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GULTON INDUSTRIES, INC.

Metuchen, N. J.

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INVESTIGATION OF BATTERY ACTIVE NICKEL OXIDES

BY

P. Ritterman and H. N. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 34178

GULTON INDUSTRIES, INC.
Alkaline Battery Division
Metuchen, New Jersey

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FINAL REPORT

INVESTIGATION OF BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman and H. N. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

June 11, 1965

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Solar and Chemical Power Branch
W. J. Nagle

GULTON INDUSTRIES, INC.
212 Durham Ave.
Metuchen, N. J.

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SUMMARY

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A study of the compounds formed on a nickel oxide electrode with respect to charged stand, charge rate, state of charge, and during overcharge, has been made. This was done using X-ray diffraction, differential thermal analysis, chemical analysis, and spectography. Most of the work was done by means of X-ray diffraction.

It was found that the active compounds of the electrode are essentially β NiOOH and $Ni(OH)_2$ during ordinary conditions of charge and discharge. During overcharge, an unstable compound is found having the X-ray patterns listed by ASTM files for γ NiOOH. These patterns were obtained by means of X-ray monitoring a two plate cell during overcharge. Data for decay of this compound during open circuit stand are also presented. In some cases, the lines of the compound disappear completely. One case is shown where after extended stand, γ NiOOH seems to decay into a compound whose X-ray patterns fit $4Ni(OH)_2 \cdot NiOOH$.

Differential thermal analysis has indicated the existence of a compound of nickel at the "graphitic" level which differs from both β NiOOH and $Ni(OH)_2$.

Initial cycling data and testing are also presented for sintered plate nickel and tubular graphite types of positive plates. author

An experiment for stabilizing the sintered plate nickel oxide electrode by means of formation at various rates and temperatures has been started.

INTRODUCTION

A. PURPOSE

Work performed under this contract was directed (1) toward an identification of the nickel oxide compounds formed during charge and discharge of the electrodes; (2) to determine when they are formed; (3) to determine which factors (such as current density and temperature) affect the charge process; (4) to relate the shelf loss process to these compounds, and (5) to determine the compounds which disappear during discharge of these electrodes.

In order to accomplish this, a three phase program was devised.

Phase I was directed toward a study of shelf life changes in the nickel electrode at room temperature and certain low and elevated temperatures.

Phase II dealt with the forms of nickel oxides appearing at various states of charge, and also with the appearance of unstable oxides during dynamic overcharge.

Phase III dealt with methods of preparation of positive sintered plate electrodes which are stable at high temperatures with respect to shelf and cycle life.

B. MEETINGS

Two meetings between Gulton and NASA Lewis personnel were held during the contract period at Gulton Industries in Metuchen, N.J.

The meetings took place on September 1, 1964 and January 5, 1965. At each meeting, Mr. W. Nagle represented NASA, Lewis. Drs. R. C. Shair and H. N. Seiger and Mr. P. Ritterman were present for Gulton Industries. Mr. M. Lurie, of Gulton, was also present at the first meeting.

INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman and H. N. Seiger

ABSTRACT

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A study of the compounds formed on a nickel oxide electrode with respect to charged stand, charge rate, state-of-charge, and during overcharge has been made. This was done by means of X-ray diffraction, differential thermal analysis, chemical analysis and spectrography. The majority of the work was done by means of X-ray diffraction.

It has been found that the active compounds of the electrode are essentially β NiOOH and $Ni(OH)_2$ during ordinary conditions of charge and discharge. During overcharge, an unstable compound is formed having the X-ray patterns resembling those of γ NiOOH. These patterns were obtained by means of X-ray monitoring a two plate cell during overcharge. Data of the decay of this compound on open circuit are also presented.

Differential thermal analysis has indicated the existance of a compound of nickel at the "graphitic" level which differs from both β NiOOH and $Ni(OH)_2$.

Initial cycling data and testing are also presented for sintered plate nickel and tubular graphite types of positive plates.

An experiment for stabilizing the sintered plate nickel oxide electrode by means of formation at different rates and temperatures has been started.

I. OUTLINE AND REVIEW OF PROGRAM

The three phase program was devised to study both the tubular and sintered plate positive electrodes. The electrochemical, as well as structural, differences of the two types of electrodes brought forth in Phase I, caused us to concentrate our studies on the sintered plate electrode.

A. LITERATURE SEARCH

1. Bibliography

The following articles constitute the bibliography on electrochemically formed nickel oxides.

a. Investigation of the Sintered Plate Nickel-Cadmium Battery. Final Report - Sandia Corp., 1958, A. J. Salkind, P. F. Bruins.

b. Nickel-Cadmium Cells I. Thermodynamics and X-ray Studies, A. J. Salkind, P. F. Bruins, J. of Electrochemical Society, Vol. 109, No. 5, P. 356-360.

c. Investigations on the Reaction Mechanism of the Nickel-Cadmium Cell. S. Uno Falk, J. Electrochemical Society, Vol. 107, No. 8, P. 661-667

d. X-ray Studies of Divalent and Trivalent Nickel Compounds. Cairns and Ott, J. American Chemical Soc., 55, 527 (1933) and 55, 533 (1933)

e. The Structure of Higher Nickel Hydroxides. Glemser and Einerhand, Zeitschrift Fur Anorganische Cheme 261 (1950), P. 43-51.

f. Chemical Processes at the Electrodes of Electrochemical Sources of Current. H. Bode, Angew. Chem. 73 (1961) 553-60

g. The Significance of EMF Decay Measurement; Application to Nickel Oxide Electrode. Conway and Bourgault, Trans. Faraday Society 58, 593-607 (1962)

h. Open Circuit Studies Highly Oxidized NiO Surface Absorbed O_2 Radicals. Conway and Bourgault, Canadian Journal of Chemistry 38, (1960) 1557-75.

i. Alkaline Storage Batteries - The Self Discharge of the Positively Charged Nickel Oxide Electrode. Pitman and Work, Naval Research Laboratory NRL report 4844, 4845.

j. H. N. Seiger and R. C. Shair, Paper presented at the Electrochemical Society Meeting, Fall 1962, Detroit.

k. The Nickel Oxide Electrode-3. G.W.D. Briggs and W.F.K Wynne Jones, Trans. of Faraday Society No. 405, Vol. 59, (1956) 1272-1281.

l. The Higher Nickel Hydroxide; the Oxidation of Nickel II Hydroxide. Feitknecht, Christen and Studer, Z. Anorg. U. Allgem. Chem. 283 (1956) P. 88-95.

m. The Forming Process in Nickel Positive Electrodes. D Toumi, Journal of the Electrochemical Society, Jan. 1965, Vol. 112, No. 1.

2. Review of Literature

Although various exotic compounds of nickel, oxygen and hydrogen were discussed and prepared by Cairn and Ott, Glemser and Einerhand and a number of other investigators, it was never stated that these were found to correspond to any particular state-of-charge of the positive plate. For the most part, these authors (Cairns, Ott, Glemser, Einerhand) concentrated on the chemical oxidation of nickel hydroxide rather than electrochemical.

Compounds which were claimed to have been found due to charge and discharge of a nickel hydroxide electrode are:

β NiOOH, $Ni_2O_3 \cdot 2H_2O$, $Ni_2O_3 \cdot H_2O$, $Ni(OH)_2$, $Ni_3O_2(OH)_4$, γ NiOOH

The most recent works on this subject were by Salkind and Bruins and Uno Falk. These authors present data indicating only β NiOOH and $Ni(OH)_2$ under ordinary charge and discharge conditions. Under extreme overcharge conditions, Salkind found that $Ni_2O_3 \cdot H_2O$ is also formed. These results were obtained at various states of charge and temperatures by X-ray diffraction measurement. There is a discrepancy between Salkind and Falk on the one hand, and other authors which the former investigators attributed to different procedures used in preparing the positive plates for X-ray analysis. Salkind and Falk arranged special cells which enabled X-ray work to be done on plates wet with hydroxide. The other authors washed and dried their plates, which could have caused the formation of other nickel oxide compounds.

The "graphitic" level, or second discharge level, corresponding to a plateau at a cell voltage of 0.7 volts has been hypothesized as $Ni_3O_2(OH)_4$. This compound, however, was not found by Falk or Salkind at any state of charge.

The existance of higher oxides help explain an excess capacity of 10%-15% found upon discharge of freshly charged plates. The workers about the turn of the century, and more recently Bode, have speculated the existance of the unstable and amorphous compound NiO_2.

The work of Pitman and Work attribute the 10% excess capacity to adsorbed oxygen. They also claim that the so-called "graphitic" level is due to adsorbed oxygen on the discharged $Ni(OH)_2$.

Conway and Bourgault attribute the excess capacity to a monolayer surface phase of adsorbed oxygen-containing radials such as O, OH on the conducting metal surface, or a higher oxide of nickel. They found that the volume of oxygen evolved from this phase corresponds to less than a monolayer of surface.

Toumi speaks of tetravalent nickel compounds which are formed in concentrated electrolyte and at elevated temperatures. These compounds consist of nickel oxygen and the cation of the electrolyte.

B. PLAN OF EXPERIMENTS

The plan and execution of the three phase program described in the previous Quarterly Reports is outlined below:

1. Phase I

The effect of stand on the chemical, electrochemical and structural characteristics of the sintered nickel and tubular graphite nickel electrode was investigated. These characteristics have been studied by X-ray diffraction, chemical analysis, differential thermal analysis and spectrograph.

2. Phase II

The oxides of nickel formed during overcharge of a sintered positive electrode have been studied. In order to investigate the unstable oxides which might be formed, it was necessary to study them during continuous overcharge by means of X-ray diffraction patterns. The appearance, growth, shift, and in some cases disappearance of lines not associated with nickel, nickel hydroxide and β nickel hydroxide have been followed.

The effect of state of charge and rate of charge on the structural, chemical and electrochemical characteristics of sintered nickel electrodes were studied.

3. Phase III

Experiments leading to the stabilization of nickel compounds formed during charge and overcharge in a sintered nickel electrode were begun. The effect of formation rate and temperature is presently being studied for their stabilizing influence. Electrodes will be evaluated for their performance at elevated temperatures up to 95°C. This evaluation will be performed as partial fulfillment of the extension of this contract.

II. EXPERIMENTAL RESULTS

A. EXPERIMENTAL PROCEDURE

1. Phase I

a. Preparation of Plates

(1) Sintered Plates

All sintered plates 0.035" x 2-1/8" x 1-7/8" were impregnated at one time by the continuous impregnation method of Gulton Industries. Each plate gained an average of 2.6 grams as $Ni(OH)_2$.

(2) Pocket Plates

From the batch of $Ni(NO_3)_2$ used to impregnate sintered plates described above, a portion was taken and combined with a slight excess of KOH to precipitate $Ni(OH)_2$. The precipitate was washed by decantation and then filtered through a Buchner funnel. The precipitate was further washed in the Buchner funnel and then air dried at 50°C for 3 days. The dried precipitate was ground into a powder in a mortar and pestle. Finally it was sifted through an 80 mesh sieve.

The precipitate was combined with number 2M flake graphite obtained from the Asbury Graphite Company in ratio of 7 parts nickel hydroxide to 3 parts graphite. The mixture was ground with the mortar and pestle and then wetted with KOH to form a very thick paste. The wet $Ni(OH)_2$ mix was then tamped into a hollow perforated stainless steel cylinder 1/4" O.D. x 4-1/2".

b. Construction of Cells

(1) Sintered Plates

Two positive plates were combined with 3 negative plates of the same dimension and with non-woven nylon separator made into a cell core. The core was placed into a plastic container, shimmed tightly, and then flooded with 34% KOH electrolyte. Thirty such cells have been constructed.

(2) Tubular Plates

The stainless steel tubes were filled with a mix of graphite and powdered $Ni(OH)_2$, prepared as described in the First Quarterly Report. The tube was sealed on the bottom, placed in a special jig, and then filled by tamping small amounts of active material at a time. After filling, a tab was welded to the top. Thus, the completed tubular positive electrode had the dimensions 4" x 7/32" I.D. Thirty such positive plates were constructed and surrounded with an excess of antipodic capacity in the form of sintered plate cadmium electrodes.

c. Formation

(1) Sintered Plates

Since these cells had never seen current, it was decided to give them two constant current charge-discharge cycles. The first cycle involved a 24 hour shorting period followed by a charge at 0.300 amperes for 9 hours. The subsequent discharge was carried out at 0.500 amperes to 0.0 volts. The second cycle started again with a 24 hour short. The second charge was at 0.300 ampere for 7 hours. The second discharge was at 0.500 ampere to 0.0 volts.

After this preliminary cycling the cells received 6 cycles involving a constant load discharge. The 6th cycle was necessitated by a temporary failure in recording equipment during the previous cycle. Each cycle consisted of a 24 hour short, a 7 hour charge at 0.300 amps, a discharge through a 2.4 Ω resistor to a voltage approaching zero. Each cell on each cycle was individually discharged through its own 2.4Ω resistor. Based on the results of the 6th cycle, 21 cells closest in capacity were chosen out of the group of 30 cells. These were divided into three groups: the first containing those 7 cells with the highest capacity; the second group with those 7 cells having the lowest capacity; and the remaining 7 cells constituted the last group. From these, 7 groups of 3 cells were formed with each group containing a high, middle, and low cell.

(2) Tubular Plates

Preliminary tests showed that current densities corresponding to the C/5 rate, based on theoretical capacity could not be used due to the high voltage and immediate oxygen gassing at the positive. Edison's patent #678722, by which these plates were made, called for an extended charge at a current density of 50 ma/in^2. This corresponded to 155 milliamperes, which we found was also too great.

Empirically, it was found that a 50 ma charge gave satisfactory results. It was also empirically established that a discharge rate of 50 ma corresponded essentially to the C/3 discharge rate.

Based on these results, the formations were performed. Each cell was given 5 cycles, involving a 50 ma charge for 16 hours followed by individual discharges through a 22 ohm resistor. This was followed by a 24 hour short. During the first three cycles, the cells were discharged to 0.2V before shorting. The last two discharges were taken to 1.0V.

Based on the results of the 5th discharge, 21 cells closest in capacity were chosen out of the group of 30. These, in turn, were divided into three groups of 7 cells each, according to capacity; high, medium, and low. This procedure is identical with that previously used for the sintered plate cells.

d. Preparatory Self Discharge Measurements and Analysis

(1) Sintered Plate Cells

The 21 cells selected as described above were placed in an oil bath, kept at 25°C, and were charged at 0.150A while thermostatted for a period of 20 hours. One group of three cells was allowed to stand on open circuit for 24 hours at which point these cells were taken apart and the positives of two cells stored at 25°C in KOH in the oil bath. The positives from the third cell were immediately analyzed - one dry and one wet - by X-ray diffraction. A dry plate is one which was washed in distilled water and vacuum dried. A wet plate is one which was immediately covered with a polyethylene bag. The other positives were analyzed - one wet, one dry - 24 hours afterward, and one 48 hours afterward. Two groups were removed at the end of the 20 hour charge period and remained on open circuit at a temperature of 50°C for 24 hours. At this time, one group was discharged at 0.500A to a voltage of 1.25 volts. The group that was discharged was taken apart. From this point, the plates were treated as 25°C runs described above. The undischarged group remained at 50°C for a period of 3 months, covered, to avoid evaporation. Two groups were removed at the end of the 20 hour charge and remained on open circuit at 10°C for 24 hours. One group was discharged to 1.25 volts and also treated as the 25°C runs described above. The other group remained on stand at 10°C for 3 months.

At the end of the second quarter, the sintered plate cells had completed their 3 months stand at 25°, 10°, and 50°C. From the analysis of previous X-ray data obtained during the first quarter, and as was stated in the First Quarterly Report, all X-ray work done during the remainder of the year was with the positive plates in the "wet" condition most resembling their condition within an actual cell. It was also found that little difference existed among the high, low, and medium capacity groups with respect to X-ray characteristics.

Therefore, only 4 positive plates were analyzed using X-ray diffraction; one which had stood 3 months at a temperature of 25°C, one which had the same stand time at a temperature of 10°C, and two that stood for that duration at 50°C. Three plates from the low capacity group were used for this, and as a check, an additional plate for the higher capacity group was used at 50°C.

(2) Tubular Plate Cells

Based on statistical distribution of capacity for the 21 cells, it was decided that six cells would be sufficient for this test. This was supported by the fact that in previous tests run on sintered plates, there was little difference among X-ray characteristics of the high, low, and medium group. The six cells selected had 2 representatives of each group based on the discharge of the fifth cycle. The 6 cells were placed in an oil bath, kept at 25°C, and there charged at 0.015 amperes for a period of 20 hours.

One cell was allowed to stand on open circuit in the oil bath for a period of 24 hours. At this point, the cell was taken apart, the steel tube opened, its active material placed in a sample holder, and immediately X-rayed. Another cell was removed from the oil bath after being charged and allowed to stand 24 hours at 10°C. A third was allowed to stand for 24 hours at 50°C. The latter two cells were opened, active material removed and X-rayed as described above.

The three remaining cells were allowed to stand for 3 months, with one cell kept at each of the above mentioned temperatures.

The study of the effect of prolonged stand at various temperatures of tubular nickel electrodes was completed. The 3 cells which had been on stand for three months at 10°, 25°, and 50°C were opened and the positive material X-rayed.

2. Phase II

a. Unstable Nickel Oxides

A two plate cell having a positive electrode of the dimensions 1 x 2 x 0.09 cm., and a negative electrode of the same thickness and twice the area, was contained within a polyethylene bag. The positives and negatives had tabs, extending through the bag, enabling the cell to be charged.

The cell was charged for 1 hour at the C rate (50 milliamperes) based on positive capacity. It was then placed in the goniometer of the X-ray apparatus. The charge was continued at 50 ma while the cell was being X-rayed. A sweep between the angles $2\theta = 10^\circ$ and 80° was made, and after its completion, the X-ray apparatus was returned to 10° as the charge continued. This was done for a total of 6 sweeps, corresponding to an overcharge of 350% at the C rate.

The X-ray apparatus was then shut off, and after 20 hours on open circuit, the cell was X-rayed again between the angles of $2\theta = 10^\circ$ and 80°. The cell was then discharged.

The discharged cell was placed on charge at 50 ma within the goniometer of the X-ray apparatus and continually monitored between the angle sweep of $2\theta = 12^\circ$ to 14.5°. The cell was swept between $2\theta = 12^\circ$ to 14.5°, also, while on opened circuit for an additional 4 hours. After 65 hours on open circuit, another series of sweeps were made between $2\theta = 12^\circ$ to 19°. The cell was discharged, and again charged in the goniometer at 50 ma. The sweep was increased to $2\theta = 10^\circ$ to 80°. The charge continued for 2½ hours. The cell was then swept between $2\theta = 10^\circ$ to 80° on open circuit initially, and after 16 hours.

In order to show that no "strange" lines occur due to the precipitation of KOH crystals, a cell consisting of two unimpregnated sintered plates was built and charged in the goniometer in the same manner. The cell was charged for 4 hours at 200 ma. An improved version of the two plate cell was built which allowed for a flatter surface of the positive covered with polyethylene exposed to the X-ray beam.

The area of the positive was also increased to 2.5 x 1.6 cm. The area of the negative was sufficiently increased to assure a positive limiting cell. The cell was X-rayed on open circuit between the angles $2\theta = 10^\circ$ to 80°. The cell was charged at the C rate (120 ma) for 2½ hours and X-ray monitored during overcharge at $2\theta = 10^\circ$ to 80°. The cell was again discharged and given a charge within the goniometer at 120 ma. for a total of 6 hours, during which time it was continuously swept between the angles $2\theta = 10^\circ$ to 40°. The cell was then allowed to stand on open circuit for one week. X-rays were taken, initially, after 3 hours, 65 hrs., and one week.

b. Stable Nickel Oxides

Thirty-six sintered plate cells, identical to those used in Phase I, were employed here. Although not previously planned, it was deemed advisable that, before any testing with respect to the electrochemical and chemical characteristics was begun, these cells be given formation cycles. The formation consisted of 5 cycles involving charge, discharge through a constant load (2.4 ohms) to 1.0V, followed by a dead short.

(1) Determination of C and C/10 rates

(a) C Rate

Three cells (See Table V, cells 1, 9, and 10) whose capacity on the 5th formation discharge was approximately equal, were charged at 0.75 amperes for a period of 2 hours and 45 minutes and then at 0.50 amperes for an additional 65 minutes. The cells were then discharged at 1.5 amperes.

(b) C/10 Rate

Three additional cells, 8, 4, and 27, of the 36 formed, were charged for a period of 20 hours at 0.150 ampere and then discharged at the same rate.

(2) State of Charge Tests

(a) C Rate

Charge to 200% of Capacity

Cells 1, 9, and 10 were charged at the C rate for a period of two hours. The cells were allowed to stand on open circuit for 24 hours, at which time their positive plates were X-rayed. One of the positive plates of cell 1 was also X-rayed after a 72 hour stand.

Charged 10% Beyond Vigorous Gassing

Cell 5 was rebuilt to allow positive to be visible by the removal of the shims. The cell was charged at the C rate. After vigorous gassing was noticed from the positive, the charge was continued for an additional 10% of the input necessary to start the gassing. After a 24 hour stand, the positive plate of this cell was X-rayed.

Charged 20% Below Vigorous Gassing Point

Cells 19 and 24 were charged at the C rate for a length of time 20% less than that required to achieve vigorous gassing, as had been determined previously. The positive of cell 19 was X-rayed following a 24 hour stand. The positive of cell 24 was X-rayed after a 72 hour stand.

Charged 200% - Discharged 50%

Cells 23 and 32 were charged at the C rate for two hours and then immediately discharged at the same rate for 30 minutes. The positive of cell 32 was X-rayed following a 24 hour stand. The positive of cell 23 was X-rayed following a 72 hour stand.

Charged 200% - Discharged 75%

Cell 25 was charged at the C rate for 2 hours after which it was discharged for 45 minutes at the same rate. Following a 72 hour stand, the positive of the cell was X-rayed.

Charged 200% - Discharged to Cell Voltage of Zero

Cell 28 was charged at the C rate for 2 hours and then discharged at the same rate to a cell voltage of zero. After a 72 hour stand, the positive of the cell was X-rayed.

(b) C/10 Rate

Charged 200% of Capacity

Cells 13, 16, and 18 were charged at the C/10 rate for 20 hours. A positive plate of each of the cells was X-rayed following a 72 hour stand.

Charged 10% Beyond Vigorous Gassing

Cell 7 was rebuilt in such a manner as to make vigorous gassing from the positive visible (the shims were removed). The cell was charged at the C/10 rate to a coulombic input 10% in excess of that necessary to produce vigorous gassing. After a 72 hour stand, the positive of the cell was X-rayed.

The test was repeated using cell 30, which was charged at the C/10 rate for 11 hours. After a 24 hour stand, an X-ray was made of one of its positive plates.

Charged 20% Below Vigorous Gassing Point

Cells 17 and 26 were charged at C/10 to an input equal to 20% less than that required to produce vigorous gassing. After a 48 hour stand, an X-ray was taken for the positives of both cells. The test was repeated with cell 31 by charging it for 8 hours at the C/10 rate. After a 24 hour stand, its positive was X-rayed.

Charged 200% - Discharged 50%

Cell 4 was charged 20 hours at the C/10 rate and then discharged at the same rate for 5 hours. The cell was on open circuit stand for 72 hours before its positive was X-rayed.

Charged 200% - Discharged 75%

Cell 22 was charged for 20 hours at the C/10 rate and then discharged at that rate for 7.5 hours. Following a 72 hour stand, the positive of the cell was X-rayed.

Charged 200% - Discharged to Cell Voltage Equals Zero

Cell 36 was discharged to a voltage of V=0 at the C/10 rate after it had received a 20 hour charge at that rate. This, too, was a positive capacity limited cell. After a 72 hour stand, the positive was subjected to analysis by X-ray.

3. PHASE III - Methods of Stabilization

a. Construction of Cells

27 cells were constructed using one .035" x 1-7/8" x 2-1/8" unformed sintered positive surrounded by two negative plates. The positives, as before, were manufactured entirely at Gulton Industries. Each positive contained an average of 3.4 grams active material weighed as $Ni(OH)_2$. The method of manufacture of the plate is the same as described in Phase I.

b. Formation Procedure

Cells were formed in groups of 3 at three different temperatures and three different rates. The three rates were 500 ma, 100 ma, and 35 ma, which correspond to the 2 hour, 10 hour, and 30 hour rates, respectively. The three temperatures were 10°C, 25°C, and 50°C. Thus, one group of 3 cells was formed under each of the 9 different conditions of rate and temperature.

The charge at each rate was of such duration as to equal 150% of the theoretical capacity of the cell. The discharge was to zero potential, followed by a minimum of a 2 hour short.

Cells will receive 3 formation cycles. At the time of writing, the formations are being completed.

4. Methods of Analysis

a. X-ray Diffraction

The general procedure for obtaining an X-ray pattern was as follows:

(1) Mount sample on sample holder

(2) Set full scale equal to appropriate scale factors and multiplier.

(3) Set in the culminating slits and set the machine at a sweep rate of 2° per minute. The chart speed was set equal to 30" per hour.

(4) Calculate "d" spacings from $n\lambda = 2d \sin\theta$. $\lambda = 1.5374$ (A table has been made of this for each 0.1° step.)

b. Differential Thermal Analysis

Three thin chromel-alumel thermocouples were mounted into a stainless steel block. One thermocouple in the block records ambient temperature. The other two are set with polarity in opposition to each other to record the temperature difference between the sample and the alumina standard. The X-Y recorder is used to automatically plot temperature differences between ambient and the temperature differential existing between alumina and sample. Three holes in the block hold the three thermocouples. The thermocouple measuring ambient temperature is cemented into the hole. The sample is powdered and a weighed quantity packed into the sample compartment.

The following samples were investigated by differential thermal analysis:

(1) Alumina, $Ba(NO_3)_2$.
(2) $Ni(OH)_2$ prepared in July 1964 for tubular plates
(3) $Ni(OH)_2$ more recently prepared
(4) Commercial $Ni(OH)_2$
(5) Charged sintered plates
(6) Sintered plates discharged to the "graphitic" level
(7) Completely discharged sintered plates.

c. Chemical Analysis

(1) Nickel

The determination of nickel has been done by precipitation from a basic solution as nickel dimethylgloxime.

(2) Oxygen

The determination of oxygen was done by means of reacting samples with excess of acid solution of KI followed by titration of the liberated iodine with sodium thiosulfate.

(3) Hydrogen

Hydrogen was determined by oxidizing the sample with K_2CrO_4 and $PbCrO_4$ at 600°C. The reaction occurred in a porcelain boat. A hot air blower forced the resultant steam into a weighed drying tube.

(4) Determination of Average Valence State of Nickel Compounds

Samples were dissolved in excess acidic As_2O_3. After the dissolution, the remaining As_2O_3 was determined by titration with standard $KmnO_4$. A determination of nickel by precipitation with dimethylgloxime completes the analysis.

5. Special Tests

a. Determination of Effect on Positive Plate Characteristics With Respect to Sealed and Vented Charge.

A test to show a similarity of compounds in the positive of a positive limiting cell can be based on the number of coulombs passed through anodes during charge before a rapid rise in pressure is noted.

A sealed electrolyte starved VO-6HS cell equipped with a pressure gauge and evacuated, was charged and discharged for 4 cycles in the following manner: (1) charged at 1.2 amperes until a rapid rise of pressure, with respect to time, was noted. The charge was then continued for a short time beyond this point. (2) Discharged at 3.0 amperes to 1.0V. (3) Dead shorted overnight.

After completion of the 4 cycles, the cell was flooded with KOH, vented to the atmosphere, and then resealed. Five additional cycles were now given to this cell. Each cycle consisted of; (1) 1.2 amperes charge for a time slightly beyond a rapid pressure rise (2) a discharge to 1.0V at 3 amperes (3) an overnight short (4) venting to atmospheric pressure and resealing.

b. Analysis of M-2 Graphite Flake

The graphite flake used as a conducting material on the tubular positive plates was quantitatively analyzed for impurities. This was done by means of spectrographic analysis at Ledoux & Co. in Teaneck, N. J.

c. Analysis of Sintered Nickel Electrodes at the "Graphitic" Level.

(1) By Means of X-Ray Diffraction

Three cells were charged at the C/10 rate for 18 hours and discharged to zero potential at 500 milliamperes (C/3). The cells were placed on dead short for 4 hours and again charged at the C/10 rate for 17 hours. They were discharged to 0 volts at C/5 with voltage traced by means of a recorder. Shorting and charge were repeated. The cells were then discharged to the beginning of the "graphitic" level and then allowed to stand on open circuit for 24 hours before a positive from each cell was analyzed by means of X-ray diffraction.

(2) By Means of Differential Thermal Analysis

Prepared positives at the "graphitic" level were washed with distilled water and air dried. Samples were ground in a mortar with a pestle and placed in the sample holder of the stainless steel block. Analysis was made with the D.T.A apparatus.

d. X-Ray of Various Components of the Positive Sintered Plate

X-ray diffraction patterns were obtained from $Ni(OH)_2$, polyethylene, a sintered nickel plate, a sintered nickel plate covered with polyethylene dry and a sintered nickel plate covered with wet polyethylene. After X-raying a sintered nickel plate with the wet polyethylene, the polyethylene was removed and the same plate was again X-rayed.

B. DATA

1. Phase I

a. Formation

(1) Sintered Plates

The capacities expressed as time in minutes for the two preliminary discharges and the sixth and final constant load discharge cycles are shown in Table I. The capacities are taken to a zero volt cut-off for the first two cycles and to the knee of the first voltage plateau for the sixth constant load cycle. The letters H, M, L next to cells in Table I indicate that these were selected as the matched capacity curves, and also to which group they were relegated using the letters for "High", "Medium" and "Low" capacity. This based on the sixth constant load cycle. Figure 1 shows a typical discharge curve for the sintered plate cell through the 2.4 ohm resistor.

(2) Tubular Plates

The capacities of the 30 tubular plate cells expressed in minutes to 1.0V appear in Table II. The discharges through a 22 ohm resistor, for the 1st and 5th cycles, are given. The letters H, M, L next to cells in that table, indicate that these were selected as the 21 closest in capacity, and also to which group they were relegated using the letters for "High", "Medium" and "Low" capacity, based on the discharge to 1.0V during the 5th cycle.

Figure 2 shows a typical discharge curve through the 22 ohm resistor when discharge was allowed to proceed beyond the 1.0V cut-off, as was done in the first 3 discharges.

b. Preparatory Self-Discharge Measurements and Analysis

(1) Sintered Plates

X-ray diffraction patterns were taken of positive plates on charged stand at room temperature (25°), elevated temperature (50°C) and cold temperature (10°C). Because only six X-ray patterns could be obtained in one working day, and because we wanted both "wet" and "dry" patterns at three temperatures for "High", "Medium" and "Low" capacity plates, three days were required to obtain all 18 X-ray patterns.

Table III lists the major peaks obtained from these X-rays. The X-ray patterns of all the plates were shown in the First Quarterly Report. Figures 3, 4 and 5 are examples of the initial charged stand X-rays obtained from "wet" plates stored at 25°C, 50°C and 10°C respectively. The X-ray patterns from "wet" plates on three months stand at these temperatures appear in Figures 6, 7 and 8.

(2) Tubular Plates

The six cells chosen for this test were numbers 2, 8, 10, 16, 24 and 30. All were treated as described in the previous section with respect to thermostated charge. After 24 hour stands on open circuit at temperatures of 25°C, 10°C and 50°C, X-ray diffraction patterns were obtained from active material in the positives of cell numbers 10, 30 amd 16 respectively.

After cells 2, 8 and 10 had been on stand for 3 months their active material obtained from the positive was X-rayed. The patterns obtained from these six positives were tabulated in the form of "d" spacings and intensities and appear in Table IV.

2. Phase II

a. Unstable Nickel Oxides

The experimental setup shown in Figure 9 was used for this test. The positive plate was placed face up in the goniometer. X-ray diffraction patterns were taken after the cell had received a full charge with respect to the positive. Figure 10 is the pattern obtained during the first sweep between $2\theta = 10^\circ$ and 80°. At the completion of overcharge the sweep shown in Figure 11 is complete at this point. The cell has been on continuous charge for 350% of its rated capacity at the C rate.

After a 20 hour stand the cell was again X-rayed between $2\theta = 10^\circ$ and 80° (Figure 12).

The cell was discharged and then charged within the goniometer.

Figure 13 shows the change in intensity of the X-ray diffraction pattern betwen $2\theta = 12^\circ$ and 14.5° with charge time and on opened circuit. A peak appears at 13.7° growing during charge and decaying on opened circuit. After 65 hours, the peak at 13.7° has disappeared. Figure 14 shows the X-ray diffraction patterns of the positive between $2\theta = 10^\circ$ and 80° while the cell was being charged at 50 milliamperes (the C rate).

Figure 15 shows the sweep for $2\theta = 80°$ to $10°$ with charge continuing. At the completion of this sweep, the cell had been on charge 140 minutes. Figure 16 shows a sweep between $2\theta = 80°$ to $10°$ with the cell on open circuit. Figure 17 shows a sweep between $2\theta = 10°$ to $80°$ after the cell has been on open circuit for 16 hours. Figure 18 shows a sweep between $2\theta = 10°$ to $80°$ of a sintered plate being positively charged at 200 milliamperes. Figure 19 shows the same sweep after the cell had been on continuous charge for 4 hours.

Figure 20 shows the X-ray pattern of the enlarged cell on open circuit monitored between $2\theta = 10°$ and $80°$. Figure 21 shows the X-ray pattern obtained from the same cell during overcharge. After an additional 2 hours of charge no change in the pattern was observed as shown in Figure 22. The cell was again discharged and given an extended charge for 6 hours while within the goniometer.

Figure 23 shows the X-ray diffraction pattern obtained during initial charge; two sweeps between $2\theta = 10°$ to $40°$. Figure 24 shows two sweeps between the same angles after 3 hours of charge. Figure 25 shows same after 6 hours of charge.

The cell was placed on open circuit. Figure 26 shows initial sweep and another sweep following 3 hour stand between $2\theta = 10°$ and $40°$. Figure 27 shows two sweeps between $2\theta = 10°$ and $40°$ after the cell had completed 65 hours on stand. Figure 28 shows the same after one (1) week on open circuit.

b. Stable Nickel Oxides

The capacities obtained from the 36 plates during discharge through a 2.4 ohm resistor are tabulated for the 5 formation cycles in Table V. Capacities are expressed as minutes to 1.0V.

(1) Determination of the C and C/10 Rate

(a) C Rate

Cells 1, 9 and 10 when discharged at 1.5 amperes required 46 minutes to reach 0.0V. To the nearest tenth, the C rate then was set equal to 1.2 amperes.

(b) C/10 Rate

Cells 8, 4 and 27 when discharged to 0.6V at 0.150 ampere required 9 hours and 56 minutes, 10 hours and 4 minutes and 9 hours and 48 minutes respectively. Thus, 0.150 ampere was established as the C/10 discharge rate.

(2) State of Charge Tests

The positive plates of the cells charged and discharged to the various states of charge at the C and C/10 rates were X-rayed. The "d" spacings and the intensities from the various X-ray patterns are shown in Table VI. The X-rays themselves appear in the Third Quarterly Report.

When using the beginning of vigorous gassing of the positive plate to indicate full charge it was found that 65 minutes of charge were required at 1.2 amperes, while at .150 ampere 855 minutes of charge were necessary.

3. Phase III - Methods of Stabilization

The capacities obtained during discharge of each formation cycle at the three conditions of rate and temperature are listed in Table VII. Cells are numbered 1 through 27. Cells 1 through 9 were formed at 25°C - cells 10 through 18 at 80°C and cells 19 through 27 at 10°C. Cells 1, 2, 3, 10, 11, 12, 19, 20 and 21 were formed at 500 milliamperes - cells 4, 5, 6, 13, 14, 15, 21, 23 and 24 at 100 milliamperes and cells 7,8,9, 16, 17, 18, 25, 26 and 27 at 35 milliamperes. The formation tests for cells 25 through 27 have just begun and no data are,as yet, available.

4. Methods of Analysis

a. X-Ray

The data obtained by X-ray analysis appears in various figures and tables dealing with Phases I and II.

b. Differential Thermal Analysis

Figure 29 is a Block Diagram of the D.T.A. apparatus. D.T.A. calibration with alumina and Ba $(NO_3)_2$ yielded satisfactory data. Three samples of $Ni(OH)_2$ - two of which were prepared in this laboratory and one of which was purchased - were analyzed. Results indicated a transition at temperatures of 539°F, 580°C and 660°F for the samples prepared here in July, 1964 and in early 1965 and for the purchased sample. A thermogram from a sintered nickel plate charged at the C rate appears in Figure 30. Various phase changes are indicated. Figure 31 shows a thermogram for a sintered positive charged at C/10. An even greater number of transitions are indicated here. A thermogram of a completely discharged plate, Figure 32, indicates only one transition at 583°F. Figure 33 is a thermogram of a sample of a positive plate discharged to the "graphitic" level. This differs from that obtained with the charged and completely discharged plates.

c. Chemical Analysis

(1) Nickel

The standardization showed the dimethylgloxime method for nickel to be accurate and precise. The amount of nickel found in the $Ni(OH)_2$ which was used for the tubular plates corresponded to the theoretical amount. The sample received from an outside source contained only 95% of the expected amount of nickel.

(2) Oxygen

By use of the acidified potassium iodide-sodium thiosulfate method no oxygen was found by this method for $Ni(OH)_2$ or in the discharged plate. Less than 5% of the expected amount was found for the charged plate.

(3) Hydrogen

The apparatus for the determination of hydrogen is shown in Figure 34. A discharged sintered plate was tested for hydrogen content, and an unusually high amount was found. Even though the hot air flowing through the tube first was passed through a drying agent, it is suspected that not all water vapor was removed, accounting for the unusually high value. Extra dry air completely sealed into the intake system is now being used.

(4) Determination of Average Valence State of Nickel Compounds

The valence state in a fully charged tubular graphite nickel oxide electrode was determined as equal to 2.15.

(5) Special Tests

(a) Determination of Effect On Positive Plate Characteristics With Respect to Sealed and Vented Charge.

The data obtained during charging of a VO-6HS was plotted for each cycle in the form of pressure vs. ampere hour or coulombic input. Figure 35 is a plot of results obtained from the fourth sealed charge. Figure 36 is a plot of pressure vs. coulombic input during flooded "vented charge" on the cycle immediately following the fourth and final sealed charge.

(b) Analysis of M-2 Graphite Flake

The impurities and their amounts found in the M-2 Graphite Flake used as a conducting material for the tubular plates are shown in Table VIII.

(c) Analysis of Sintered Nickel Electrode at the "Graphitic" Level

i. By Means of X-Ray

No major difference between the peaks of a completely discharged plate and those at the "graphitic" level are apparent.

ii. By Means of Differential Thermal Analysis

Figure 33 shows a thermogram of the positive plate of a cell discharged to the "graphitic" level. This thermogram is considerably different from that obtained from a completely discharged positive. The thermogram indicates several transitions for a plate discharged to the "graphitic" level, while, as previously mentioned, only a single change is indicated by the completely discharged plate.

(d) X-Ray of Various Components of the Sintered Positive Electrode Sample

An X-ray diffraction pattern consists of a pattern of the superposition of the nickel oxide electrode, aqueous potassium hydroxide and polyethylene. To resolve the effects of the contributions of each, several combinations were investigated. The major "d" spacings are given in Table IX. Figures 37 and 38 are the diffraction patterns obtained from the same wet-sintered-unimpregnated plate with (Figure 37) and without (Figure 38) polyethylene.

C. Discussion

1. Phase I

As indicated in Figures 1 and 2 a second voltage level exists in both the sintered nickel and tubular graphite type of electrodes starting at a cell voltage of about 0.7V. This potential corresponds to -0.1 to -0.2 volts (Hg/HgO reference) which happens incidentally to be in the range of oxygen consumption on a positive electrode via the perhydroxyl mechanism. X-ray data has shown that no difference between a completely discharged sintered plate and a plate discharged to the beginning of the "graphitic" level exists. Differential thermal analysis however indicates considerable difference (Figures 32 and 33) between a discharged plate and one discharged to the beginning of the "graphitic" level. The compounds corresponding to the "graphitic" level may be adjacent to the grid or amorphous. Either of these considerations would mask their appearance when analyzed by means of X-ray. From this point of view it may be assumed that the "graphitic" level is not due to any adsorbed oxygen, but rather to a compound.

The capacities of the sintered plates after the 6th cycle (Table I) chosen to comprise the 7 test groups did not vary from each other significantly, nor as may be deduced from data in Table III, was there a difference in the X-ray characteristics due to "High", Medium" or "Low" capacity.

It can be seen that differences exist between the patterns of wet and dry plates at all temperatures. The table further shows little difference between patterns of plates initially stored at room temperature and 10°C. However, at 50°C there is a difference between plates stored at that temperature and the two others. The increased number of peaks indicate that the X-rayed surfaces of plates stored at 50°C have been discharged to $Ni(OH)_2$ - as shown by the appearance of the lines at d = 2.72Å - 2.77Å. 1.56Å and 1.48Å. After the three months storage the plates stored at 10°C show only the peaks at d = 4.49Å and 2.33Å indicating that little or no change in the structure has occurred on stand. At 25°C the lines at d = 2.72Å and 1.57Å have appeared. At 50°C the lines at d = 2.67Å, 1.57Å and 1.47Å appeared (Table X). The heights of active nickel oxide peaks in relation to the nickel peaks increased during the 3 month storage. The higher the stand temperature, the greater the relative increase. This is hypothesized to be due to a migration of active material causing greater masking of the previously intense nickel peaks. (Compare Figures 3,4,and 5 with Figures 6,7,and 8)

The necessity for low charge rates with respect to both surface areas and theoretical capacity indicates a major difference between tubular plates and sintered nickel plates. The behavior possibly explains why the original Edison process, using graphite had been abandoned in favor of a process employing flake nickel. The evolution of oxygen during charge at current densities recommended by Edison for initial treatment resulted in a very ineffective charge.

The "d" spacings and intensity obtained from X-ray data of active material of the tubular plates are shown in Table IV for plates stored 24 hours at 10°C, 25°C and 50°C and for similar plates stored at those temperatures for 3 months. The table reveals the formation of additional spacings after extended stand, especially for the material kept at 50°C. The decrease in intensity of d = 2.32Å to 2.34Å after extended storage would indicate that in a tubular electrode this line is associated with a form of nickel oxide which undergoes change during stand. This particular "d" spacing has been associated with $Ni(OH)_2$. The disappearance of 1.47Å on extended stand, also associated with $Ni(OH)_2$ would indicate that we are dealing with a different phase of $Ni(OH)_2$ than that found in a sintered nickel plate. Different phases of $Ni(OH)_2$ have been suggested recently by Toumi. These along with the poor charge acceptance of the tubular plates, even at low current density, would indicate them to be of little value in this program. Thus, investigation of the tubular plate was not included in Phase II.

2. Phase II

a. Unstable Nickel Oxides

The initial experiment showed the existence of "strange lines" which arise during overcharge, remains while overcharge is continued and wane during open circuit. This is shown in Figures 10, 11 and 12 respectively.

While scanning the cell between 2θ = 12° to 14.5° during charge, and subsequent opened circuit, the behavior of the peak at 13.7° indicated the formation of an unstable compound (Figure 13). A tabulation of the peaks corresponding to the "d" spacings during the subsequent X-ray monitored charge, overcharge and open circuit was made. As Table XI shows, a peak occurred at d = 6.95 (2θ = 12.7°). This peak formed during the overcharge and decayed during stand. It has completely decayed after 16 hours of stand. No other decaying peaks were formed.

The X-ray patterns obtained during overcharge of the enlarged cell indicated the formation of 3 peaks corresponding to γ NiOOH as listed by the ASTM files.

The X-ray diffraction patterns obtained during subsequent charge and on open circuit are tabulated along with their intensities in Table XII. As on previous overcharge γ NiOOH is produced. The characteristics d = 6.95Å, 3.41Å, 2.33Å are present to a significant intensity (ASTM - 6.90, 3.43, 2.37). In addition a very intense line d = 6.79Å has appeared. On initial open circuit the γ NiOOH lines are intense, as is 6.79A. After 3 hours on open circuit stand the γ line 6.95Å has vanished, while 6.79Å is present and has gained in intensity. The two other lines associated with γ NiOOH are still present and have also gained in intensity. After 65 hours on open circuit the line d = 7.35Å has appeared and d = 6.79Å has diminished in intensity. Line 2.33Å has disappeared while 3.41Å has increased in intensity. After 168 hours both 7.35Å and 6.79Å have vanished. The lines d = 7.62Å and 3.85Å have appeared. These two lines are associated with the compound $4Ni(OH)_2$ - NiOOH.

The changing of "d" spacings on open circuit rather than the decay may be attributable to the concentration and amount of electrolyte in the cell. Although the KOH was never allowed to crystalize, the amount and concentration in the cell could not be rigorously controlled. During overcharge the cell lost some amount of water. This was replaced with diluted KOH. It is of interest to note that it has been reported by other investigators, that strange lines have been found due to washing and drying plates. It is conceivable from the data observed here that appearance of strange lines and their stability is a function of the oxidation state of the electrode and also a function of the concentrated electrolyte. The control experiment which allowed for tremendous overcharge on a sintered plate showed that no strange lines appeared as a result of KOH drying out by itself.

b. Stable Nickel Oxides

The "d" spacings and their intensities at various states of charge are shown in Table VI. This has been done for both the C and C/10 rates. Due to the discrepancy between gassing point and capacity at the C/10 rate, additional tests were run taking 10 hours as full charge and charging 10% above and 20% below this value as shown in the table. All the positive electrodes showed lines at d = 4.50Å to 4.70Å. Since these peaks are associated with both the charge and discharge states no significance to this can be assigned.

The peak appearing at line d = 3.73Å - 3.77Å shown in Table VI and those at d = 3.62Å - 3.73Å in Table XI can be assumed to be the same. These peaks appear during charge and overcharge and do not decay on stand. At the C of rate charge and discharge (1.2 amperes) this line appears in all plates except when completely discharged.

At the position for the line d = 2.32Å - 2.36Å no peak appears for the four (4) plates which were considerably overcharged and not discharged. This line appears for all the other plates.

In order to quantitatively determine the state of charge of the nickel oxide electrode by means of X-ray diffraction, it may be necessary to consider the depth of penetration of X-rays into the sintered plate electrode. The diffraction patterns obtained from a plate which has been discharged 50% appear the same as those obtained from a plate discharged 75%. The formation of nickel compounds during charge and discharge of the sintered plate electrode can occur by one of the two following mechanisms: - (1) Atom transfers at the electrolyte/active material interface with charge transfer at the active material/grid interface - (2) Both charge and atoms transfer at the electrolyte/active material interface. The data would indicate the first mechanism correctly describes the process occurring during charge and discharge of the sintered plate positive electrode.

3. Phase III - Stabilization

The main objective of this work is to ultimately produce cells with sintered plate nickel oxide electrodes that have a minimal capacity loss due to storage at elevated temperatures.

a. The preliminary efforts are covered at this time, because this Phase III work is the basis of continued investigations. Formation charges were carried out at 10°C, 25°C and 80°C as described previously. Rates employed varied from 35 to 500 milliamperes. The results of three formation cycles are shown in Table VII.

At 80°C the capacity of the plates appear to increase with cycling although they start with low capacities. Formation at 10°C and 25°C both yield the same capacity, which is greater than at 80°C and is independent of rate over the variety of rates used.

4. Methods of Analysis

a. X-Ray

The discussion in Phases I and II have already dealt with X-ray and its value as a method of analysis.

b. Differential Thermal Analysis

The single transition which was found to occur for pure $Ni(OH)_2$ corresponds to that found for the completely discharged plate (Figure 31). This substantiates the evidence that the active material of completely discharged plates consists of $Ni(OH)_2$. The plate charged at the C rate (Figure 29) indicates the presence of some $Ni(OH)_2$ as well as other compounds. The plate charged at the C/10 rate has an even greater number of transition regions than that at the C rate (Figure 30). The plate discharged to the graphite level indicates there may be compounds different from both the charged and discharged plate as seen in Figure 33. These compounds remain to be identified.

c. Chemical Analysis

(1) Nickel

The analysis of nickel compounds by the dimethylgloxime method is quite satisfactory. The utility of the method is evaluated on the basis of a quantitative separation of the oxide from elemental nickel. Thus, in the tubular plate, the method is eminently suitable. In sintered plates, however, separation by the NH_3-NH_4Cl solution and glycine solutions are less than perfect. This difficulty does, indeed, prevent a formula weight determination of the sintered plate. The electric chemical behavior of the tubular plate, however, differs considererably from that of the sintered plate, and even at very low current densities cannot be charged to any extent. Thus, the determination of a useful formula weight by means of analyzing the active material of the tubular plate cannot be accomplished.

(2) Oxygen

The KI method for the determination of active oxygen was found unsatisfactory. An alternate method, the thermal decomposition and subsequent absorption, should be more meritorious.

(3) Hydrogen

The passage of dried hot air through the tube led to erroneous results. A completely closed entrance system using extra dry compressed air is now being used.

5. Determination of Average Valence State of Nickel Compounds

The valence found for nickel in a charged tubular graphite plate corresponds to the fact that its utilization was less than 10%. In order to achieve meaningful results from a sintered nickel plate, the nickel itself must be mechanically removed.

6. Special Tests

a. Determination of Effect on Positive Plate Characteristics With Respect to Sealed and Vented Charge

Sealed cells generally are semi-dry while vented cells contain mobile electrolyte. The question of study of open cells was raised and an experiment was devised to provide insight into the answer. The coulombic efficiency of a semi-dry cell was compared to a vented-flooded cell. Reasoning that similar coulombic inputs would result in the formation of the same compounds or species, a decision could be made based on experimental results.

It is concluded from use in pressure at nearly the same time for the same cell in the two different conditions, that the coulombic efficiencies are also nearly the same. From these data then, is the justification of carrying out experiments in the flooded unsealed manner.

b. Analysis of M-2 Graphite Flake

The results of the analysis of the graphite flake indicate that, except for aluminum and silicon the material is pure.

c. Analysis of Sintered Nickel Electrode at the Graphitic Level

The difference in results obtained from analysis using D.T.A and X-ray was explained in the discussion of Phase I of this report.

d. X-ray of Various Components of the Sintered Positive Electrode Sample

The effect of wetting a sintered plate with KOH and covering with polyethylene was investigated (Figures 36 & 37). The absence of a peak at $2\theta = 36.2°$ (d = 2.47Å) when polyethylene is removed proves that the peak is due merely to an interaction with KOH and the polyethylene. Such an interaction had not been previously considered and it had been assumed that this peak was due to a nickel compound. Corrections for this finding have been made through out this report.

There is a further indication in comparing the two curves in Figures 37 and 38 that an effect similar to the above again occurs at the line $2\theta = 19.5°$ (d = 4.54Å). This line, however, has now been shown to be characteristic of active nickel oxides, as well as of the wetted material. The intensityof the peak (d = 4.50Å-4.70Å) in the various tables has not, however, been amended because of difference in scale factors. Further work and study will be necessary to make the appropriate corrections.

D. Conclusions

1. The electrochemical behavior and structure of the active material of tubular electrodes differ considerably from that of the sintered plate electrode.

2. No difference was found among "High", "Medium" and "Low" capacity plates with respect to compound formation.

3. During extended stand in the charged state, especially at high temperature there is an indication of crystal growth and also a masking of sintered nickel surface.

4. Under ordinary plateau conditions of charge and discharge the compounds formed in a sintered nickel positive electrode are essentially $\beta NiOOH$ and $Ni(OH)_2$.

5. Evidence for nickel compounds other than $Ni(OH)_2$ are found at the "graphitic" level.

6. During high rate overcharge of sintered plates an unstable compound which has peaks associated with $\gamma NiOOH$ is formed.

7. Under certain conditions $\gamma NiOOH$ was found to decay into a stable compound whose peaks seem to resemble those listed for $4Ni(OH)_2 \cdot NiOOH$.

8. The state of charge of a positive plate cannot as yet be determined in a quantitative manner by our present analytic techniques.

III. RECOMMENDATIONS AND FUTURE WORK

A. X-Ray Techniques

1. To eliminate any possible interactions between polyethylene and KOH during X-ray, samples should be stored in sealed bags wet with hydroxide. These are to be opened just before X-ray and just the wet sample monitored. The duration of one X-ray sweep is less than 40 minutes and it is unlikely that a drying of the viscous KOH would occur during that time. The drying effect, if any, could be further checked by scanning the sample between small intervals of 20 and looking for changes in patterns with time. This could be done for fresh samples at various degree intervals. An alternative to this would be covering and uncovering a wet positive with polyethylene during short scanning periods and comparing patterns.

2. Interference from polyethylene may also be eliminated by having the sample stored in a tent-like cover thus by-passing the reflection of the polyethylene. This type of setup would be most advantageous in the evaluation of the overcharge data.

B. Storage of Plates

The effect of stand time on the positive electrode should be made both in the presence and absence of the sintered negative electrode. These will be done at various temperatures.

C. Effect of Current Density State of Charge and Temperature

A more intense study involving differential thermal analysis, chemical analysis and X-ray diffraction directed toward a quantitative, as well as qualitative determination of materials of the nickel oxide electrode will be made at various current densities, state of charge and temperature.

D. Stabilization of Nickel

1. Doping

Doping of the inclusion of a foreign material within the structure of nickel oxide and hydroxide crystals of a nickel oxide electrode has been found to function as a stabilizing force. The doping of the electrode will be subdivided into those elements near nickel in the periodic table and the alkali and alkaline earth elements. These will be introduced into the electrode during impregnation in amounts of 5, 10 and 20 mole %.

2. Formation

Impregnated sintered nickel plaques will be formed at various rates and temperatures.

3. Other Methods of Stabilization

A literature search will be made to seek other means of nickel oxide stabilization.

4. Evaluation

The charge retention on open circuit stand, voltage level, charge efficiency during discharge, as well as utilization will be evaluated by electrochemical means at room and elevated temperatures.

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APPENDIX

MIXED SOLUTION ELECTRODES

Because of the shift of X-ray lines, it had been suggested that $Ni(OH)_2$ and NiOOH form mixed solutions. This can be tested by investigating the slope of the Nernst equation.

Consider the reaction:

$$(1)\quad NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$$

The Nernst equation is given by:

$$(2)\quad E = E^\circ - 0.06 \log \frac{[NiOOH]\ a_{H_2O}}{[Ni(OH)_2]\ ^2OH^-}$$

Since the concentration of electrolyte is not altered much by the state-of-charge, one may write

$$(3)\quad E = E^{\circ 1} - \log \frac{[NiOOH]}{[Ni(OH)_2]}$$

The concentrations are stated as mole fraction. Let N = mole fraction of $Ni(OH)_2$ and N_o = mole fraction of NiOOH. Since $N_o + N_r = 1$, equation (3), becomes:

$$(4)\quad E = E^{o1} - 0.006 \log \frac{1-NR}{N_r}$$

Tue equation can hold only when an electrode is poised in the sense that the argument of the logarithm does not approach zero nor infinity. Hence, the change of open circuit potential of a positive electrode may be determined at, say, 50% charged and 10% charged. N_r is 0.5 and 0.9 respectively for these conditions. The change of potential between these points is calculated to be 57 mv. Such a change is additional evidence for a solid solution.

Conway and Gileadi (Electrochemical Society Meeting, Boston, 1962) were able to show that over a range of oxidation from 20% to 50% charged, the nickel oxide exhibits a constant reversible potential. Up to 10% charged, there is, perhaps a surface phase that is being charged. Alternatively, the βNiOOH may have reached its limit of solubility in $Ni(OH)_2$.

The fact that Conway and Gileadi's careful measurements show a constancy over 10% to 50% State-of-Charge implies that at least for the major part, that βNiOOH is insoluble in $Ni(OH)_2$. The calculated change between these points is 57 mv and the measurements were made to one-tenth of a millivolt. No doubt exists as to the conclusion.

TABLE I

CYCLING DATA

SINTERED NICKEL PLATES

CELL NO.	TIME TO 0 VOLTS PRELIMINARY CYCLE		TIME TO KNEE OF FIRST PLATEAU 6TH CONSTANT LOAD CYCLE	
	1	2		
1	164	142	150	M
2	190	146	185	
3	175	145	150	M
4	170	157	150	M
5	182	160	147	M
6	164	110	70	
7	161	150	70	
8	175	161		
9	175	157	165	H
10	175	161	147	M
11	162	95	142	L
12	165	153	130	
13	178	157	155	H
14	120	95	154	H
15	162	130	147	M
16	170	159	138	L
17	160	152	135	L
18	165	155	70	
19	165	144	85	
20	155	141	145	L
21	170	148	152	H
22	170	148	150	M
23	160	144	182	
24	168	148	152	H
25	160	142	138	L
26	160	142	180	
27	155	143	140	L
28	155	143	157	H
29	165	141	150	H
30	170	144	138	L

TABLE II

CAPACITIES OF TUBULAR CELLS DISCHARGED THROUGH 22 OHM RESISTOR

CELL NO.	CYCLE #1 MINUTES TO 1.0V	CYCLE #5 MINUTES TO 1.0V	
1	146	168	M
2	145	193	H
3	157	191	H
4	168	192	H
5	162	200	
6	96	105	
7	190	205	
8	177	175	M
9	169	187	M
10	175	173	M
11	184	256	
12	172	193	H
13	182	195	H
14	160	172	M
15	170	166	M
16	191	190	H
17	127	127	
18	100	103	
19	133	115	
20	116	130	
21	132	162	L
22	137	154	L
23	159	169	M
24	150	160	L
25	125	145	L
26	106	75	
27	131	133	L
28	167	190	H
29	122	130	L
30	144	162	L

TABLE I

LIST OF "d" SPACINGS
FIGURES 2 - 19 OF
FIRST QUARTERLY REPORT

Fig. No.	Treatment of Plate				"d" Spacings Other Than Obtained From Nickel or Polyethylene							
	Temp.	Stand Time Before X-Ray	Condition of Plate	Cell No.								
2	25°C	24 Hours	Wet-Unwashed	21	4.68	3.75				2.34		
4	25°C	48 Hours	Wet-Unwashed	5	4.68	3.72				2.36		
6	25°C	72 Hours	Wet-Unwashed	20	4.61	3.73				2.34		
3	25°C	24 Hours	Washed-Dry	21	4.68					2.34		
5	25°C	48 Hours	Washed-Dry	5	4.65					2.32		
7	25°C	72 Hours	Washed-Dry	20	4.63					2.34		
8	50°C	24 Hours	Wet-Unwashed	28	4.73	3.73			2.73	2.35	1.57	1.48
10	50°C	48 Hours	Wet-Unwashed	15	4.60	3.69			2.71	2.34	1.57	1.48
12	50°C	72 Hours	Wet-Unwashed	27	4.60	3.77	3.02	2.97	2.77	2.36	1.57	1.48
9	50°C	24 Hours	Washed-Dry	28	4.66						1.56	1.48
11	50°C	48 Hours	Washed-Dry	15	4.65						1.56	1.48
13	50°C	72 Hours	Washed-Dry	27	4.63						1.56	1.48
14	10°C	24 Hours	Wet-Unwashed	24	4.63					2.36		
16	10°C	48 Hours	Wet-Unwashed	10	4.54					2.36		
18	10°C	72 Hours	Wet-Unwashed	25	-					-		
15	10°C	24 Hours	Washed-Dry	24	4.61					2.32	-	-
17	10°C	48 Hours	Washed-Dry	10	4.63					2.32	1.56	1.48
19	10°C	72 Hours	Washed-Dry	25	4.59					2.31	1.53	1.48

TABLE IV

INTENSITIES OF "d" SPACINGS OBTAINED FROM ACTIVE MATERIAL OF TUBULAR POSITIVE ELECTRODE*

Cell No.	Storage Temp.	Time On O.C.**	"d" Spacings							
			4.49-4.61	3.59-3.68	2.99	2.61-2.68	2.32-2.34	2.29-2.28	2.25	1.47
8	10°	3 Months	9	5	----	4	----	6	----	----
2	25°	3 Months	10	5	----	5	10	----	----	----
24	50°	3 Months	7	12	9	8	10	8	5	----
30	10°	24 Hours	11	6	----	8	38	----	----	4
10	25°	24 Hours	10	----	----	5	40	----	----	5
16	50°	24 Hours	10	4	----	6	35	----	----	4

* "d" Spacings due to graphite are not included

** O.C. - Opened Circuit

TABLE V

PHASE II - CAPACITIES OF SINTERED PLATE CELLS WHEN DISCHARGED THROUGH 2.4 OHM RESISTOR

CELL NO.	CYCLE #1	CYCLE #2	CYCLE #3	CYCLE #4	CYCLE #5
			Minutes to 1.0V		
1	188	184	169	164	172
2	191	193	182	174	180
3	163	157	151	150	148
4	166	165	147	155	159
5	182	186	167	187	179
6	190	198	177	167	178
7	169	165	149	153	163
8	180	174	166	162	168
9	174	179	171	171	174
10	184	177	169	177	173
11	234	190	174	206	185
12	197	179	166	164	192
13	176	185	163	203	166
14	195	199	176	176	167
15	193	193	173	168	152
16	197	190	175	201	166
17	160	173	156	161	163
18	190	197	172	174	165
19	185	192	170	172	176
20	186	198	171	210	169
21	181	238	167	188	156
22	193	195	170	196	158
23	208	193	177	186	180
24	186	207	173	173	177
25	196	182	167	165	177
26	196	189	171	175	161
27	172	185	162	161	168
28	173	173	163	197	177
29	199	192	173	174	169
30	184	181	166	161	152
31	183	179	172	154	153
32	177	171	163	159	180
33	128	161	150	155	148
34	128	182	164	163	154
35	195	192	169	172	177
36	188	191	173	190	157

TABLE VI

INTENSITIES OF "d" SPACINGS AT VARIOUS STATES OF CHARGE OF SINTERED POSITIVE ELECTRODES*

			"d" Spacings				
Figure	Treatment	Charge & Discharge Rate	4.50-4.70	3.77-3.73	3.58	2.71	2.32-2.36
12	200% Charge 24 Hr. Stand	1.2 Amps	28	12	--	--	--
13	200% Charge 72 Hr. Stand	1.2 Amps	30	18	--	--	--
14	10% Beyond Vigorous Gas.	1.2 Amps	25	7	--	8	11
15	20% Below Vigorous Gas.	1.2 Amps	28	8	--	--	7
16	200% Charge, 50% Discharge	1.2 Amps	24	8	--	--	12
17	200% Charge, 75% Discharge	1.2 Amps	25	7	--	--	8
18	200% Charge, Complete Discharge	1.2 Amps	30	--	5	--	6
19	200% Charge	0.150 Amps	18	--	--	--	--
20	10% Beyond Vigorous Gas.	0.150 Amps	18	--	--	--	--
21	11 Hour Charge	0.150 Amps	8	8	--	--	8
22	20% Below Vigorous Gas.	0.150 Amps	5	8	--	--	6
23	8 Hour Charge	0.150 Amps	8	--	--	--	10
24	200% Charge, 50% Discharge	0.150 Amps	5	--	--	--	8
25	200% Charge, 75% Discharge	0.150 Amps	8	--	--	--	7
26	200% Charge, Complete Discharge	0.150 Amps	4	--	--	10	8

* "d" Spacings due to Nickel and Polyethylene are not included

TABLE VII

CAPACITY ON STABILIZATION FORMATION

Cell No.	Cycle #1	Cycle #2	Cycle #3	Rate	Temp.
1	.95AH	.99AH	.98AH	500 ma	25°C
2	.99AH	1.04AH	1.04AH	500 ma	25°C
3	.98AH	1.04AH	1.03AH	500 ma	25°C
4	1.03AH	1.06AH	1.04AH	100 ma	25°C
5	1.01AH	1.03AH	1.00AH	100 ma	25°C
6	1.02AH	1.04AH	1.00AH	100 ma	25°C
7	.83AH	.80AH	.81AH	35 ma	25°C
8	.84AH	.81AH	.80AH	35 ma	25°C
9	.83AH	.80AH	.78AH	35 ma	25°C
10	.28AH	.49AH	.59AH	500 ma	80°C
11	.29AH	.48AH	.59AH	500 ma	80°C
12	.28AH	.50AH	.64AH	500 ma	80°C
13	.64AH	.68AH	.69AH	100 ma	80°C
14	.59AH	.64AH	.66AH	100 ma	80°C
15	.60AH	.71AH	.65AH	100 ma	80°C
16	.40AH	.68AH	--	35 ma	80°C
17	.48AH	.70AH	--	35 ma	80°C
18	.47AH	.68AH	--	35 ma	80°C
19	.94AH	.90AH	.96AH	500 ma	10°C
20	.94AH	.96AH	.97AH	500 ma	10°C
21	.91AH	.91AH	.91AH	500 ma	10°C
22	.95AH	.99AH	--	100 ma	10°C
23	.96AH	1.01AH	--	100 ma	10°C
24	.98AH	1.05AH	--	100 ma	10°C

TABLE VIII

QUANTATIVE ANALYSIS VIA SPECTROGRAPH OF M-2 GRAPHITE FLAKE

IMPURITY	RELATIVE AMOUNT
Aluminum	0.5 %
Barium	0.002%
Calcium	0.02 %
Cobalt	0.001%
Copper	0.002%
Iron	0.5 %
Magnesium	0.02 %
Manganese	0.01 %
Molybdenum	0.002%
Silicon	1% - 10%
Titanium	0.005%
Vanadium	0.005%

TABLE IX

X-RAY "d" SPACINGS OF X-RAY SAMPLE COMPONENTS*

$Ni(OH)_2$	Polyethylene	Sintered Plate	Sintered Plate Covered With Polyethylene
4.56	4.10		
2.69			4.12
2.34		2.03	2.03
1.56		1.76	1.76
1.48		1.24	1.24

KOH WETTED SINTERED PLATE COVERED WITH POLYETHYLENE	KOH WETTED SINTERED PLATE
4.12	
4.53	2.03
2.47	1.76
2.03	1.24
1.76	
1.24	

* "d" Spacings given in angstrom units

TABLE X

X-RAY "d" SPACINGS AND INTENSITIES OF SINTERED PLATES ON 3 MONTHS STORAGE AT 10, 25 and 50°C

Figure	Temperature	
6	25°C	4.61(20) - 2.37(10) - 2.72(5) - 1.57(5)
7	50°C	4.59(19) - 2.34(10) - 1.57(6) - 1.47(8)
8	10°C	4.49(22 - 2.33(5)

* "d" Spacings given in angstrom units

Relative intensities indicated by Parentheses

TABLE XI

INTENSITIES OF "d" SPACINGS OBTAINED FROM SINTERED POSITIVE ELECTRODES DURING CHARGE, OVERCHARGE AND OPEN CIRCUIT STAND

		"d" Spacings				
Figure	Treatment	6.95	4.40-4.50	3.73-3.62	2.94	2.66
14	Charge 50 ma	--	16	8	--	--
15	Overcharge 50 ma	72	15	8	--	--
16	Initial Opened Circuit	18	18	6	5	8
17	Opened Circut - 16 Hours	--	20	7	--	--

* "d" Spacings due to Nickel and Polyethylene are not included

TABLE XII

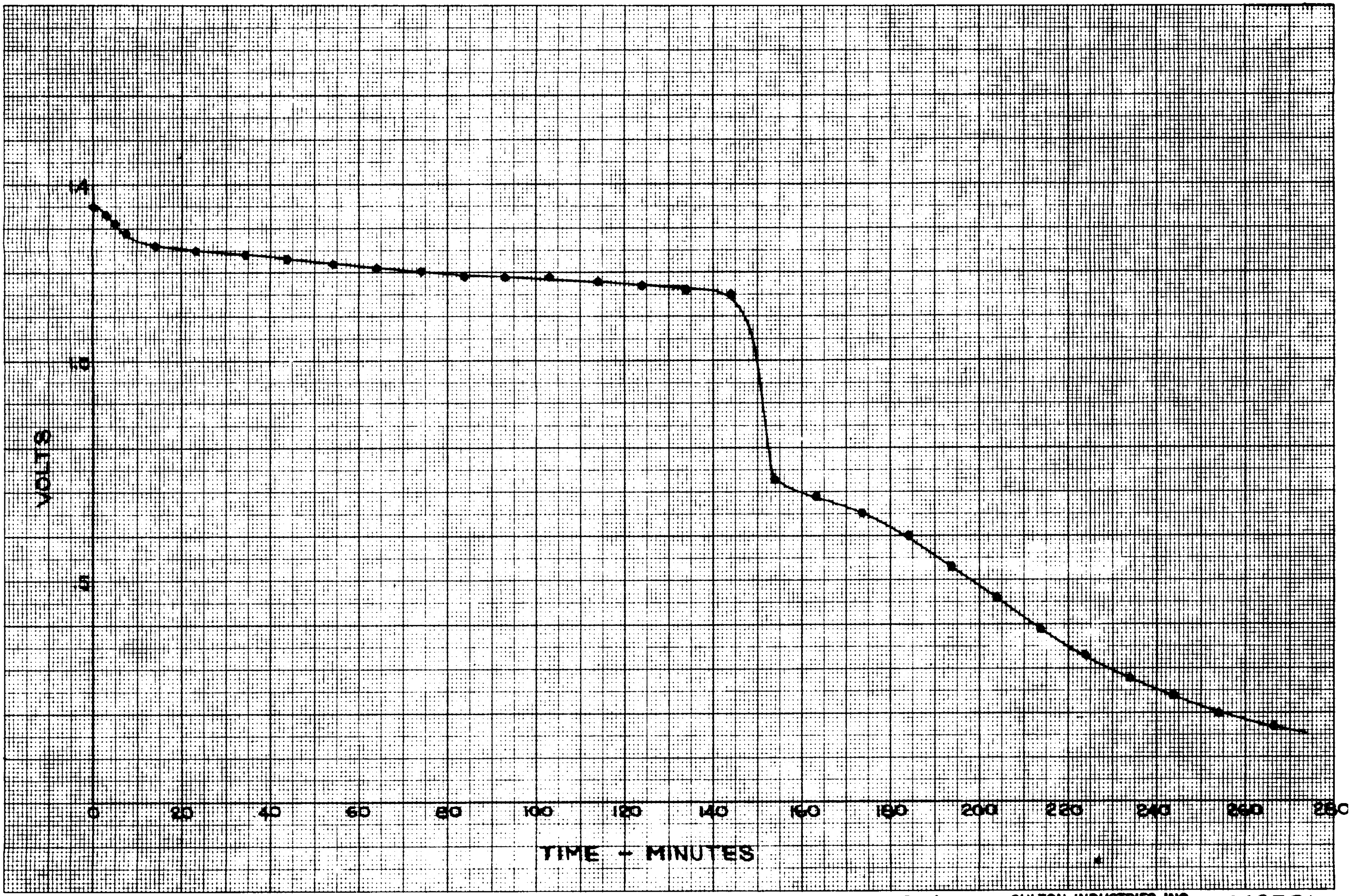
"d" SPACINGS AND INTENSITIES FROM SINTERED POSITIVE ELECTRODE DURING CHARGE, OVERCHARGE AND EXTENDED OPEN CIRCUIT STAND (FIGURES 23 - 28)

Time On Charge at 120 ma	"d" Spacings and Intensities*
Initial	4.66(20) - 3.62(10)
3 Hours	6.90(6) - 4.66(26) - 3.70(13)
6 Hours	6.95(22) - 6.79(37) - 4.60(18) - 3.77(10) - 3.41(10) - 2.97(25) 2.33(13)
Open Circuit	
Initial	6.97(23) - 6.79(35) - 4.60(22) - 3.77(8) - 3.41(10) - 2.97(10) 2.33(27) - 2.30(15)
3 Hours	6.79(45) - 4.60(22) - 3.77(8) - 3.41(17) - 2.97(12) - 2.33(50) 2.30(15)
65 Hours	7.35(22) - 6.79(25) - 4.53(18) -3.77(40) - 3.41(45)
168 Hours	7.62(15) - 4.66(30) - 3.85(23) - 3.67(12) - 2.36(11)

* "d" Spacings given in angstrom units

Relative intensities indicated by parentheses

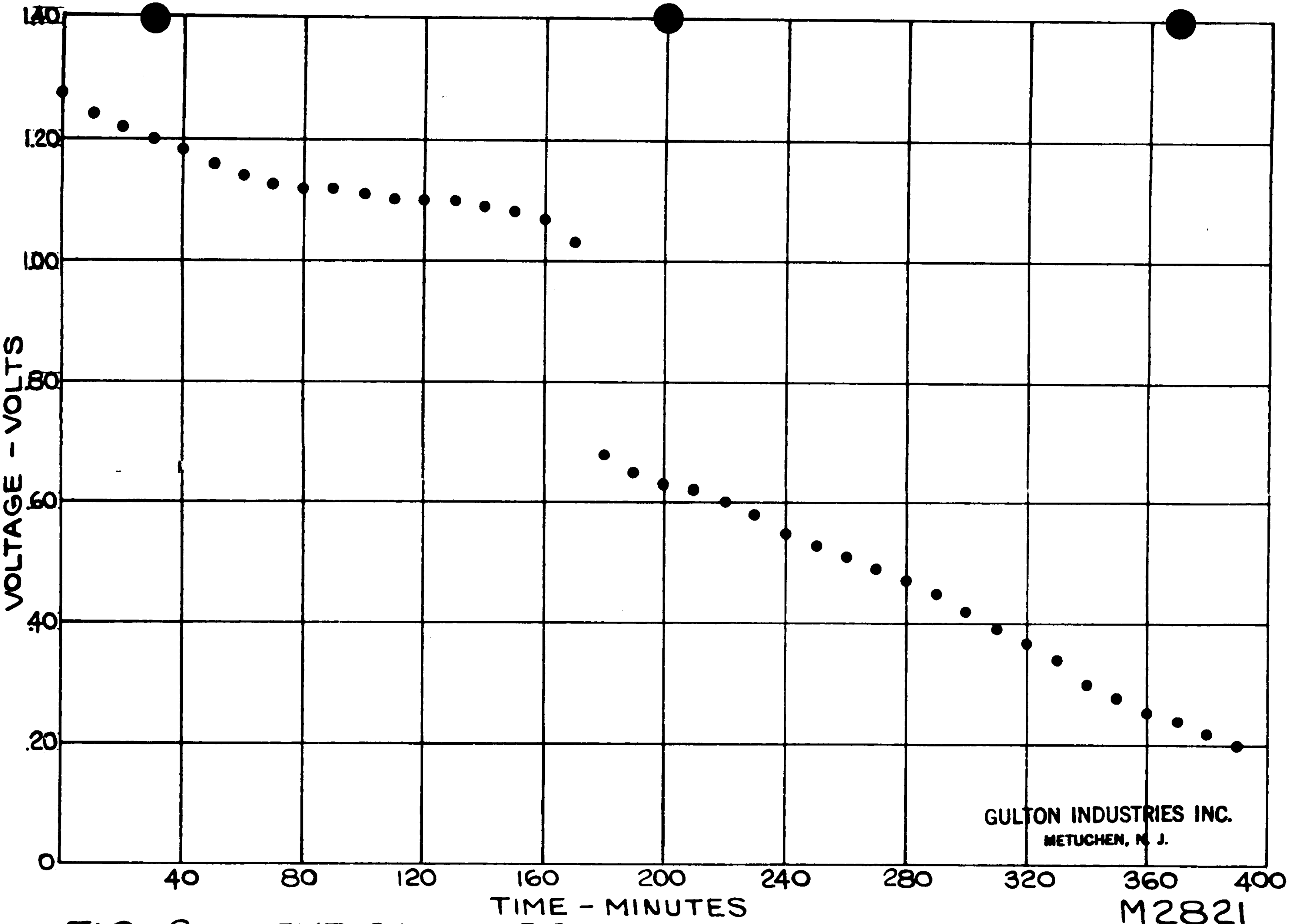
FIG. 1



TYPICAL DISCHARGE CURVE CONSTANT LOAD = 2.4Ω
CELL 7, CYCLE 2

GULTON INDUSTRIES INC.
METUCHEN, N. J.

M2581
AB5400



M2821

FIG. 2 TYPICAL DISCHARGE CURVE TUBULAR PLATE CELL
DISCHARGED THRU 22Ω RESISTOR TO 0.2 VOLTS

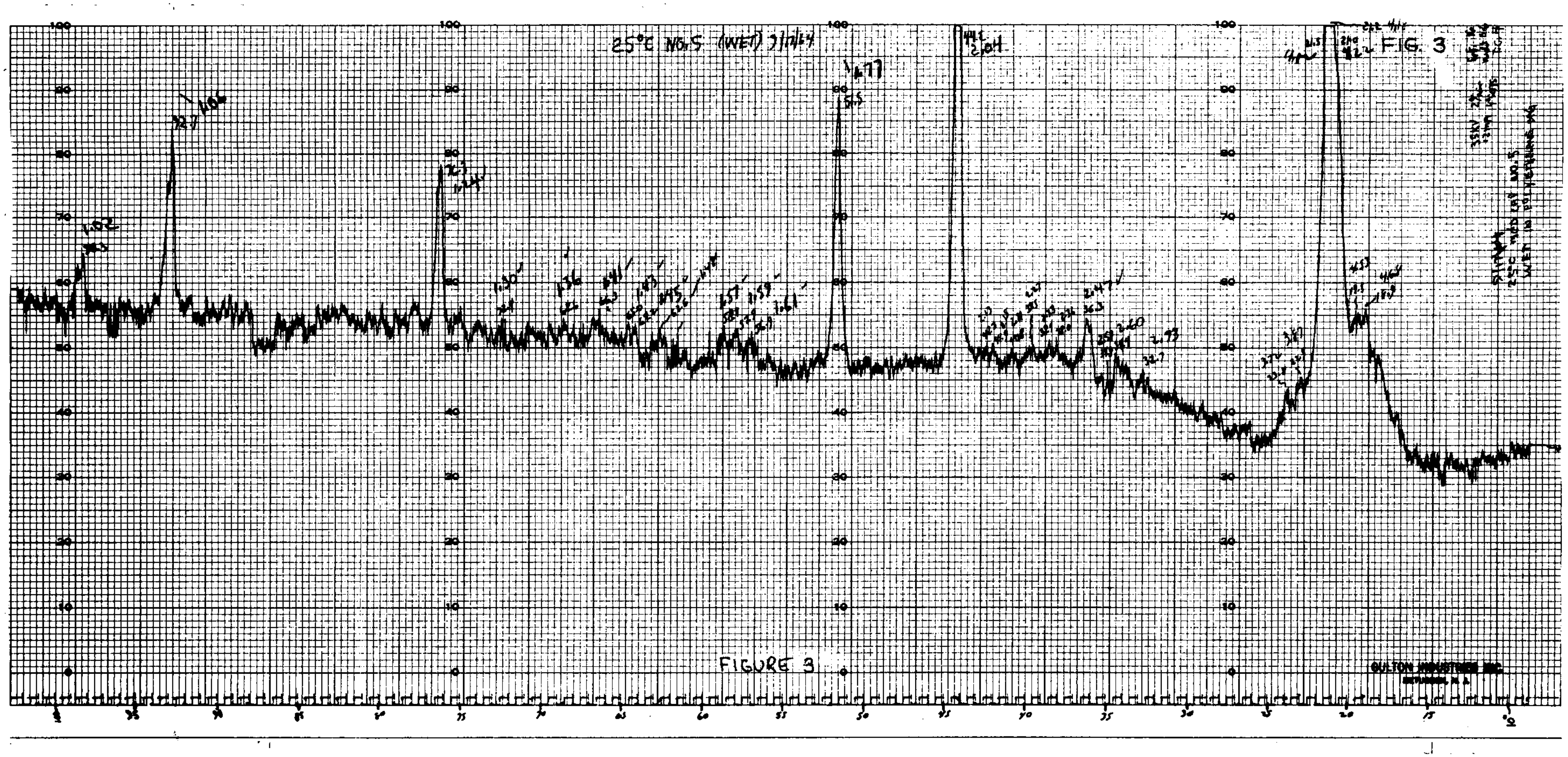


FIGURE 3. X-RAY PATTERN OF INITIAL CHARGED STAND AT 25°C

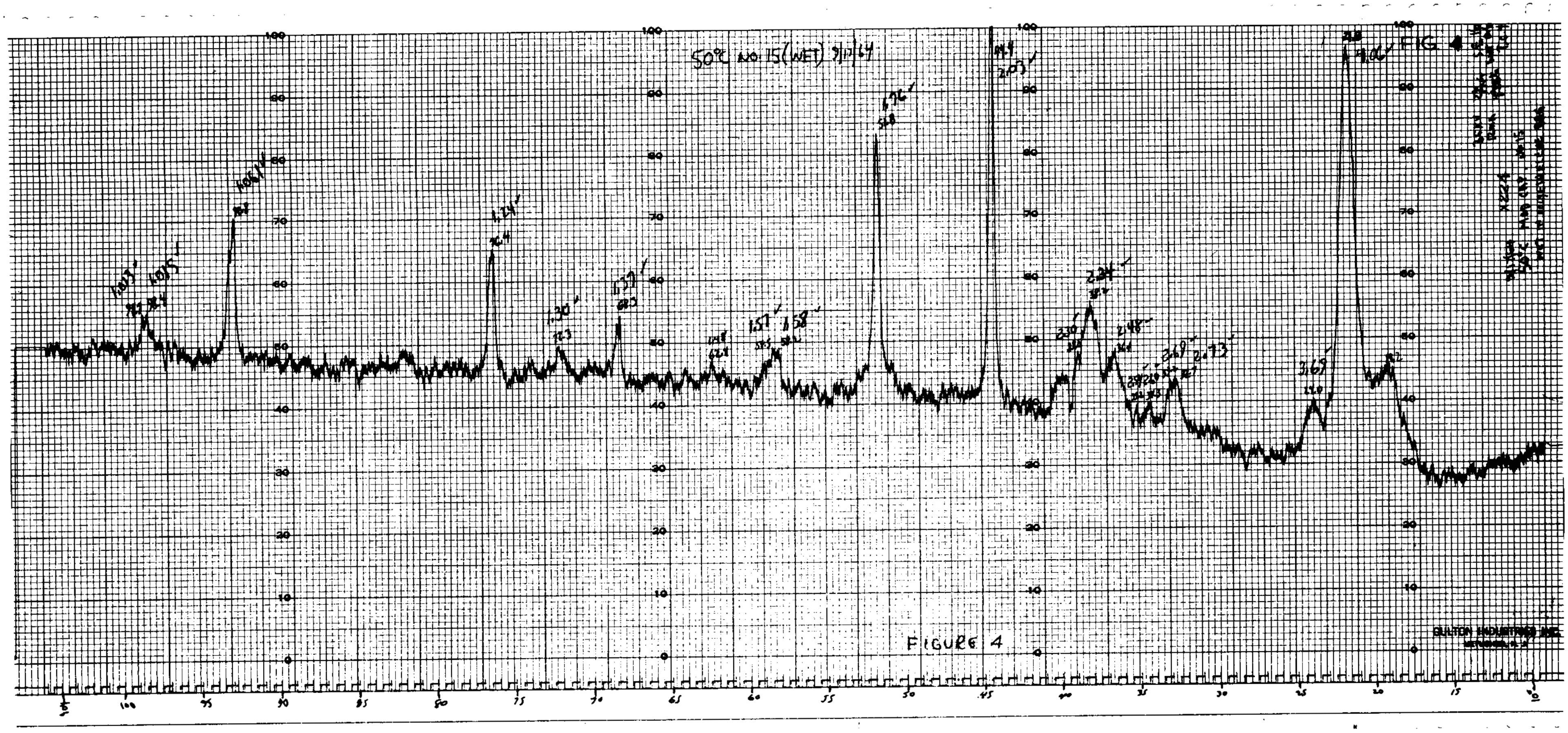


FIGURE 4. X-RAY PATTERN OF INITIAL CHARGED STAND AT 50°C

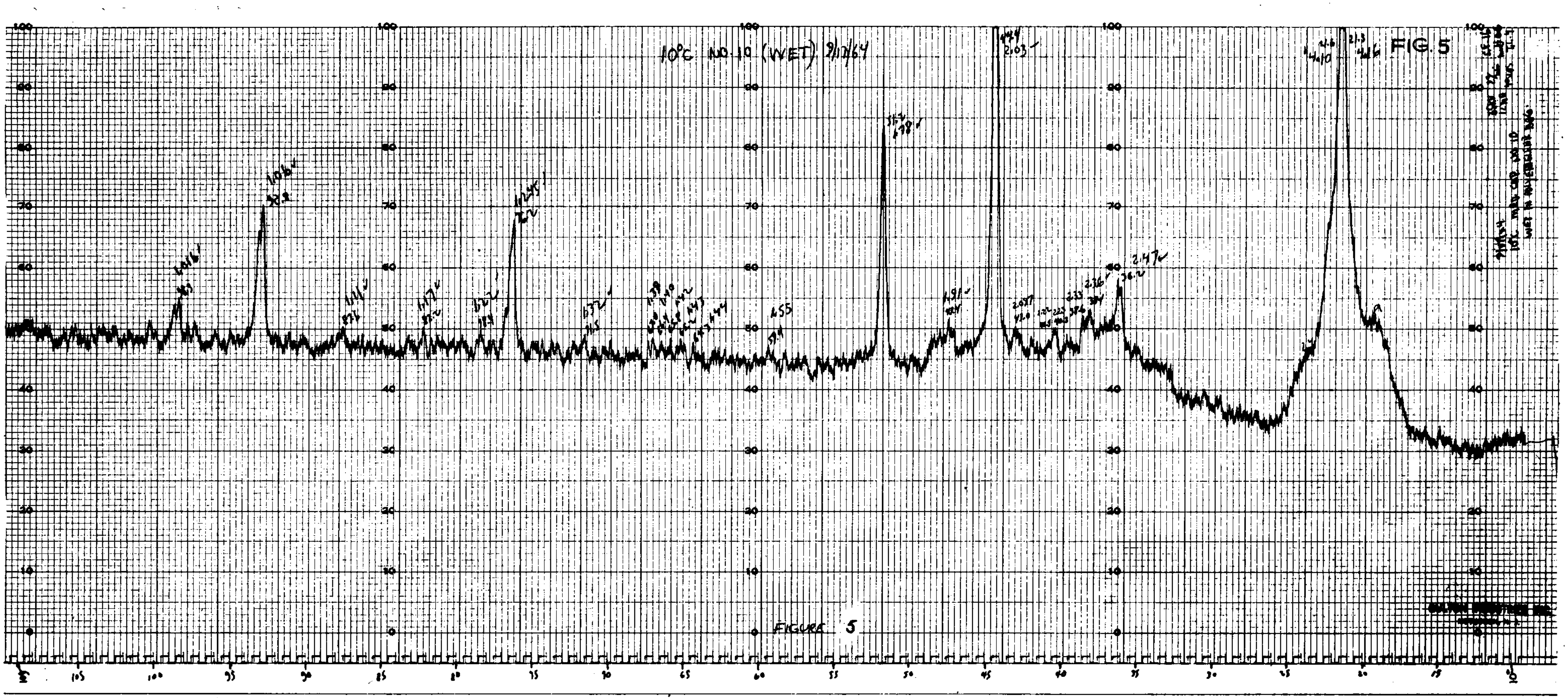


FIGURE 5. X-RAY PATTERN OF INITIAL CHARGED STAND AT 10°C

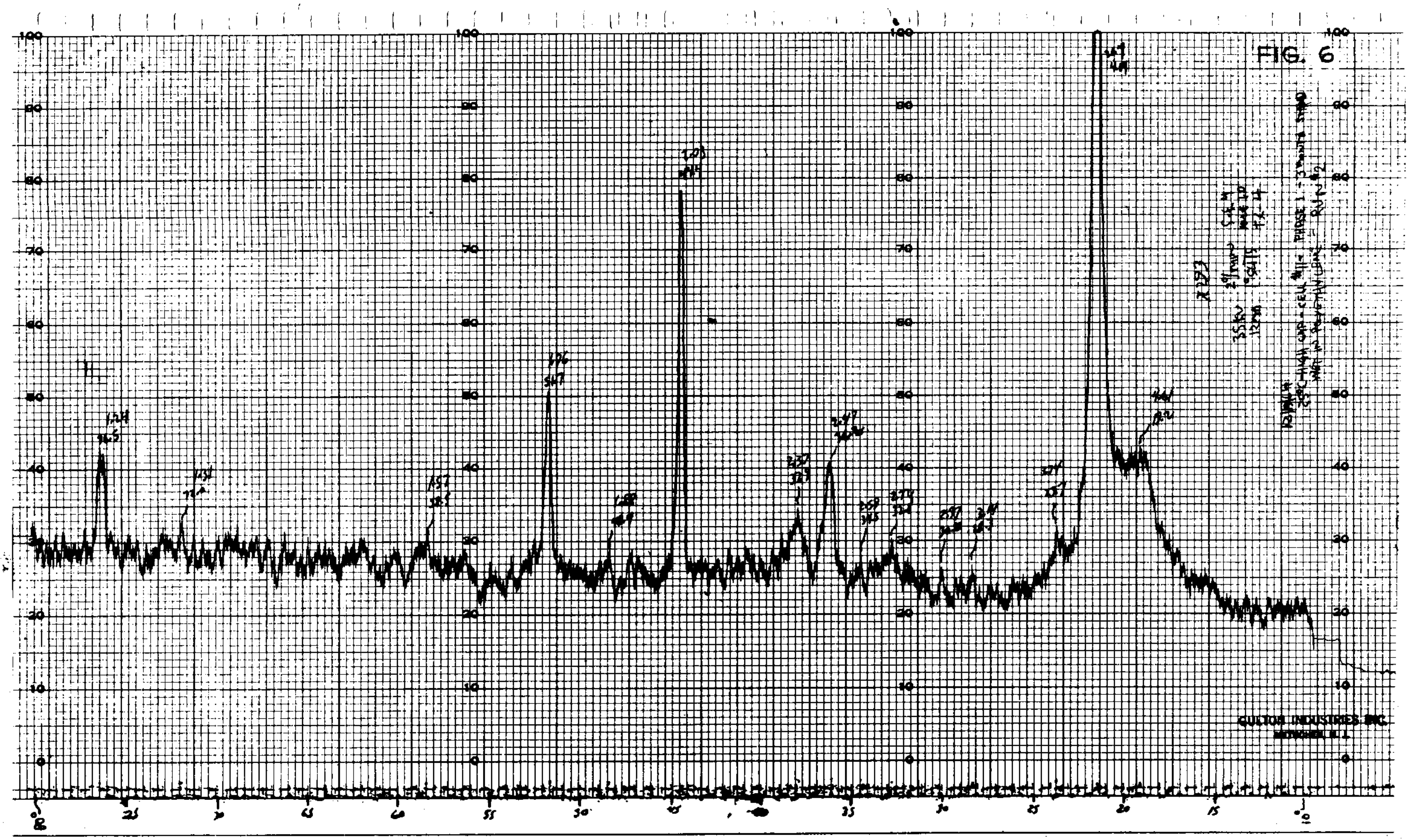


FIGURE 6. X-RAY PATTERN OF 3 MONTH CHARGED STAND AT 25°C

FIG. 7

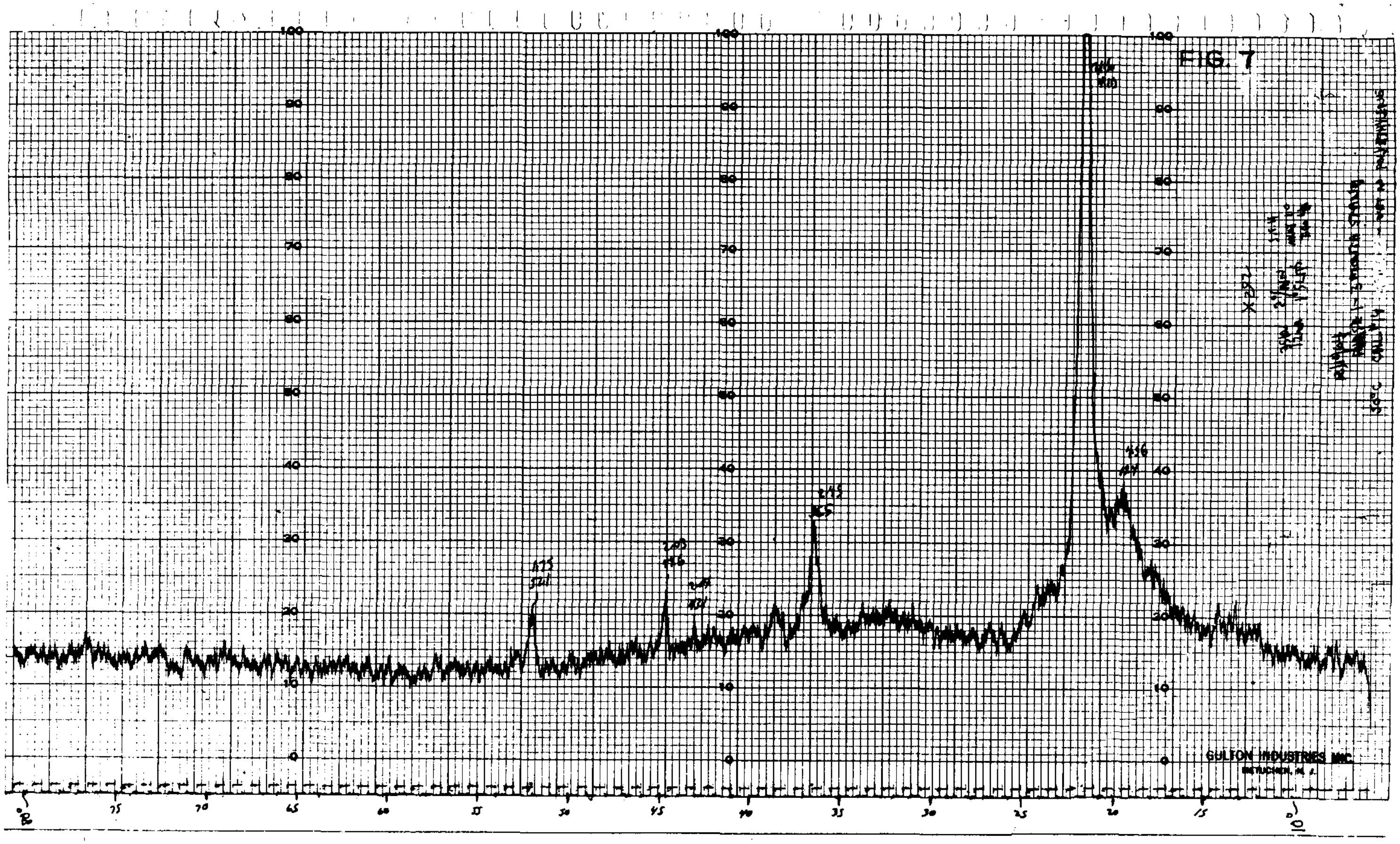


FIGURE 7. X-RAY PATTERN OF 3 MONTH CHARGED STAND AT 50°C

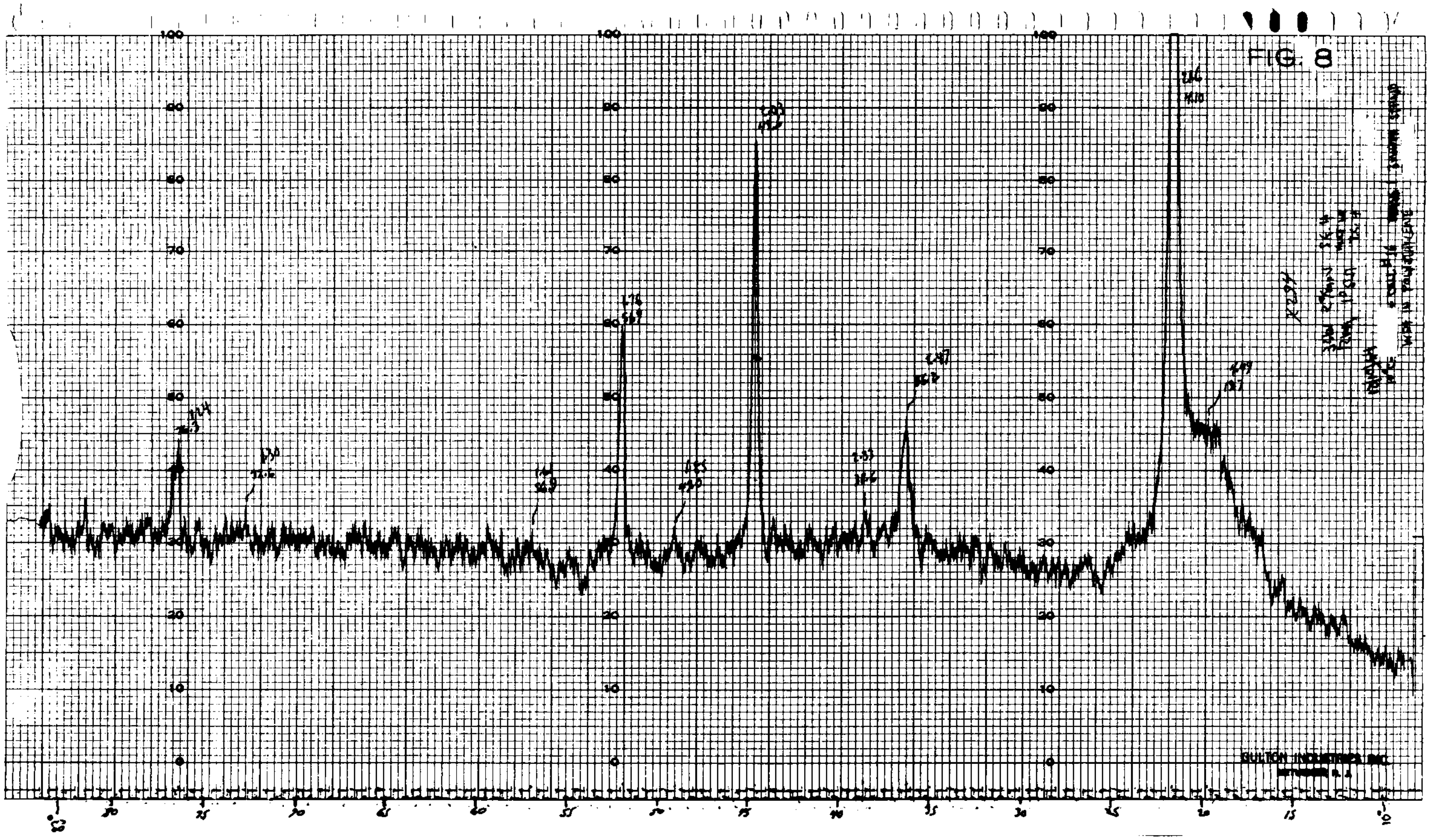
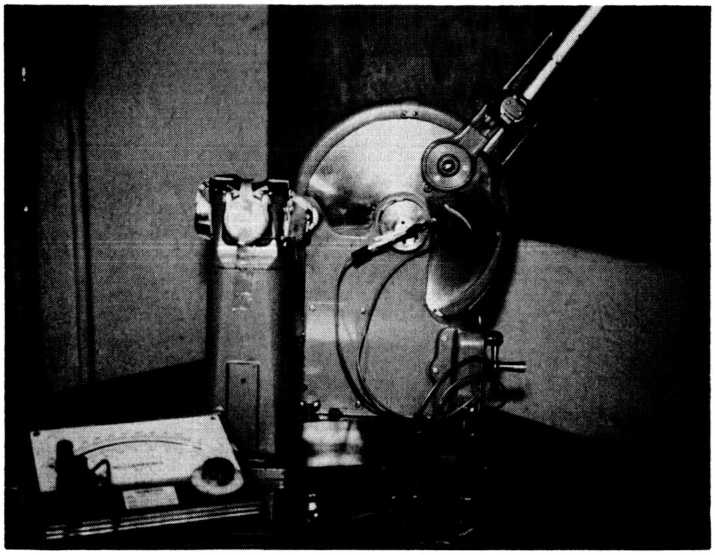
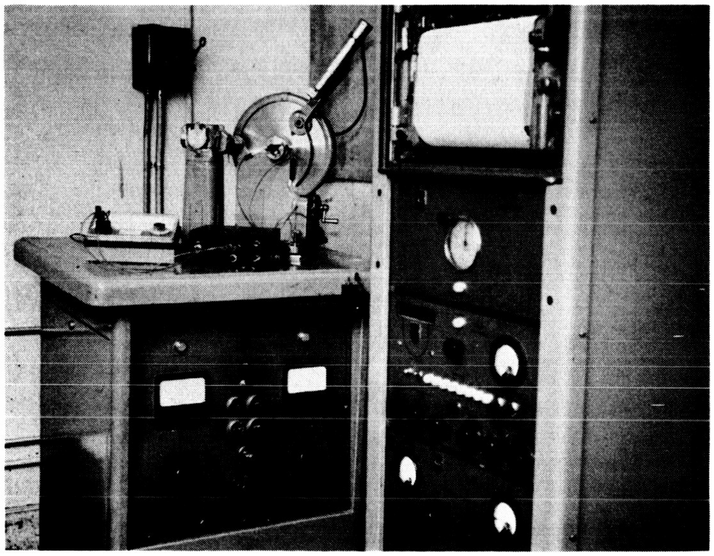


FIGURE 8. X-RAY PATTERN OF 3 MONTH CHARGED STAND AT 10°C

UNSTABLE NICKEL OXIDE EXPERIMENTAL SETUP



CLOSE-UP SHOWING CHARGER, METER, CELL AND GONIOMETER



LONG SHOT SHOWING X-RAY APPARATUS
RECORDER, CHARGER, METER, AND CELL

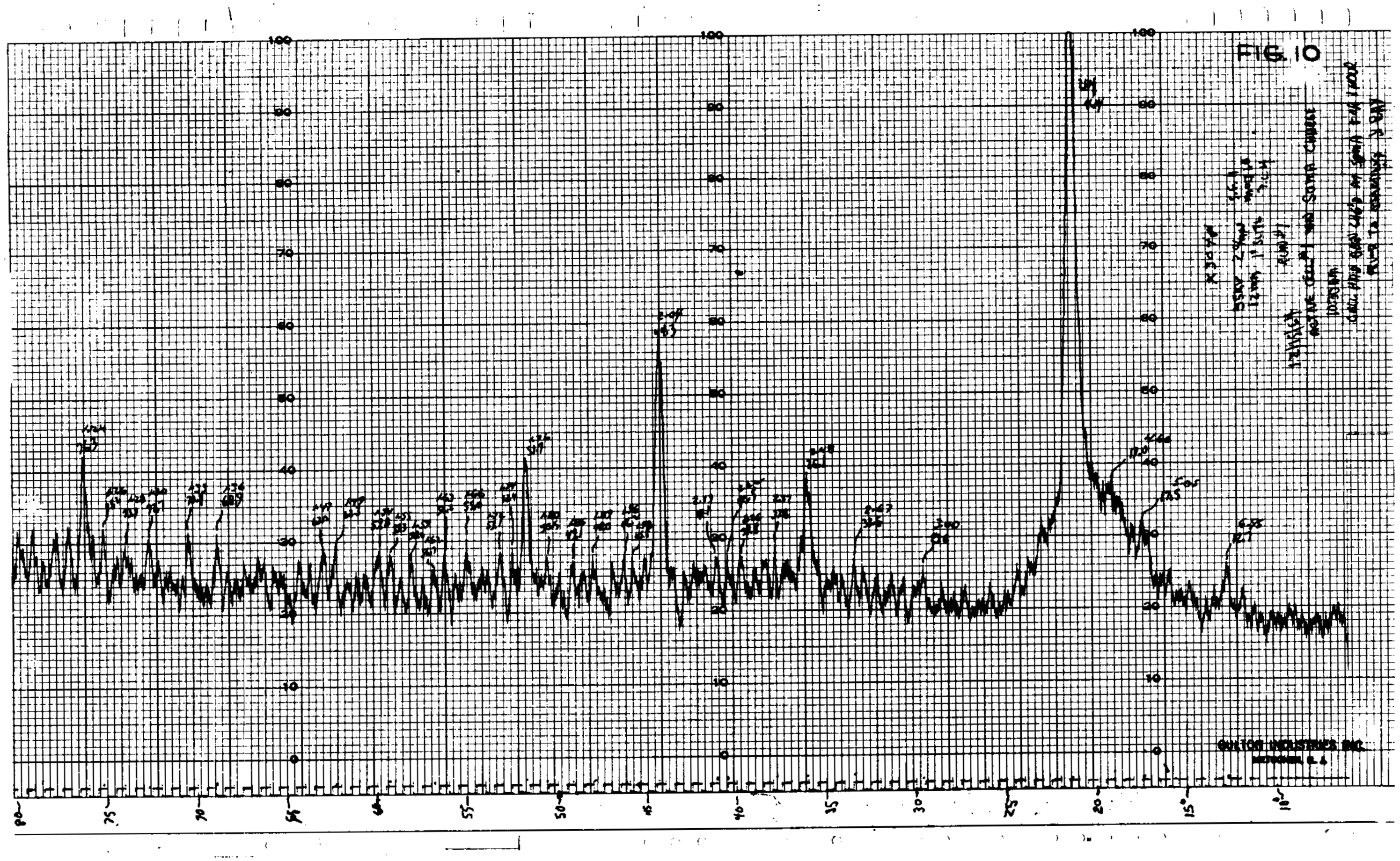


FIGURE 10. X-RAY PATTERNS OF INITIAL SWEEP SINTERED PLATE POSITIVE ELECTRODE WHILE ON CHARGE AT 50 MA

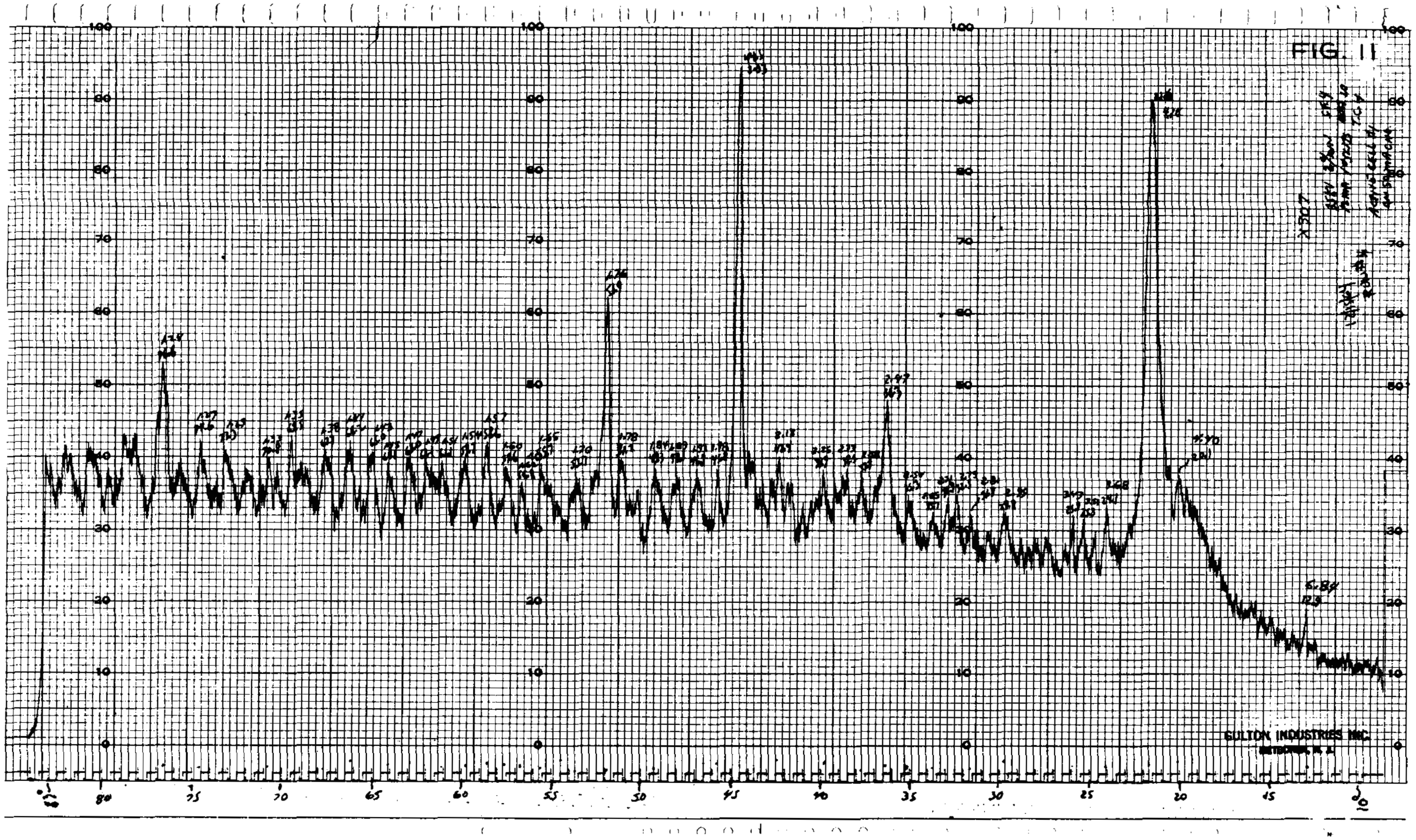


FIGURE 11. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE FINAL SWEEP OF OVERCHARGE CELL ON CHARGE AT 50 MA

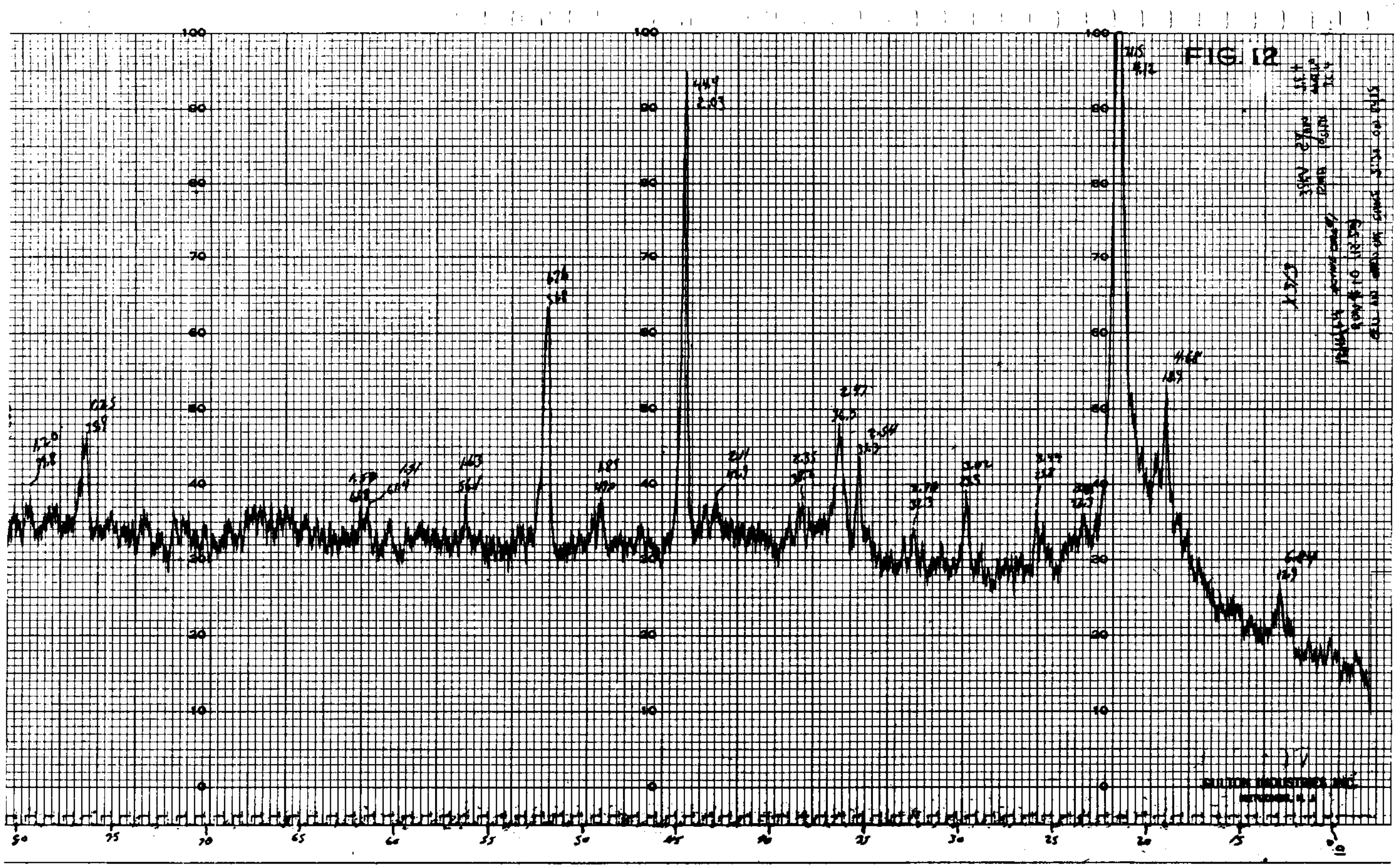


FIGURE 12. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE AFTER OPEN CIRCUIT STAND

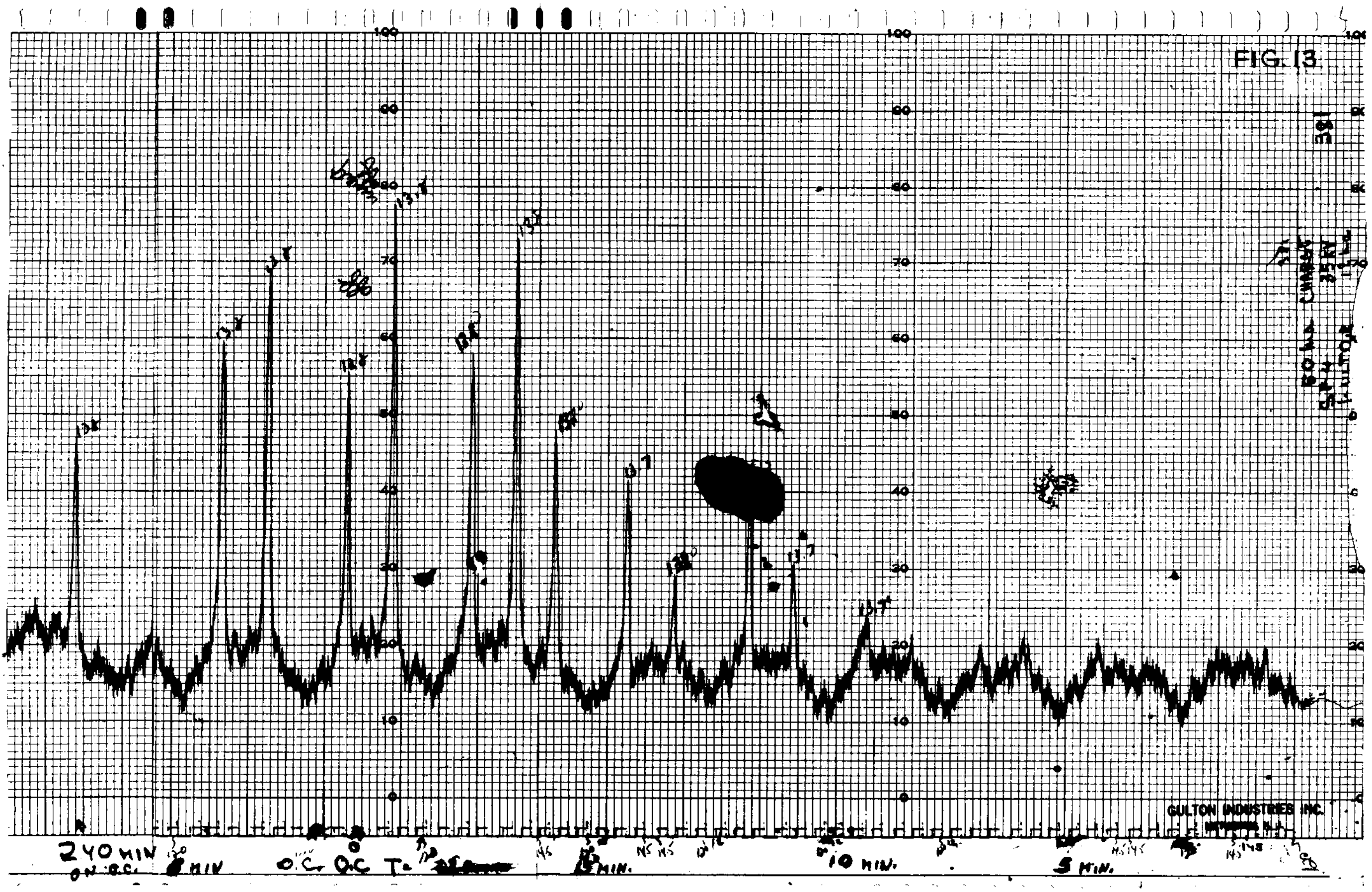


FIGURE 13. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODES DURING CHARGE AT 50 MA AND FOLLOWING OPEN CIRCUIT SWEEP BETWEEN $2\theta = 12^\circ$ to 14.5°.

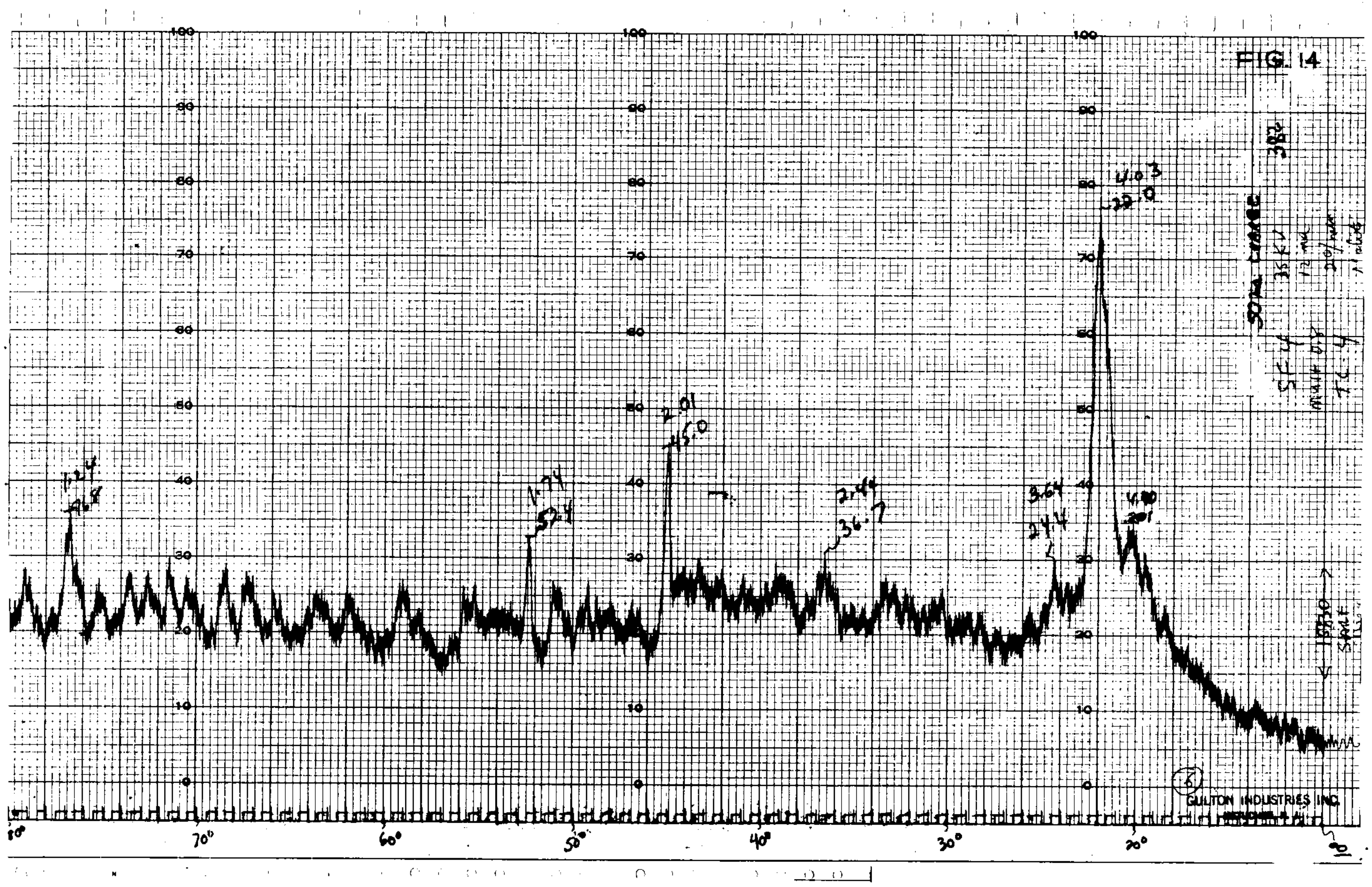


FIG. 14

FIGURE 14. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE BETWEEN 2θ = 10° to 80° WHILE ON CHARGE AT 50 MA

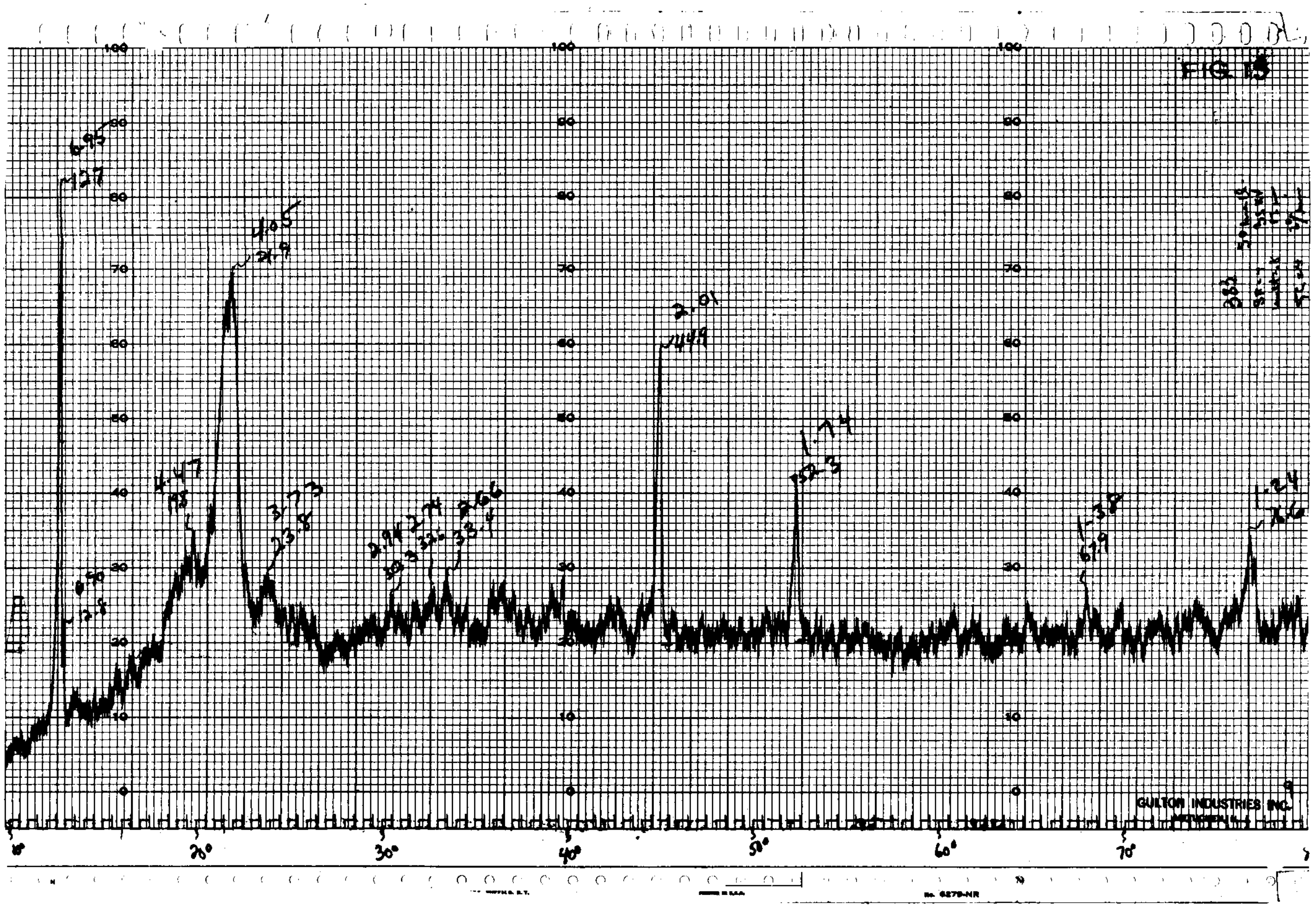


FIGURE 15. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE BETWEEN $2\theta = 10^{\circ}$ to 80° ON CHARGE AT 50 MA FOR 140 MINUTES

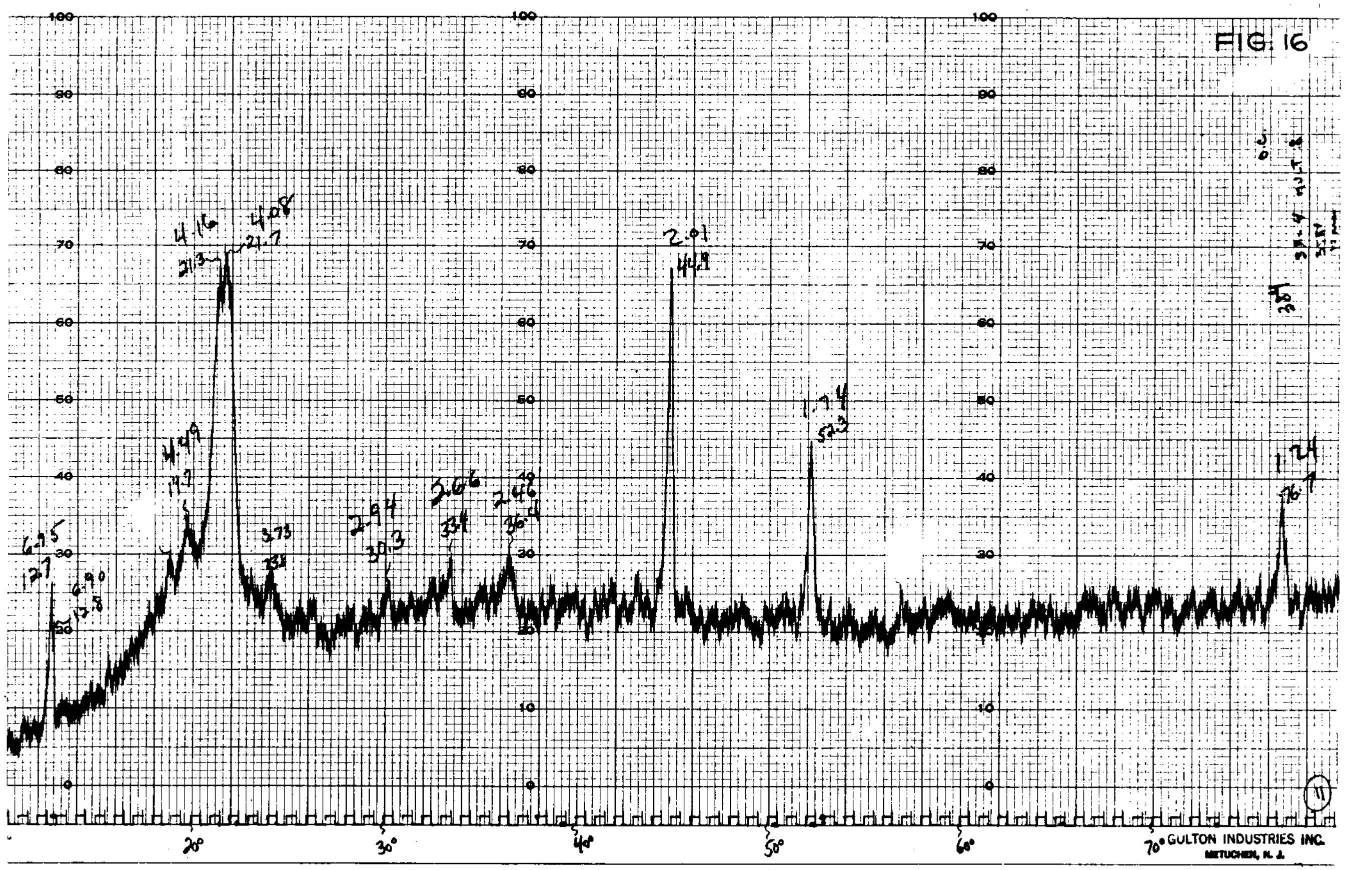


FIGURE 16. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE BETWEEN $2\theta = 10^{\circ}$ to 80° ON INITIAL OPEN CIRCUIT

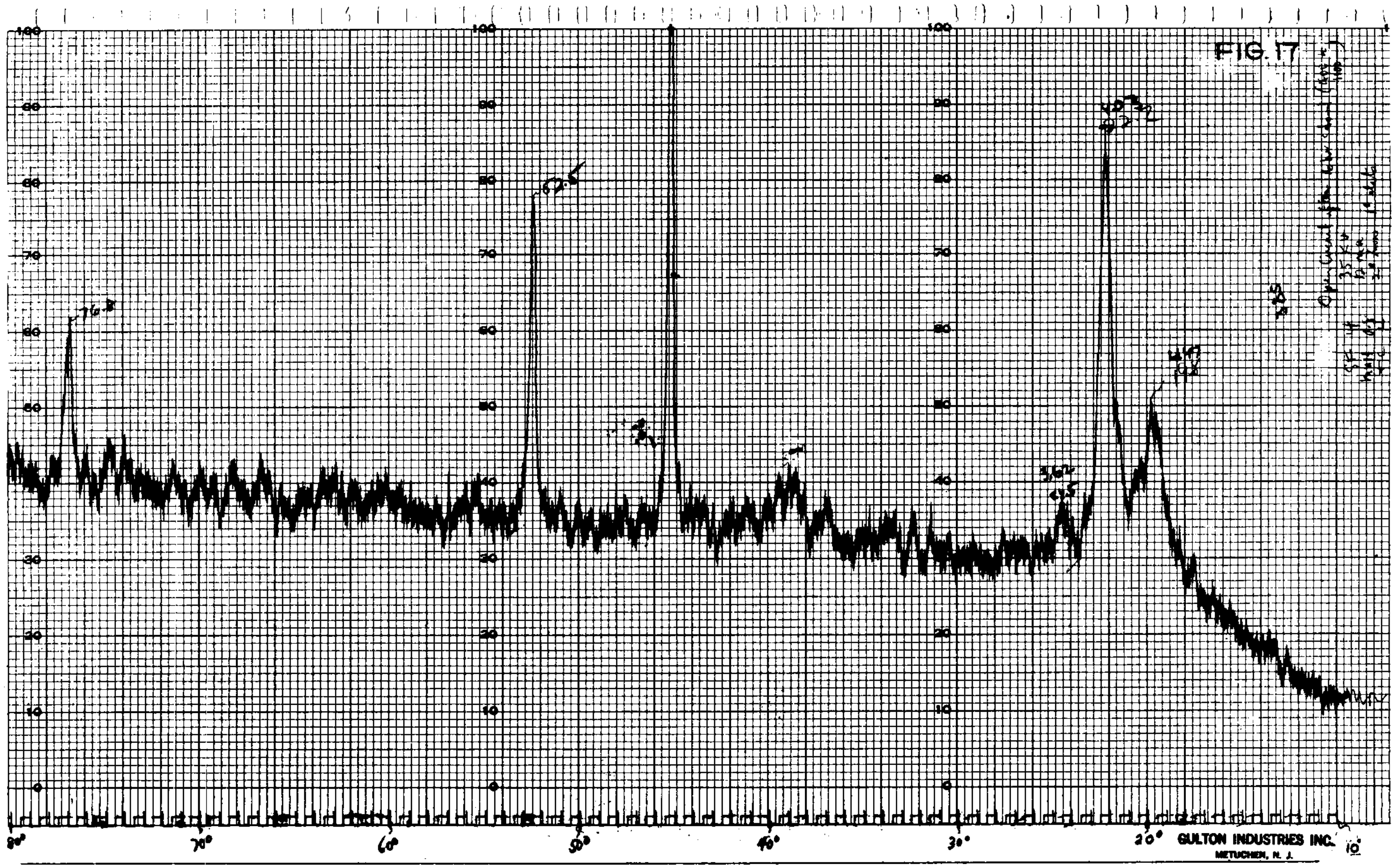


FIGURE 17. X-RAY PATTERN OF SINTERED PLATE POSITIVE ELECTRODE BETWEEN $2\theta = 10^{o}$ to 80^{o} AFTER 16 HOURS ON OPEN CIRCUIT

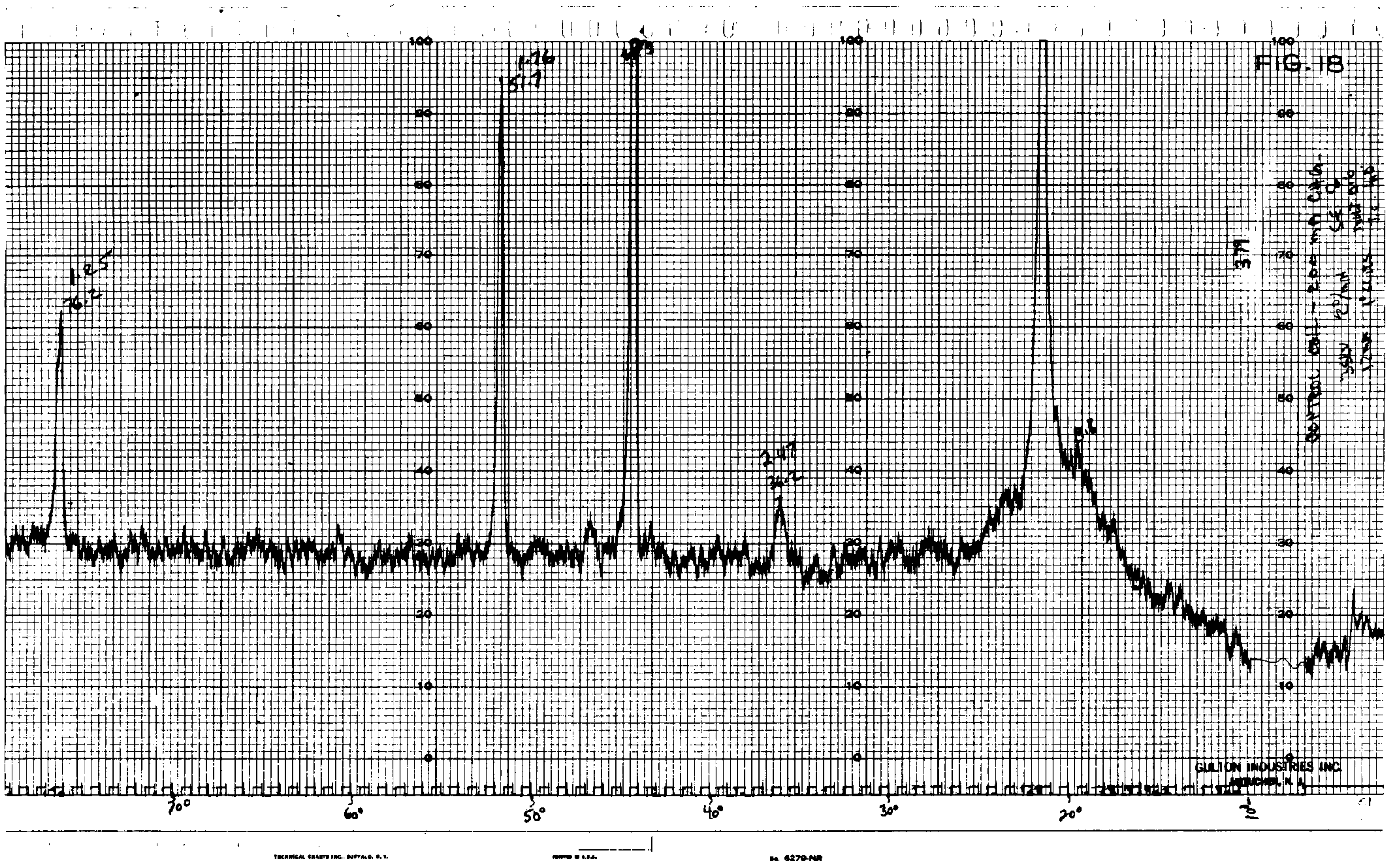


FIGURE 18. X-RAY PATTERN FOR UNIMPREGNATED SINTERED PLATE DURING INITIAL CHARGE

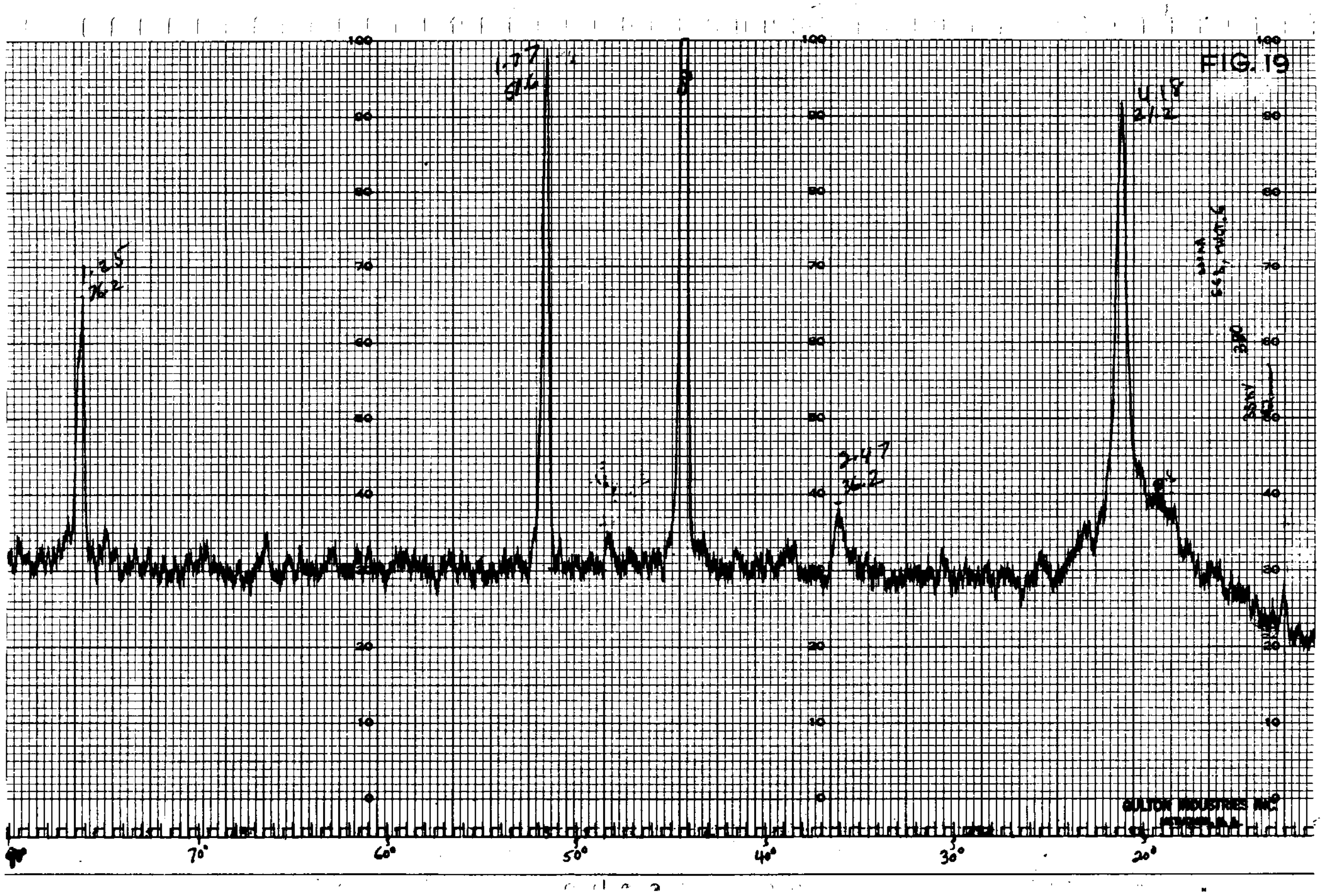


FIGURE 19. X-RAY PATTERN FROM UNIMPREGNATED SINTERED PLATE AFTER BEING ANODIZED FOR 4 HOURS

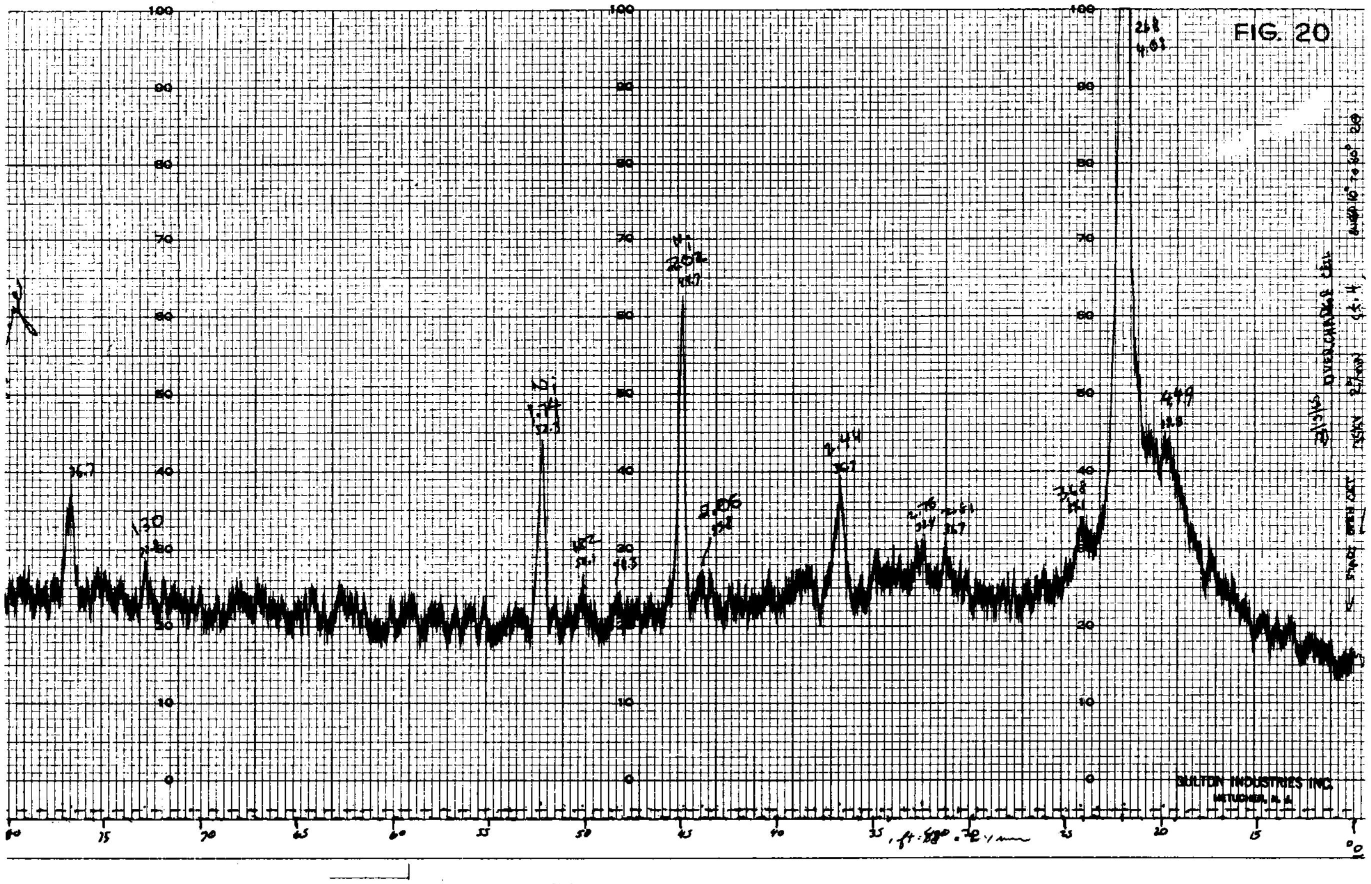


FIG. 20

FIGURE 20. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE ON OPEN CIRCUIT

FIG. 21

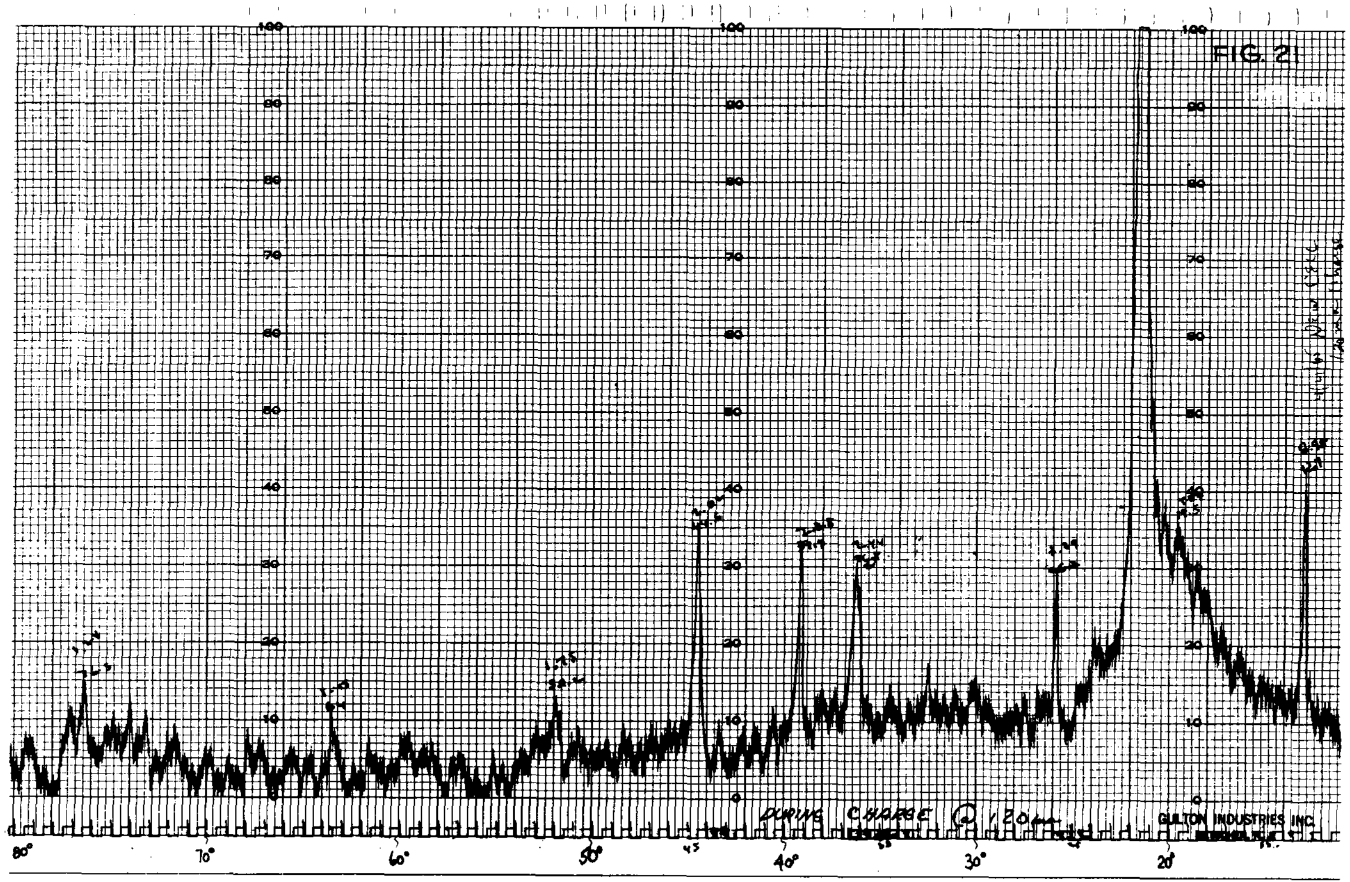


FIGURE 21. X-RAY PATTERNS OF ENLARGED CELL POSITIVE ELECTRODE DURING OVERCHARGE AT 120 MA

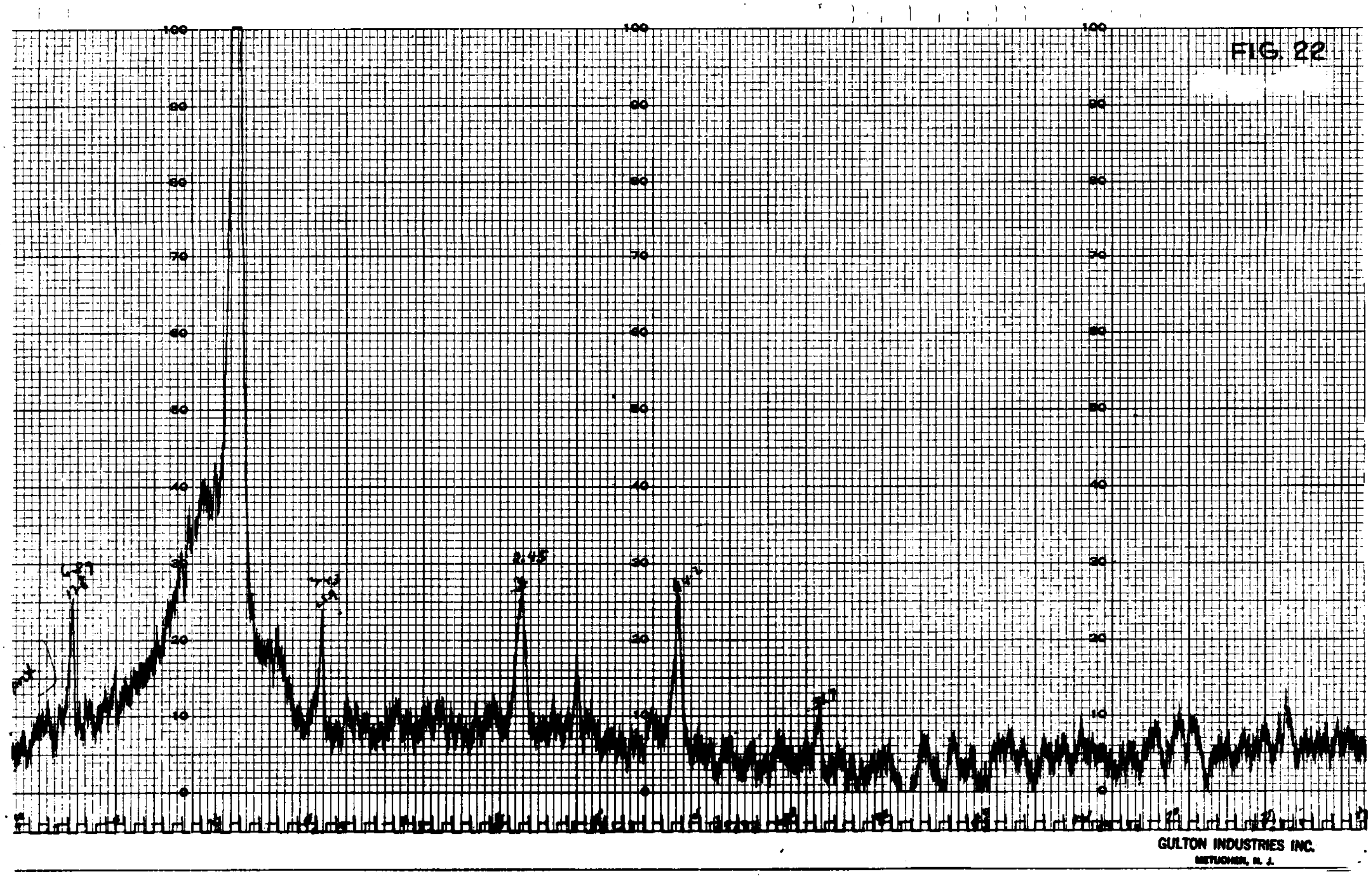


FIG. 22

FIGURE 22. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE AFTER AN ADDITIONAL 2 HOURS OF OVERCHARGE

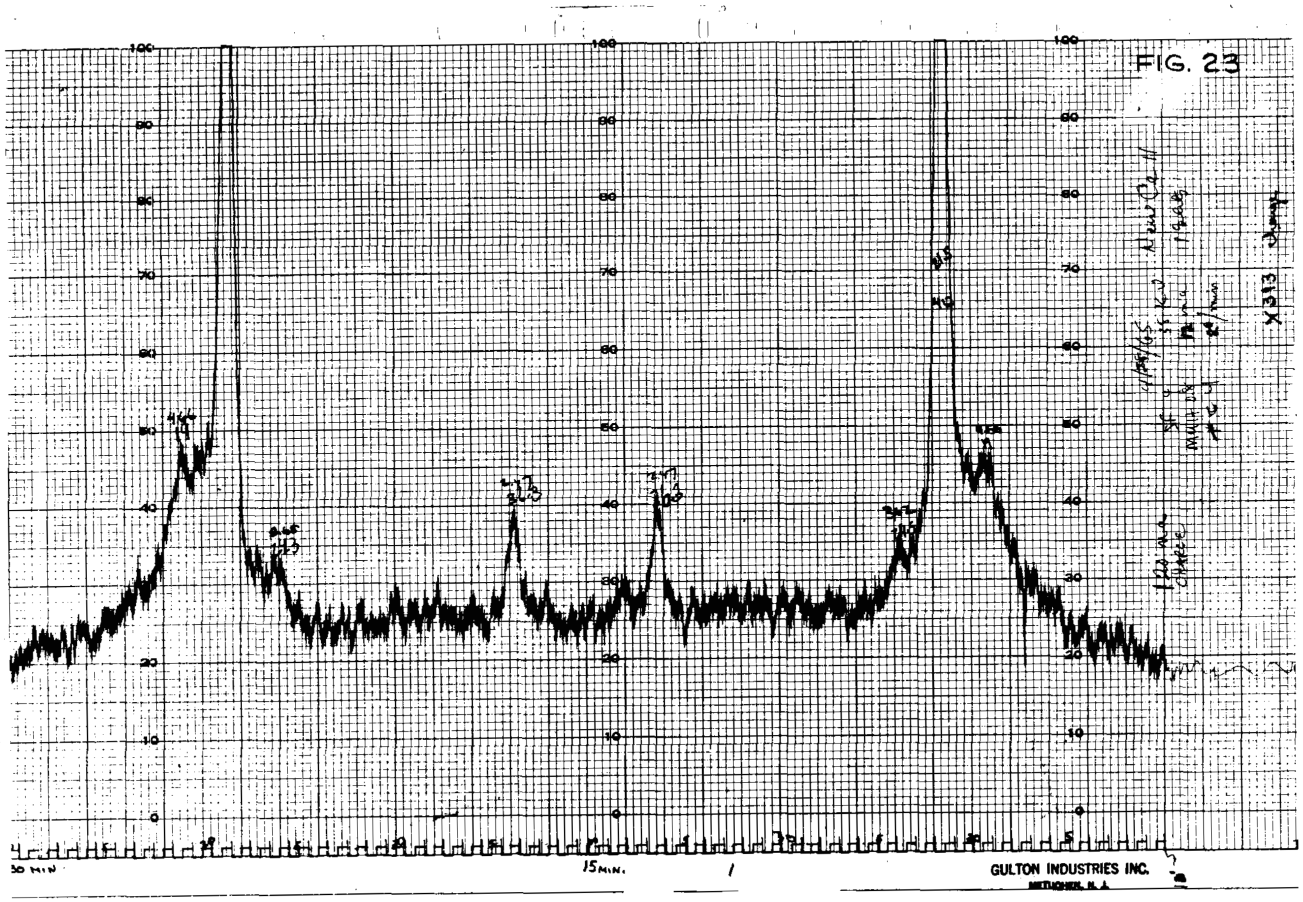


FIGURE 23. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE - TWO SWEEPS BETWEEN 2θ = 10° to 40° DURING INITIAL CHARGE

FIG. 24

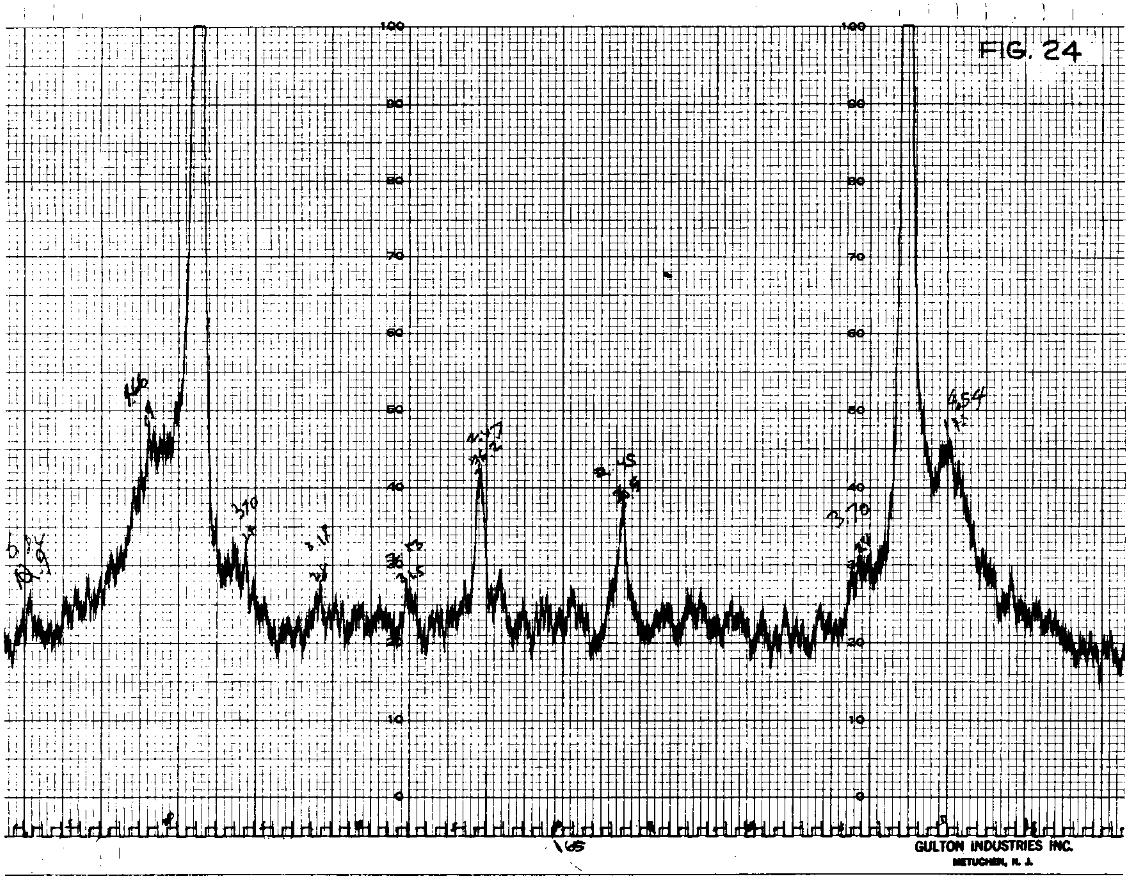


FIGURE 24. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE - TWO SWEEPS BETWEEN $2\theta = 10^{\circ}$ to 40° AFTER 3 HOURS OF CHARGE

FIG. 25

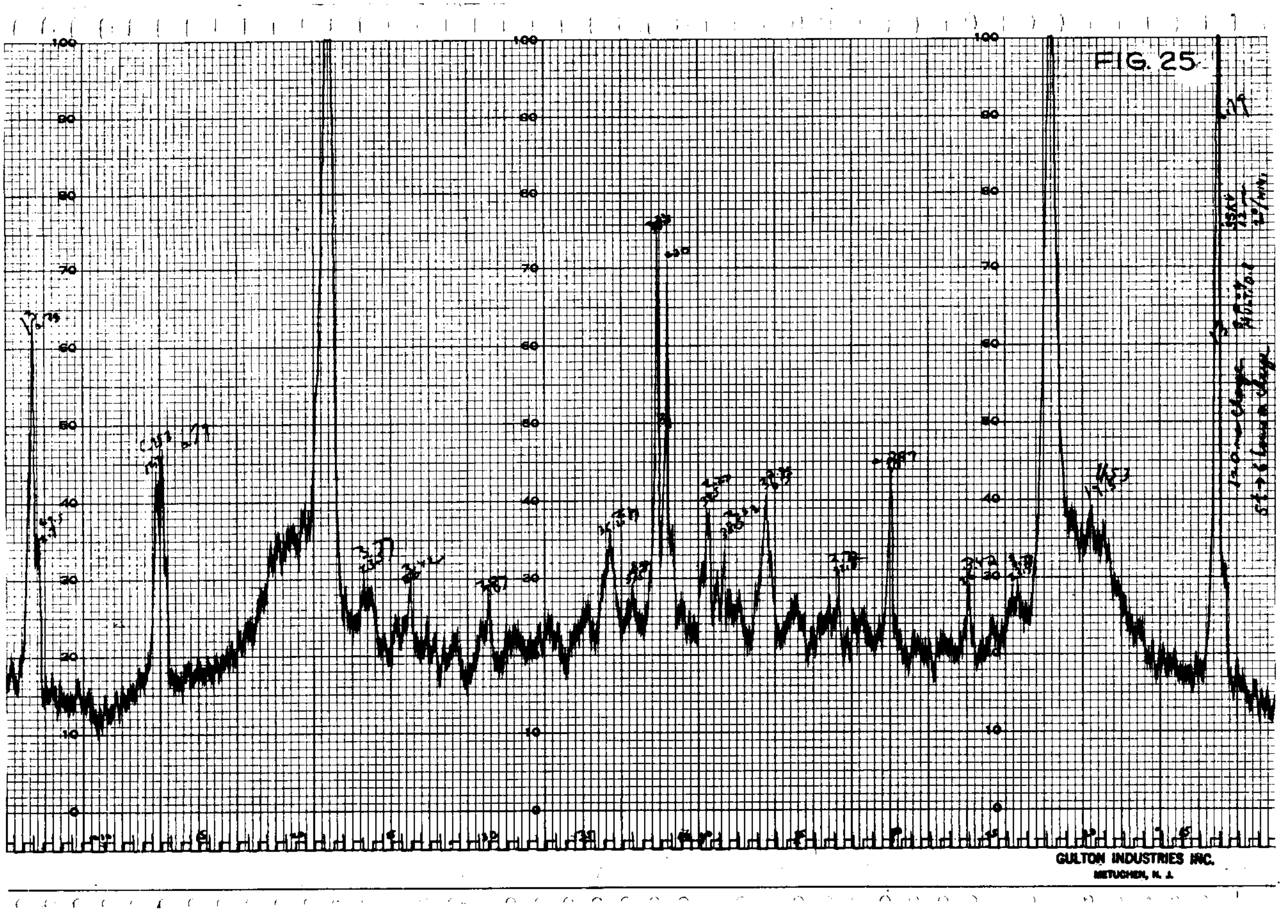


FIGURE 25. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE - TWO SWEEPS BETWEEN $2\theta = 10^\circ$ to 40° AFTER 6 HOURS OF CHARGE

FIG. 26

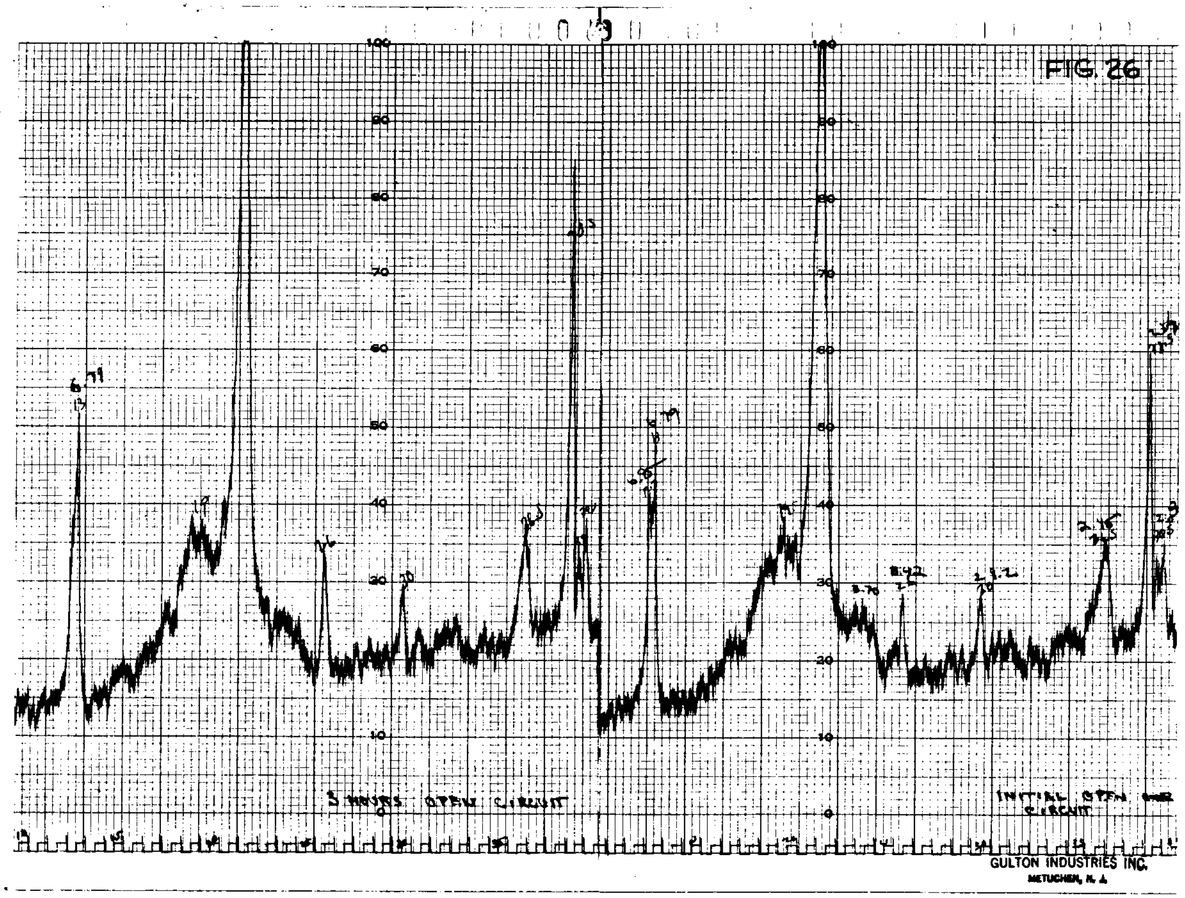


FIGURE 26. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE BETWEEN $2\theta = 10^{o}$ to 40^{o} ON INITIAL OPEN CIRCUIT AND AFTER 3 HOURS OPEN CIRCUIT STAND

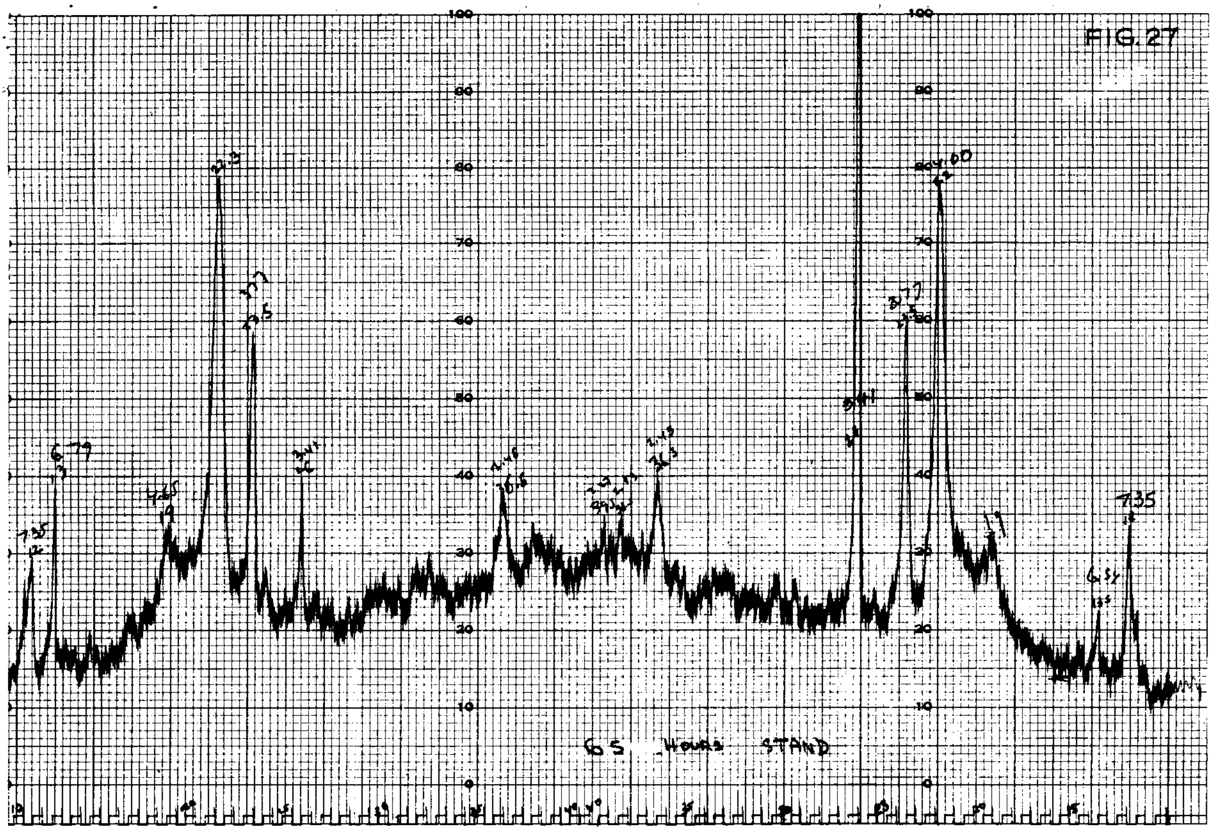


FIGURE 27. X-RAY PATTERN OF ENLARGED CELL POSITIVE ELECTRODE - TWO SWEEPS BETWEEN 2θ = 10° to 40° AFTER 65 HOURS OPEN CIRCUIT STAND

FIG. 28

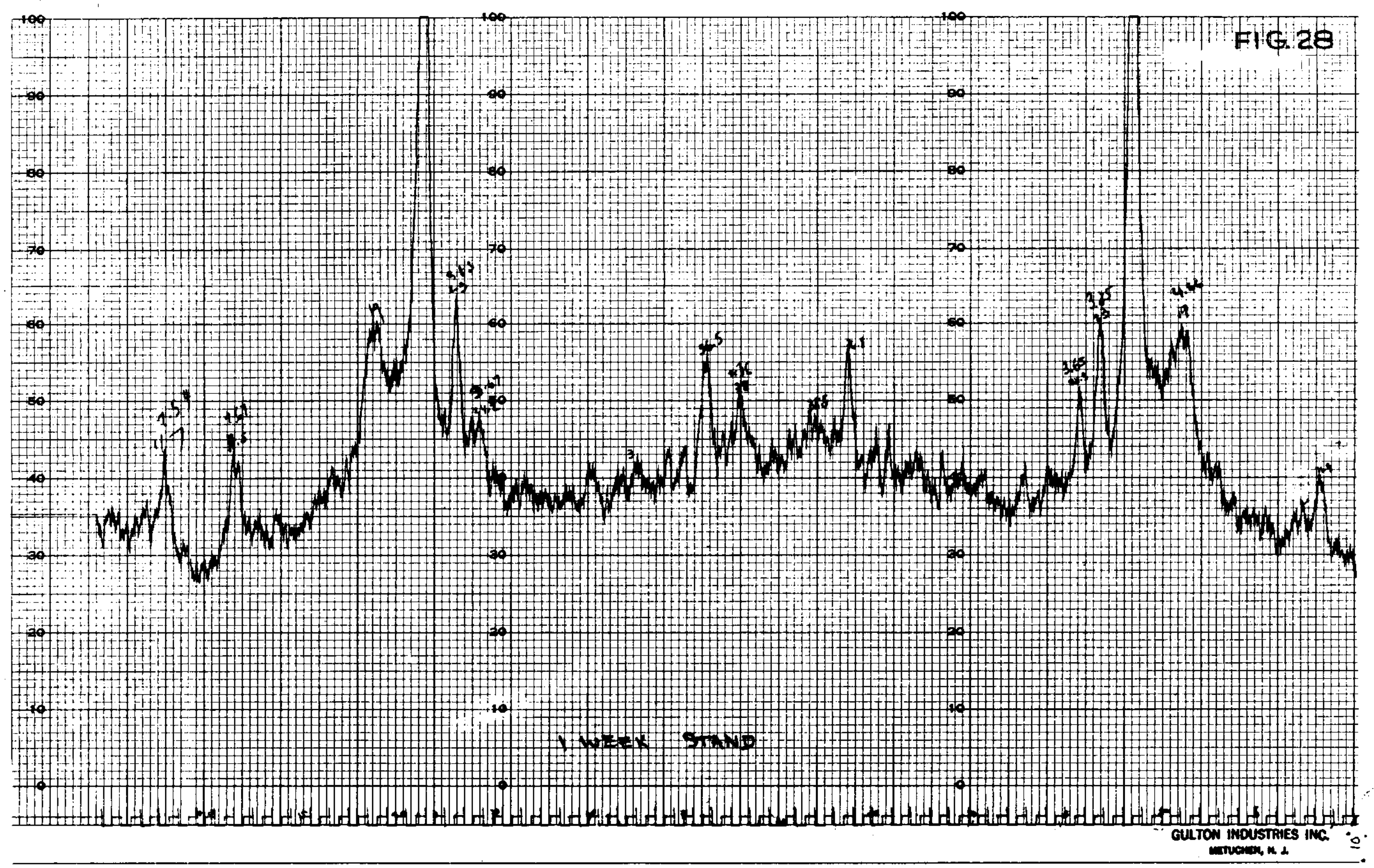


FIGURE 28. X-Ray PATTERN OF ENLARGED CELL POSITIVE ELECTRODE - TWO SWEEPS BETWEEN 2θ = 10° to 40° AFTER 1 WEEK OPEN CIRCUIT STAND

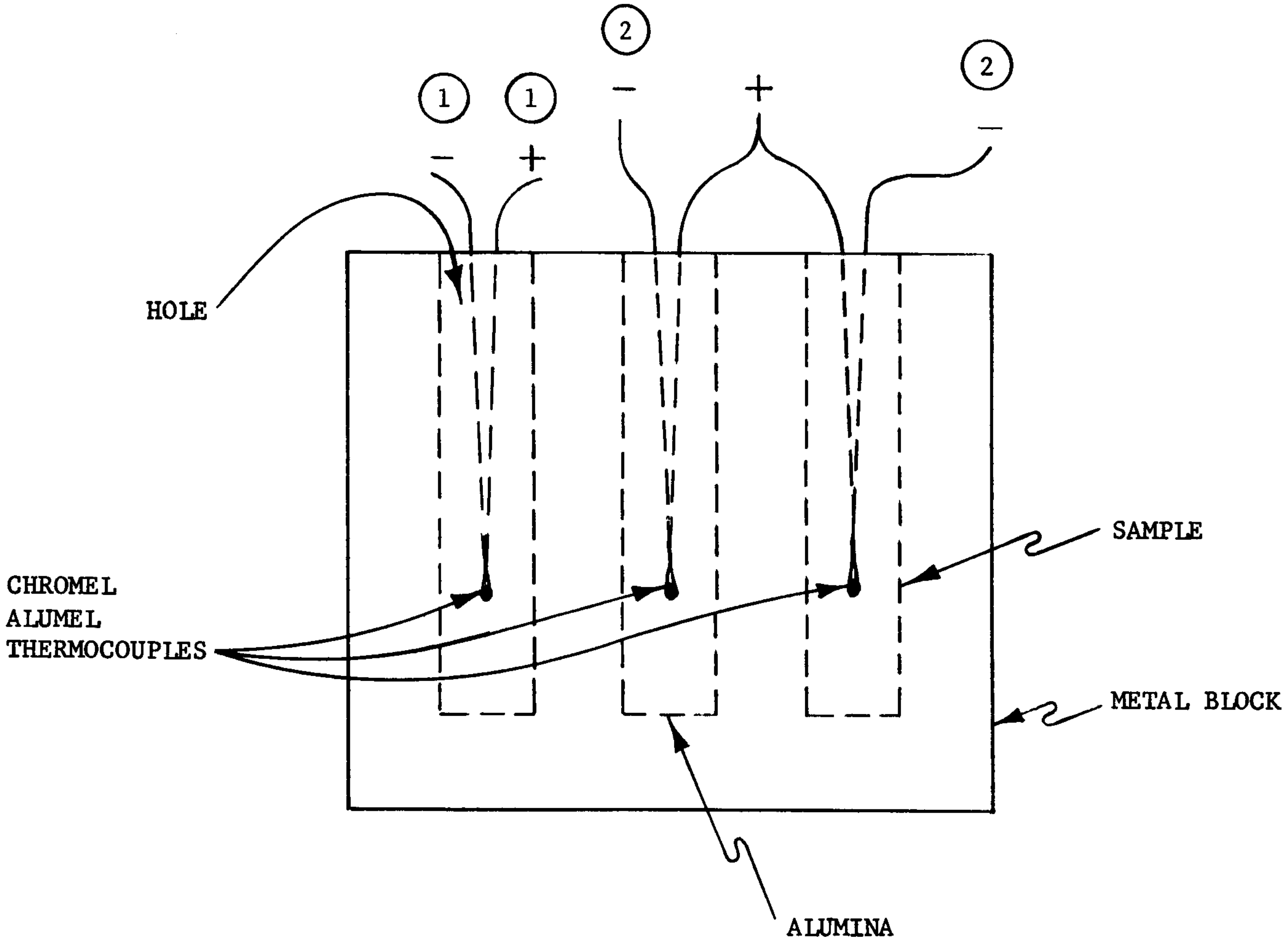


Fig. 29 - D.T.A. HEATING BLOCK
1-1 To Abscissa of the X-Y Recorder
2-2 To Ordinate of the X-Y Recorder

M2646
AB8400

FIG. 30

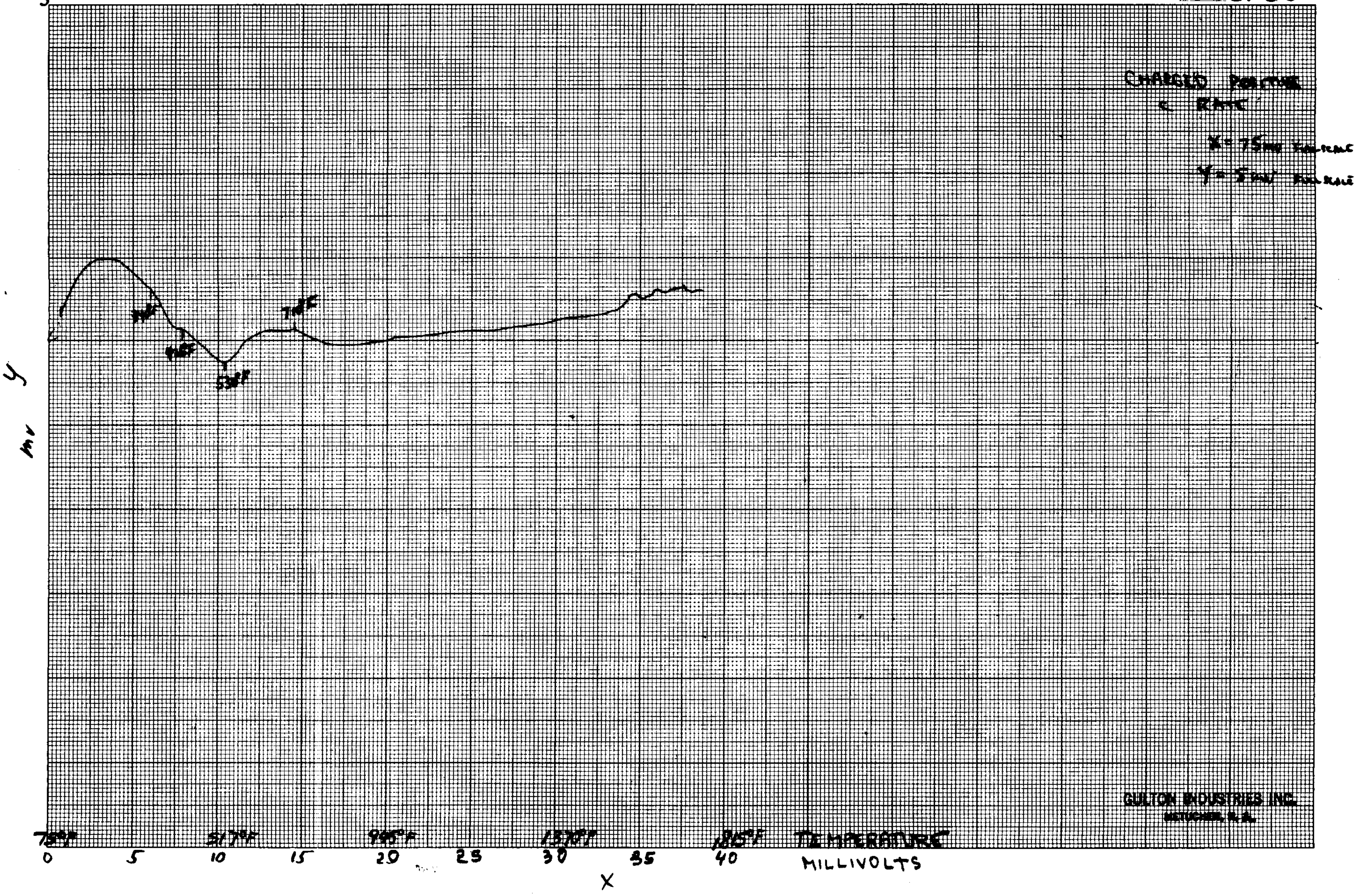
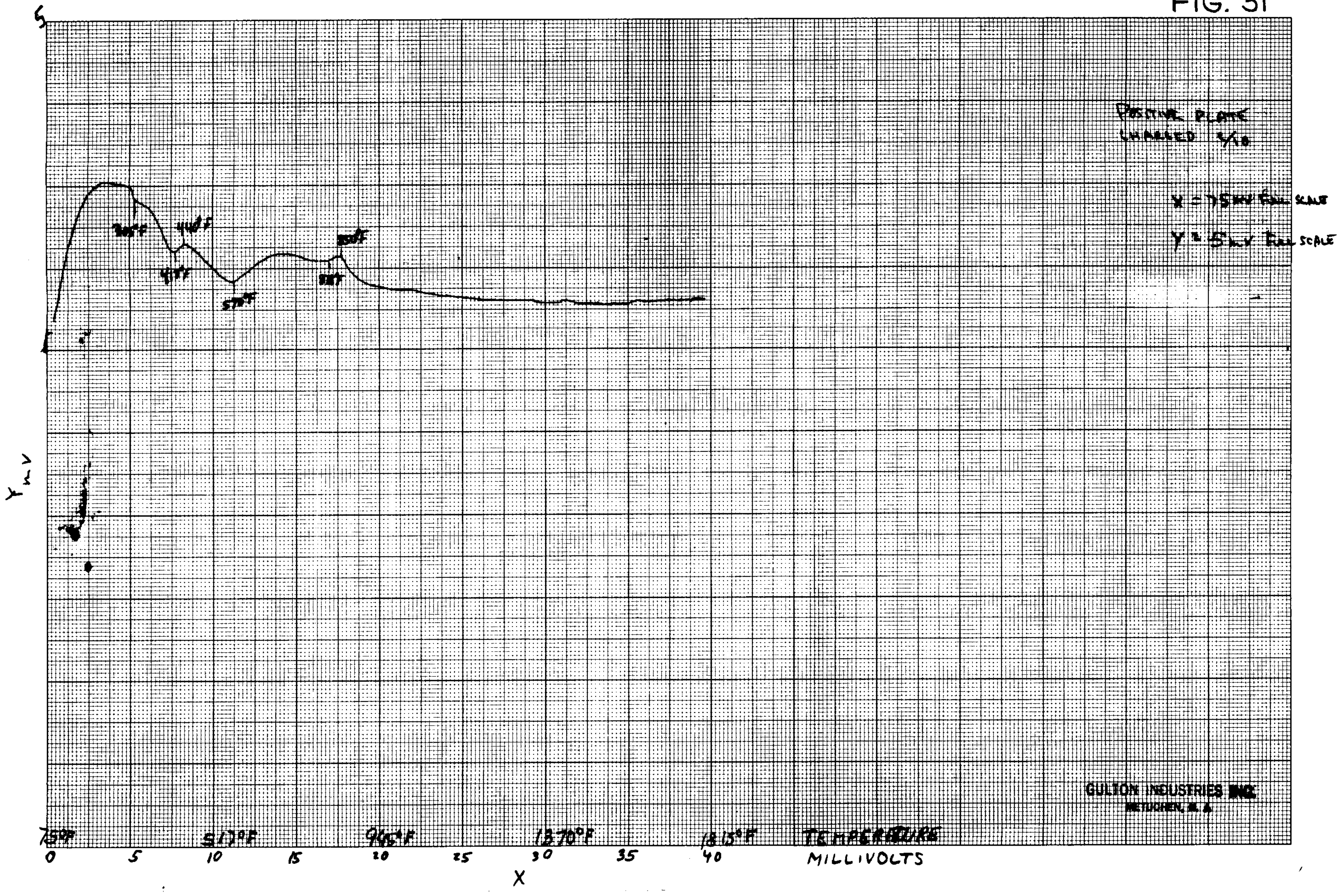

CHARGED POSITIVE
C RATE
X = 75mv full scale
Y = 5mv full scale
5
y
mv
415°F
538°F
718°F
75°F
517°F
995°F
1370°F
1815°F
TEMPERATURE
0
5
10
15
20
25
30
35
40
MILLIVOLTS
X
GULTON INDUSTRIES INC.
METUCHEN, N.J.

FIG. 31



POSITIVE PLATE
CHARGED 5/10

X = 75 mV FULL SCALE

Y = 5 mV FULL SCALE

FIG. 32

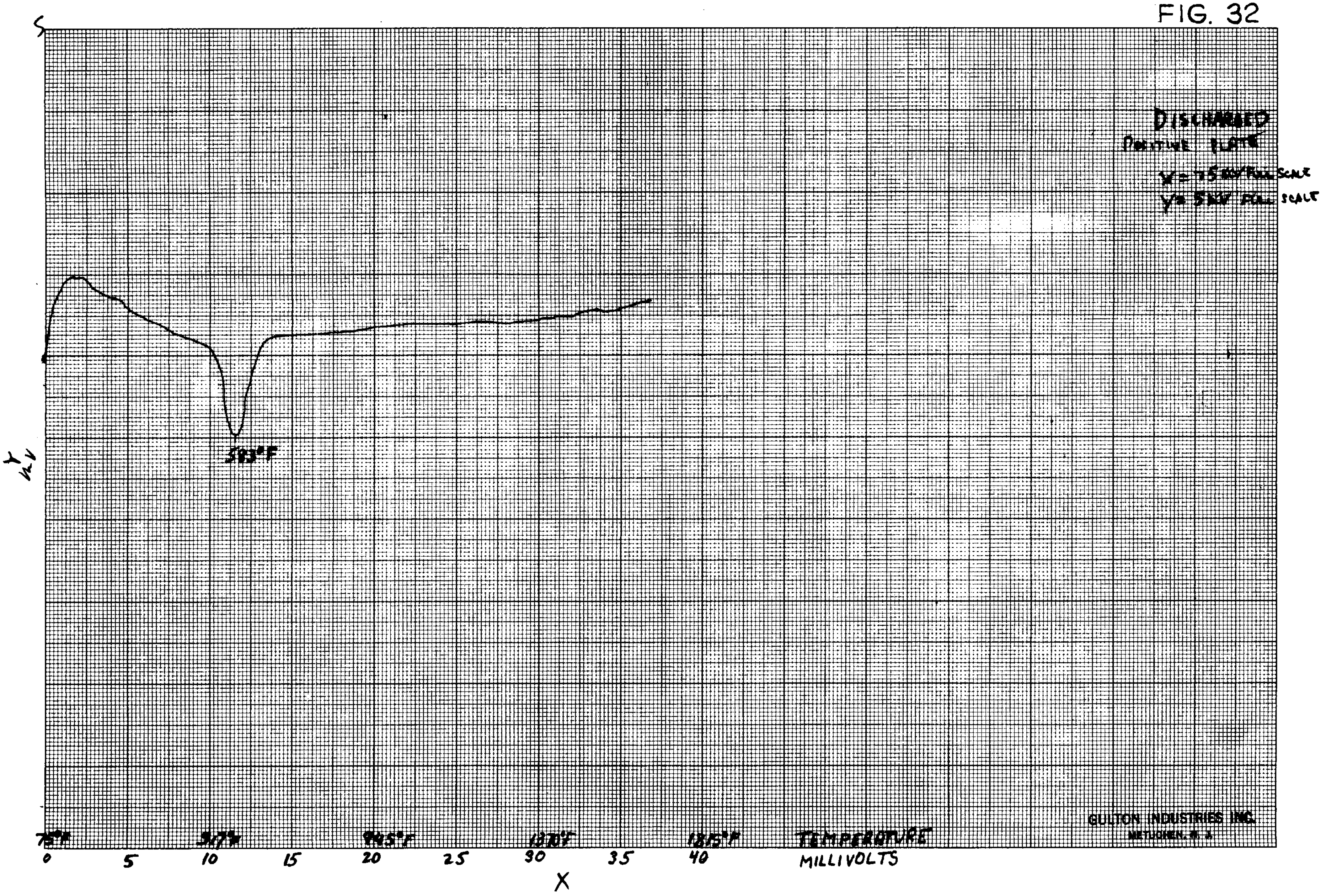
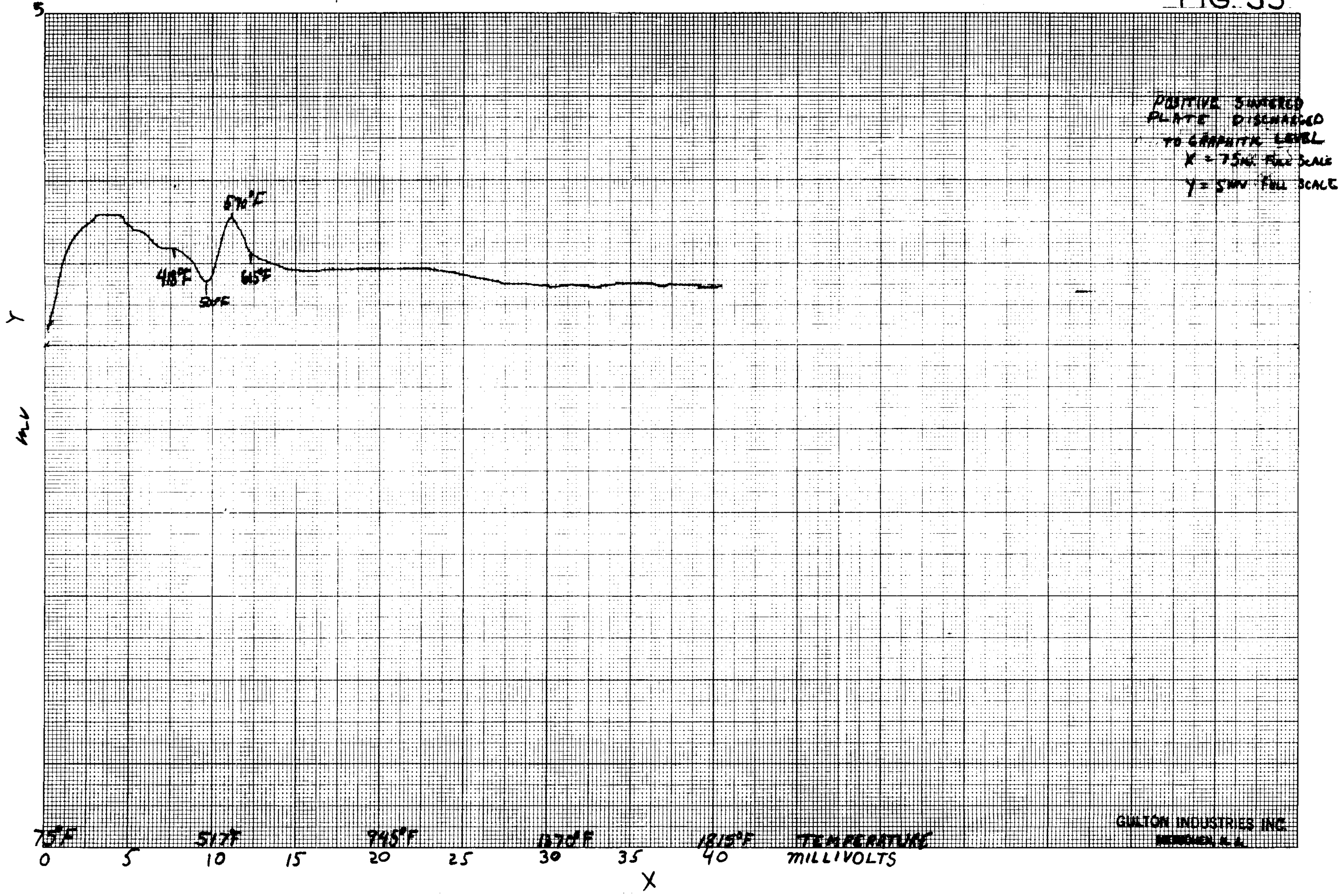

DISCHARGED
POSITIVE PLATE
X = 75 mV FULL SCALE
Y = 5 mV FULL SCALE
583°F
5
Y
mV
75°F
517°F
945°F
1370°F
1815°F
TEMPERATURE
0
5
10
15
20
25
30
35
40
MILLIVOLTS
X
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIG. 33


POSITIVE SINTERED
PLATE DISCHARGED
TO GRAPHITE LEVEL
X = 75MV FULL SCALE
Y = 5MV FULL SCALE
5
Y
MV
576°F
418°F
504°F
615°F
0
5
10
15
20
25
30
35
40
75°F
517°F
945°F
1370°F
1815°F
"TEMPERATURE"
MILLIVOLTS
X
GULTON INDUSTRIES INC.
METUCHEN, N.J.

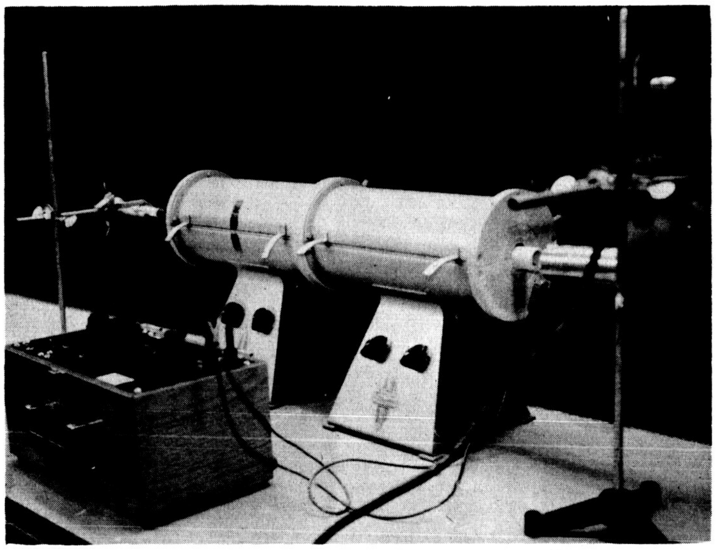


FIGURE 34 APPARATUS SET UP FOR HYDROGEN DETERMINATION

M2945

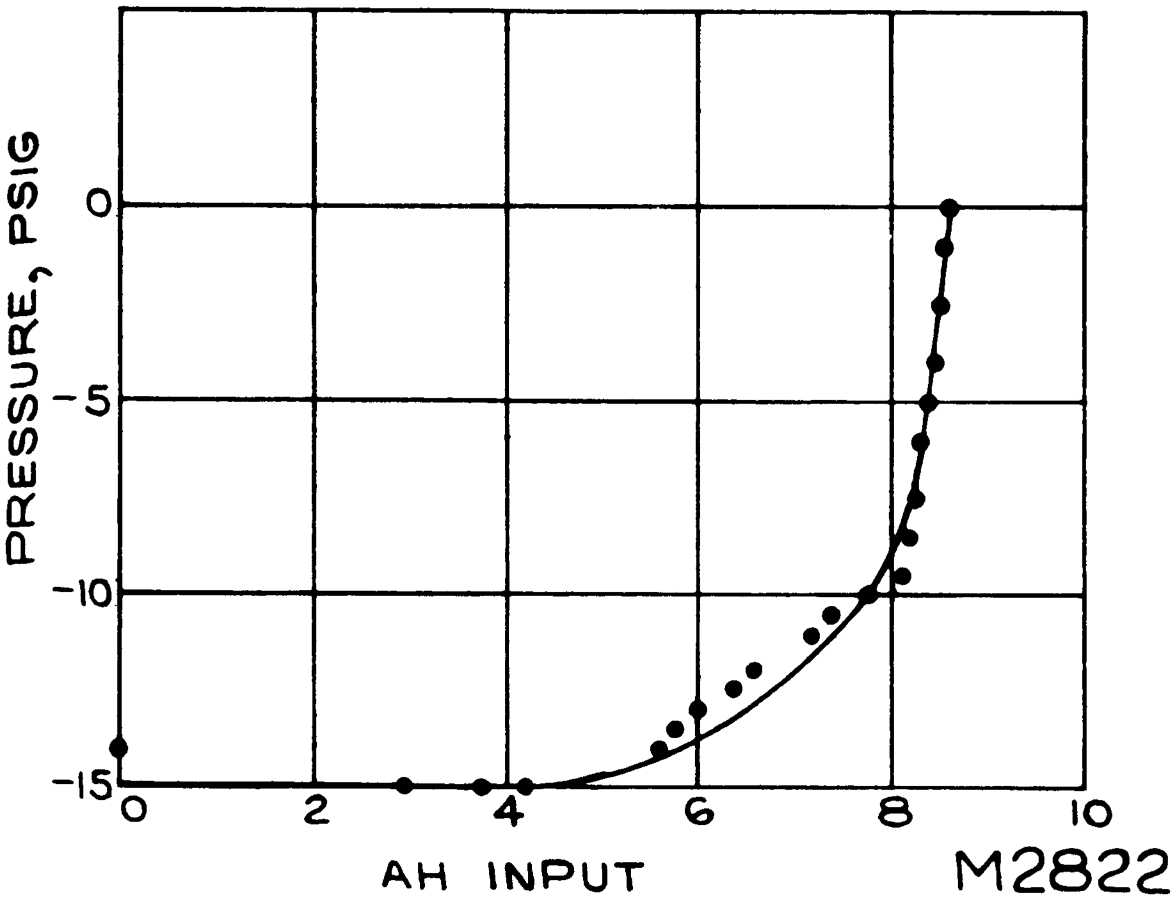


FIG. 35 FINAL SEALED-STARVED CHARGE

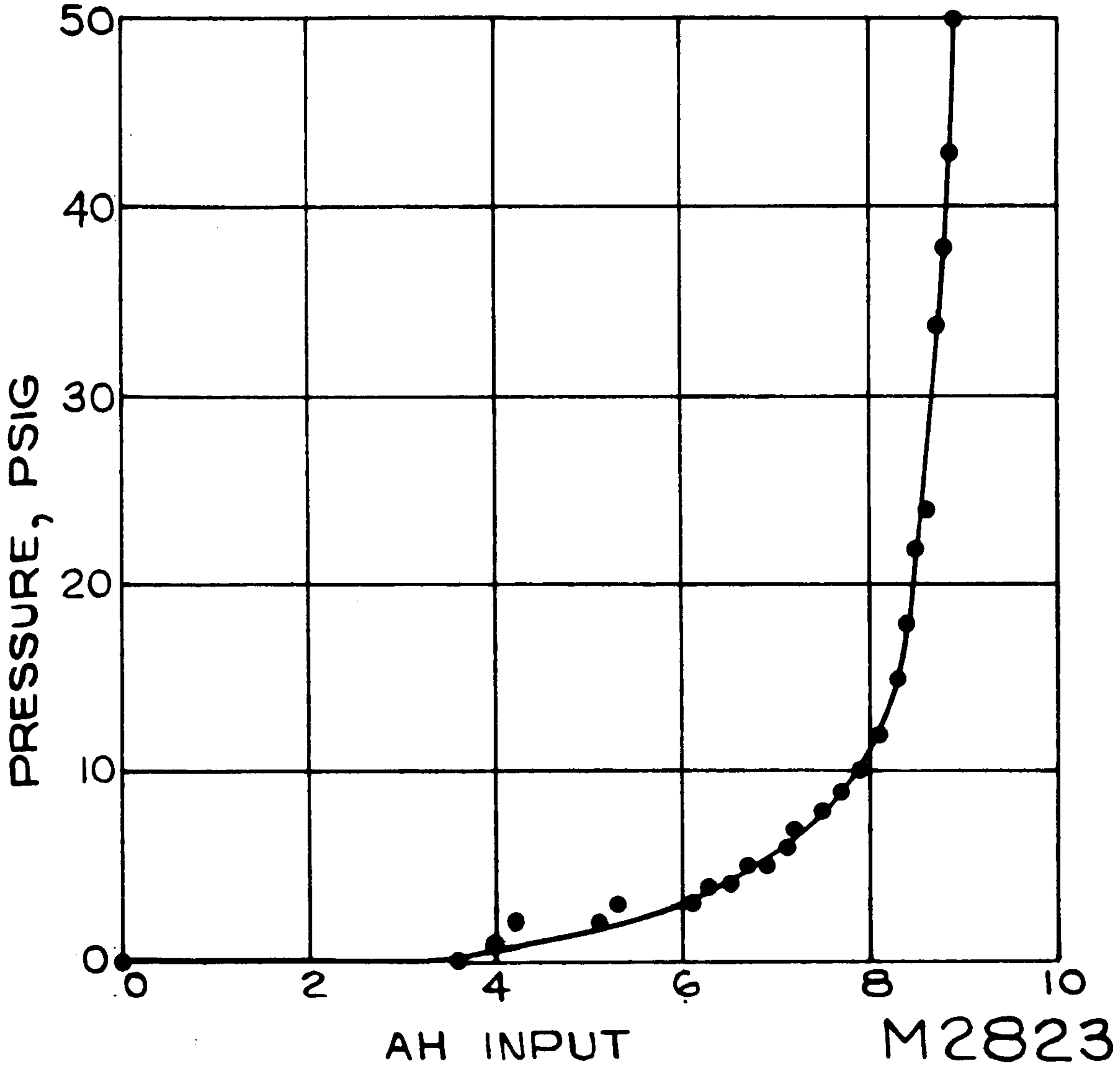


FIG. 36 FIRST FLOODED CHARGE

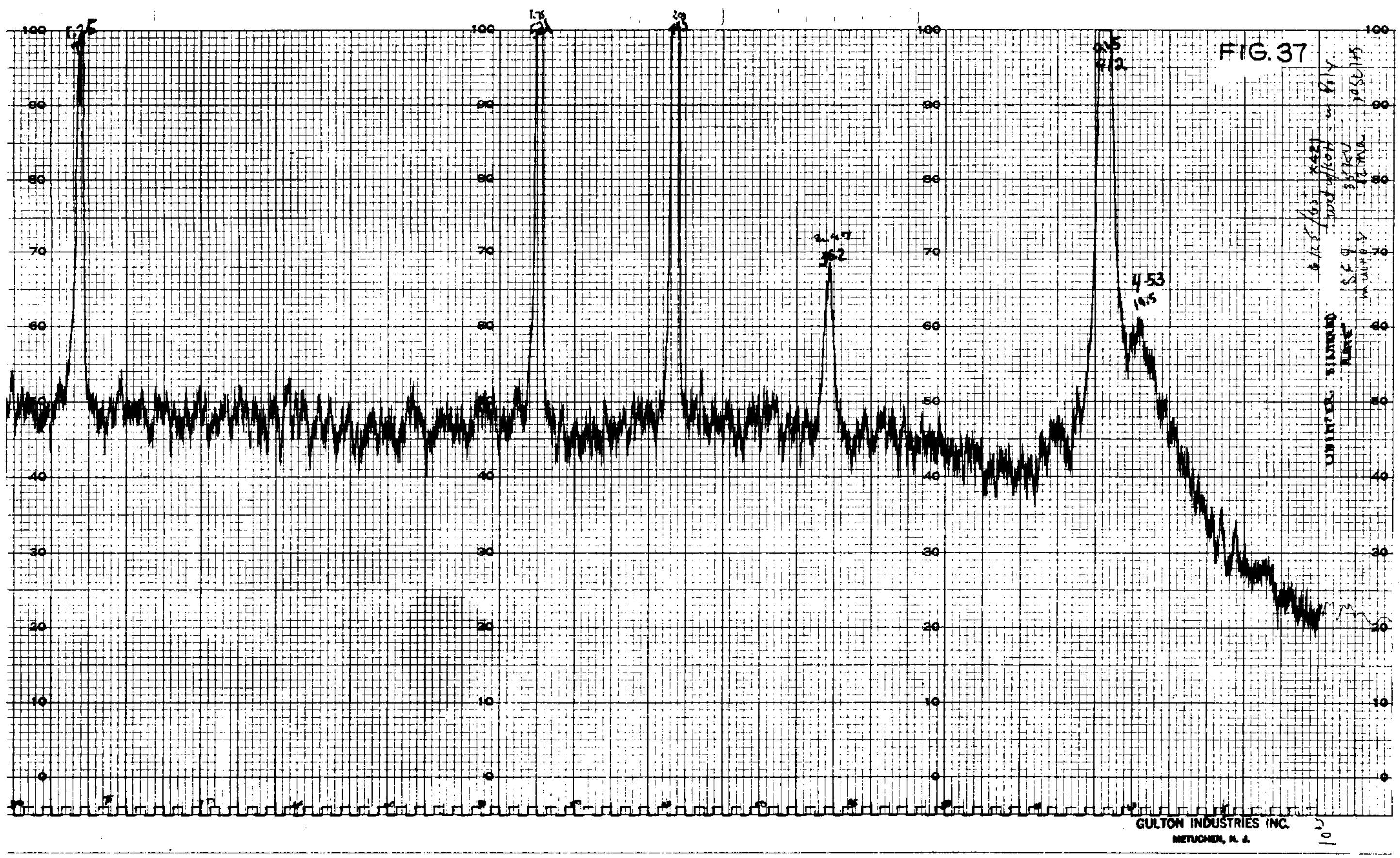


FIGURE 37. X-RAY PATTERN UNIMPREGNATED SINTERED NICKEL PLATE WET WITH KOH AND COVERED WITH POLYETHYLENE

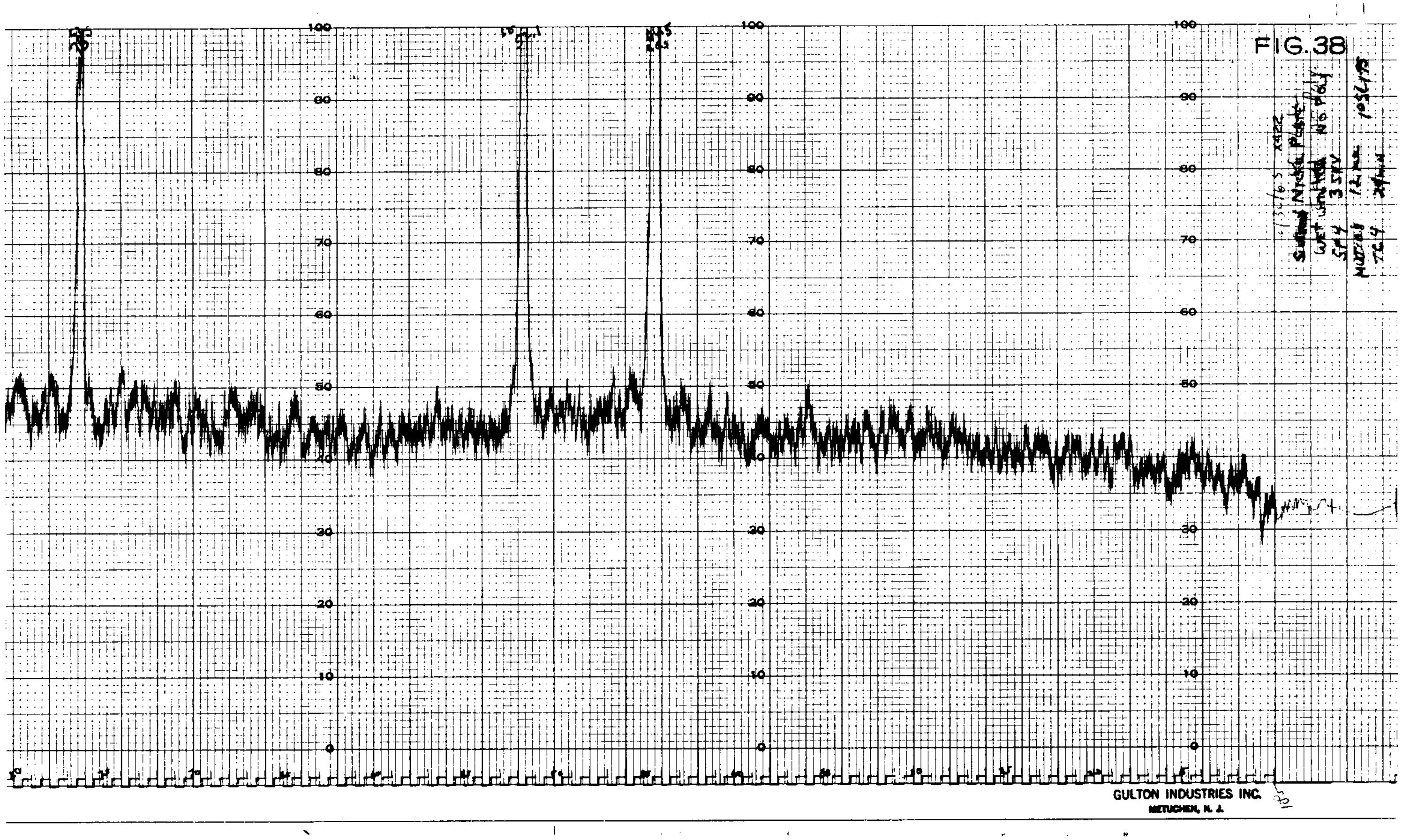


FIGURE 38. X-RAY PATTERN OF SINTERED NICKEL PLATE STILL WET WITH KOH BUT POLYETHYLENE REMOVED

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