NASA CR-54957

INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

By

P. Ritterman, S. Lerner, and H. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-7620

GULTON INDUSTRIES, INC.

Alkaline Battery Division
Metuchen, New Jersey

NOTICE

Requests for copies of this report should be referred to

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Attention: AFSS-A
Washington, D. C. 20546

NASA CR-54957

THIRD QUARTERLY REPORT

INVESTIGATION OF BATTERY ACTIVE NICKEL OXIDES

BY

P. Ritterman, S. Lerner and H. N. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

March 12, 1966

CONTRACT NAS 3-7620

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.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

INVESTIGATION OF BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman, S. Lerner and H. N. Seiger

SUMMARY

26274

Further X-ray studies of the sintered plate nickel oxide electrode indicates no noticeable structure change occurs until the electrode has been at least 90% charged. The structure of the charged state is a disordered $Ni(OH)_2$ structure. Overcharge causes production of an active material which is completely amorphous to X-ray. Considerable overcharge results in production of γ NiOOH. Structures of the charged and discharged states are presented pictorially.

A study of the effect of stand at various temperatures on structure was begun.

Formation treatment was found to have little effect on stability of electrodes.

Positive electrodes with cobalt additives were shown to retain 75% of original capacity after charged stand at 65°C, for 7 days, as compared to less than 50% for controls.

INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman, S. Lerner and H. N. Seiger

ABSTRACT

X-ray diffraction patterns are shown which indicate no structural differences between discharged and up to 90% charged plates.

X-ray patterns of fully charged and overcharged electrodes show amorphous and γ NiOOH structures.

A pictorial view of the $Ni(OH)_2$ structure is presented.

X-ray patterns of plates after initial stands at 10°C, 25°C and 50°C are shown.

Plates formed at C/30, 10°C; C/10, 25°C; and C/10, 80°C were compared for charge retention at room and elevated temperatures, and no significant differences were found.

Cobalt doped positives were shown to be superior to pure $Ni(OH)_2$ controls on charged stand tests.

I. INTRODUCTION

A. PURPOSE

Investigations performed under this contract include the following: (1) Identification and characterization of materials formed at the positive electrode of a sintered plate Ni-Cd cell at various temperatures and states of charge; (2) various means of stabilization of the positive electrode material at elevated temperatures; and (3) studies of the utilization efficiency, voltage, and cycling characteristics of the positive electrodes which have been improved by stabilization.

B. STATUS OF PROGRAM AT THE BEGINNING OF THE QUARTER

X-ray diffraction techniques have been used as the means of determining nickel structure. It has been shown that no differences in structure were apparent between the completely discharged state and the 75% charged state. This was found true for both the C/2 and C/10 charge rate.

A study of the effects of formation rate and temperature revealed that plates formed at C/10 and 80°C, and those formed at C/30 and 10°C were superior, with respect to their stability and utilization. Thirty plates were formed, with ten in each formation group, at C/10-80°C, at C/30-10°C, and at C/10-25°C. The latter formation condition served as the control.

The effects of additives on stabilization have shown, thus far, that 20 atom % cobalt results in increased stability as well as increased utilization of active material impregnated into the plate.

II. OUTLINE OF PROGRAM

The program has been divided into two parts. The first involves investigations into the qualitative and quantitative nature of the sintered nickel oxide electrode. These investigations will be carried out by use of chemical, electrochemical, and X-ray diffraction techniques as methods of analysis. The second part concerns itself with methods of stabilizing the charged state of the sintered nickel oxide electrode. The stabilization methods include (1) additives (the inclusion of foreign materials within the structure of nickel oxide crystals), (2) formations at various currents and temperatures, and (3) any other means of stabilization deemed feasible will be presented for approval to the NASA Project Manager. Plates made by these methods will be evaluated with respect to charge retention and performance on charge and discharge.

The details of this program have been discussed in the First and Second Quarterly Reports and are reviewed below.

A. IDENTIFICATION AND CHARACTERIZATION OF BATTERY ACTIVE MATERIAL EXISTING IN THE NICKEL OXIDE ELECTRODES

1. Variables Investigated

Three effects on active electrode material structure are being studied:

a. State of charge
b. Rate of charge
c. Effect of stand

Stand effects are being investigated at elevated (50°C), cold (10°C) and room temperature, both in the presence and absence of the antipode (cadmium electrode).

Three plate cells consisting of single positive plates surrounded by excess negative capacity in the form of two sintered cadmium electrodes are being used for all tests.

2. Methods of Analysis

a. Chemical Means

The formula weight will be determined by a quantitative determination of nickel, hydrogen, and oxygen. A determination of nickel valence will also be made

(1) Nickel

Total nickel will be determined by electroplating on a platinum grid.

Methods of separating Ni^o from the active nickel oxides will be explored.

(2) Hydrogen

A washed and dried sample will be mixed with K_2CrO_4 and $PbCrO_4$ and heated to 600°C. The hydrogen in the sample will be converted to water vapor.

(3) Oxygen

Oxygen will be determined by difference with respect to nickel and hydrogen.

(4) Nickel Valence

The valence of nickel will be determined by iodiometric titration and concurrent analysis for active nickel.

b. X-ray Diffraction

All X-ray diffraction data are obtained with uncovered samples. Two goniometer scan speeds are used, one at 2° per minute, the other at 1/8° per minute.

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation and Various Temperatures and Rates

Formations have been performed at C/2, C/10, and C/30 and temperatures of 10°, 25°, and 80°C for each rate. These cells were formed at each rate and each temperature for 3 cycles.

2. Additives

Impregnating nickel solutions will be prepared containing 5%, 10%, and 20% metal atoms of Co, Ba, Mn, Li, Mg, Na, Be, and Ca. These will be incorporated by use as the salt of the nitrate ion.

For each quantity and additive type, 10 plates will be impregnated.

3. Other Techniques of Stabilization

Other means beside the impregnation used by Gulton Industries will be explored. These will include molten salt impregnation and anodic, as well as cathodic impregnation of sintered plaques from dilute solution of nickel salts.

C. PRELIMINARY EVALUATION

Electrodes stabilized by the above described methods are evaluated in the following manner.

1. Stand

All cells will be charged at the C rate for 2 hours and then immediately discharged at C/5 to 0.0 V.

The charge will be repeated and following a particular stand condition, the cell will be discharged at C/5 to 0.0 V.

The stand condition will be varied with respect to time and temperature.

Immediate discharge capacity determinations will be made after each stand test.

2. Electrochemical Stabilization

Samples of each group shall be cycled for 4 cycles at C/10 charge -- C/5 discharge at room temperature. Cell voltage versus time will be recorded. Cells will be evaluated for capacity, reproducibility of results from cycle to cycle with respect to capacity, efficiency and voltage level.

D. EVALUATION OF IMPROVED MATERIAL

After establishing a superior material, or group of superior materials, the following tests will be made.

1. Decomposition of Charged Positive

Cells prepared with the superior positive will be exposed to stand at temperatures up to 95°C. Charge retention will be obtained as has been described above.

2. Investigation of Sintered Plate Parameters

After establishing a loading factor which meets the approval of the NASA Project Manager, investigation will be made concerning establishment of (a) optimum formation techniques, (b) charge acceptance as a function of charge rate, and determination of point of oxygen evolution at various rates, (c) utilization factors at various discharge rates and utilization factors for depth of discharge from 25% to 100%.

Details of these tests have been described in the previous Quarterly Reports.

III. EXPERIMENTAL PROCEDURES & RESULTS

A. EXPERIMENTAL PROCEDURES

1. Determination of Battery Active Material Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State of Charge

In the previous quarter, it was determined that the structure of the positive plate was unchanged between the fully discharged and 75% charged state. X-rays were taken during this quarter of plates in the 90% state of charge and overcharged beyond 100%. These X-rays were taken using a slow $1/8^o$ per minute scan rate. Six cells which were part of the twenty selected for testing during the second quarter, were shorted through a 1 ohm resistor for 16 hours. One cell was left completely discharged. The five remaining cells were charged at 500 ma (C/2) for 1½ hours, 1 hour and 48 minutes, 2 hours, 2 hours and 40 minutes, 4 hours, and 11 hours.

b. Effect of Stand Time at Various Temperatures

(1) Construction of Cells

Thirty cells, consisting of 1 positive and 2 negatives, were assembled. Each positive plate had dimensions of 1-7/8" x 2-1/8" x .035" and contained 3.4 grams of $Ni(OH)_2$.

(2) Formation Procedure

All cells were formed at 100 ma. The charge lasted for 15 hours, then discharged until the cells reached zero volts. Upon completion of discharge, the cells were shorted for 2 hours. This procedure was repeated twice more.

(3) Selection of Cells and Test Procedures

Based on the capacity of the third formation cycle (Table I), 24 cells, most alike in capacity, were charged at 100 ma for 20 hours at room temperature. Twelve of the cells were then disassembled in the charged state and their positives placed in beakers of 34% potassium hydroxide. The other 12 cells remained as they were. Four plates and four cells were placed in an oven at 50^oC. A like number of cells and plates were placed in a cold box at 10^oC, and the remaining cells and plates were kept at room temperature. After a stand of 24 hours, a plate and a cell were removed from each temperature ambient, the cells disassembled, and all plates X-rayed. After 48 hours, another cell and plates were removed from each ambient and the positive plates X-rayed. The remaining cells and plates will be retained at their respective temperatures for a three month period, at which time all positives will be X-rayed.

c. High Valence Nickel Oxide

With the hope of producing a standard for X-ray, a nickel oxide compound was prepared by slow addition of a solution consisting of .34N NaOCl and 6.45N in KOH to 200 ml of .17N $Ni(NO_3)_2$ solution. When the resulting precipitate had settled, the supernatant liquid was removed by decantation and the solid washed twice with fresh base. The sample was stored in a beaker of 34% KOH.

d. Oxidation State of Nickel

The oxidation state of nickel in the compound described above was determined in the following manner.

The sample was placed in a beaker of alkaline KI. The sample was then dissolved by addition of dilute sulfuric acid until the Ph reached 1.5. The iodine liberated by the reduction of nickel in oxidation states greater than 2 to Ni^{++} is titrated with a standard solution of $Na_2S_2O_3$. The total amount of nickel present was determined by electroplating on a platinum grid. A sintered plate was also analyzed by this method.

e. Preparation of $Ni(OH)_2$

Pure $Ni(OH)_2$ was prepared as another X-ray standard by addition of KOH to $Ni(NO_3)_2$ solution. The resulting precipitate was filtered through a Buchner funnel, washed and dried. It was analyzed for nickel valence using the method described in (c.) above.

2. Stabilization

a. Formation

(1) Effect of Stand

The evaluation of the positive plates formed at 10°C - 35 ma, 25°C - 100 ma, and 80°C - 100 ma was performed in the following manner.

Six cells from each group of ten were charged at 1 ampere for 2 hours and then immediately discharged at 200 ma and room temperature to 0.0V. After an overnight short, they were again charged at 1 ampere for 2 hours. The cells were disassembled and the positives allowed to stand in separate beakers of KOH, at room temperature, for a period of 3 days, and then discharged at 200 ma at room temperature to 0.0V. Cells were again shorted overnight and test procedure described above was repeated at a 50°C and 65°C three day stand for the charged positives.

(2) Effect of Cycling

The four remaining cells from each group were cycled 4 times. Each charge was for a period of 16 hours at 100 ma, followed immediately by a discharge at 200 ma to a cell voltage of 0.0V. All cells were shorted for 2 hours between cycles.

b. Additives

(1) Effect of Stand

Four cobalt containing positives (20 atom percent cobalt) and four controls were charged at 1 ampere for 2 hours, and then immediately discharged to 0.0V at 200 ma and room temperature. The cells were then shorted overnight and again charged at 1.0 ampere for a 2 hour period. In the charged state, the cells were disassembled and positives stored for a 1 day period at 65°C. Following this, the individual positives were returned to their respective antipodes. The rebuilt cells were discharged at 200 ma at room temperature. The test was repeated with the stand time extended to 7 days.

(2) Preparation of Plates

Ten plates containing 20 atom percent of Beryllium, impregnated to a weight gain of 3 grams, were prepared. Plates with other additives at the 20 atom percent level are presently being impregnated.

B. EXPERIMENTAL DATA

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State of Charge

Figure 1 shows X-ray diffraction patterns obtained by slow scan between 10° and 40°. Three peaks obtained correspond to the three major peaks of $Ni(OH)_2$. Patterns of the discharged state, 75% charged, 90% charged, and 100% charged and 133% charged are shown.

Figure 2 shows the diffraction patterns obtained from 200% to 550% charged.

b. Effect of Stand at Various Temperatures

The capacities of the 30 cells on their final formation discharge are listed in Table I. Numbers marked with an asterisk indicate the 24 cells chosen.

Figures 3, 4, 7, 8, 11, and 12 are X-ray patterns obtained from stored plate positives. Figures 5, 6, 9, 10, 13, and 14 are X-ray patterns obtained from stored cell positives. Figures 3, 5, 7, 9, 11 and 13 are X-ray patterns after a 24 hour stand. Figures 4, 6, 8, 10, 12 and 14 are X-ray patterns obtained after a 48 hour stand. Figures 3, 4, 5, 6 are from plates stored at 10°C. Figures 7, 8, 9, 10 are from plates stored at room temperature. Figures 11, 12, 13 and 14 are from plates stored at 50°C.

c. High Valence Nickel Oxide and Oxidation State

The oxidation state of the nickel in the high valence oxide was determined to be 3.07. Table II shows the data used in determining the average valence.

The X-ray pattern obtained from the prepared compound is shown in Figure 15.

d. Nickel Hydroxide Standard

Three major peaks from the X-ray diffraction pattern of $Ni(OH)_2$ are shown in Figure 16.

2. Stabilization of Nickelic Oxides and Hydroxides

a. Formation

(1) Effect of Stand

The capacities obtained from the cells with different formation histories are listed in Table III--for immediate discharges, and discharges after a 3 day stand at room temperature, 50°C, and 65°C. The immediate discharge capacities were taken initially and before each elevated temperature testing.

The effect of stand is shown in graphic form in Figure 17, using the average value of the immediate discharge capacity as 100% charge retention.

(2) Effect of Cycling

Table IV shows the capacities of 4 cells in each group for 4 consecutive cycles. Figure 18 shows a typical discharge curve for each formation group.

b. Additives

(1) Effect of Stand

Table V shows the capacities of 4 cobalt positive cells without a stand, after a 1 day stand at 65°C, and a 7 day stand at 65°C when discharged to the 1.0V and 0.0V end points. Results of 4 control cells are also shown. These are shown graphically in Figure 19, taking immediate discharge capacity as 100% charge retention.

(2) Preparation of Plates

Table VI lists weight gains of plates containing the beryllium additive (20 atom %).

C. DISCUSSION

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrode

a. Structure of Nickel Hydroxide

Pure nickel hydroxide crystallizes with a hexagonal closest packed oxygen layer structure having space group P$\bar{3}$M(4). In this, each nickel atom is surrounded by six oxygen atoms and each oxygen has three nearest neighbor nickel atoms. There is one $Ni(OH)_2$ molecule per unit cell. Figure 21 shows a photograph of a three dimensional representation of one $Ni(OH)_2$ unit cell.

b. Effect of State of Charge on Structure

A semi-quantitative study of the effect of state of charge on structure was made by obtaining the integrated intensities (areas under the peaks) of the X-ray reflections shown in Figures 1 and 2. These intensities are shown in Table VIII and were obtained by normalizing the area under the various peaks, setting the 001 ($d = 4.60\text{-}4.70$ Å) equal to 100.

If reference is made to Figures 1 and 2 and Table VIII, it is apparent that until the positive is fully charged (100%) there is little or no change in the basic nickel hydroxide structure.

In the X-ray patterns the 001 reflections arise from planes in the "c" or inter-layer direction, while the 100 reflections arise from planes in the "a" or intra-layer direction, as shown in the drawing, Figure 22. As the cell is charged, the Ni^{+2} is oxidized to Ni^{+3} with the simultaneous loss of a proton to the solution (Figure 23). As the positive is fully charged and overcharged, the $Ni(OH)_2$ structure becomes disordered, first in one plane (100) and then in the other (001).

c. Effect of Stand on Structure

The results of Figures 3 through 14 are summarized in Table VII, with respect to an estimate of the intensities of the reflections of the 001, 100 and 101 planes of the $Ni(OH)_2$ structure, corresponding to the d values of 4.62, 2.73 and 2.32 Å. The intensities are given as a function of area under the curve. Results show that plates stored at 10°C, by themselves, retain their amorphous structure (which corresponds to the fully charged, better, overcharged state) than plates stored as cells at that temperature.

At room temperature storage time seems to affect structure more than whether a plate was stored by itself or as part of a cell. Plates stored for 24 hours show peaks corresponding to the 001 plane. Those stored 48 hours show peaks at all planes indicating a greater order and lower state of charge.

The 100 plane, which is usually the least intense line, is the predominant one when plates are stored at 50°C, especially for the 48 hour stand.

The 001 plane, which usually is retained until a state of considerable overcharge is reached, becomes the least predominant at 50°C.

This behavior at 50°C cannot yet be explained with relation to self discharge of the plate. During the Fourth Quarter, after the plates completing the 3 month stand have been X-rayed, additional information concerning the effect of high temperature storage will become available.

d. Nickel Oxides and Oxidation State

The apparent success in determining the valence of a higher nickel oxide will help in the analysis of a charged sintered nickel plate, if the method proves applicable. The high valence compound was shown to be amorphous (Figure 15) and cannot be identified further by formula weight determination since it is unstable when removed from its alkaline surroundings.

2. Stabilization of Nickelic Oxides and Hydroxides

a. Formation

The results of comparison of charge retention characteristics of plates formed at various rates and temperatures are summarized in Figure 16. No significant differences are shown with respect to stability at room, or elevated, temperatures between plates with differenct formation treatment. On the basis of capacity, however, the results given in Table III and Table IV and Figure 17 indicate that a slightly greater capacity for plates formed at C/30, and 10°C was exhibited than the control, while those formed at C/10 and 80° exhibit a lower capacity. The reproducibility of capacity with cycling is not affected by different formation conditions.

b. Additives

Figure 19 clearly shows the superiority of charge retention by the cobalt additives in the positives over that of the control positives.

Figure 20 is a typical discharge curve obtained from control and cobalt additive positives on immediate discharge and after stand for 7 days at 65°C. The cobalt doped positives have greater absolute capacities as well as greater charge retention.

IV. CONCLUSIONS

1. No structural change is detectable in the active material of the sintered nickel oxide electrode until after the plate is 90% charged.

2. At a level of overcharge between 50%-100%, the structure of the active material becomes amorphous.

3. The charge retention and utilization characteristics of cobalt additive in positives are considerably superior to those of pure $Ni(OH)_2$ positives.

4. Formation procedure, with respect to rate and temperature, has little effect on charge retention characteristics, but does affect utilization.

5. A recrystallization from the amorphous material occurs after considerable high rate overcharge, forming a compound whose structure is compatible to that associated with γ NiOOH.

V. FUTURE WORK

A. A quantitative study of the intensities of the X-ray reflections at various states of charge will be undertaken.

B. An attempt will be made to refine the structure of nickel hydroxide in so far as the interlayer oxygen distance is concerned. Also, the structure of γ NiOOH will be examined.

C. Since, in the conversion from $Ni(OH)_2$ to β NiOOH, we are interested in the positions of the protons which are invisible to X-rays, the possibility of using neutron diffraction techniques to elucidate these positions will be looked into.

D. A small cell will be constructed which will alow the positive to be X-rayed while under continuous charge.

E. A technique to enable the method of determining the oxidation state of nickel to be applied to the sintered positive will be investigated.

F. A technique to study the sintered electrode by infrared analysis will be investigated. This will allow determination of the formula weight of the active material at various states of charge.

G. The positive electrodes will be studied microscopically to determine grain size of active material at different states and rates of charge.

H. Additional cobalt doped plates will be prepared and evaluated with respect to charge efficiency, discharge efficiency, and the other parameters to be evaluated as a superior material.

J. Nickel positives containing other additives at the 20 atom % level will be evaluated.

REFERENCES

1. Second Quarterly Report NASA CR-54654, "Investigation of Battery Active Nickel Oxides", Ritterman and Seiger, Contract NAS 3-4178, Dec. 12, 1965
2. P. Bro and D. Cogley, Unpublished Report
3. Ibid
4. R. W. Cairns and E. Ott, J. Am. Chem. Soc., 55, 527 (1933)
5. F. P. Kober, J. Electro Chem. Soc., 112, 1064, (1965)

TABLE I

CAPACITY ON FINAL FORMATION - STAND CELLS

	CELL NUMBER	CAPACITY	
		To 1.0V	To 0.0V
*	1	.98	.98
*	2	1.03	1.03
*	3	.93	.94
*	4	.97	.97
*	5	.95	.95
*	6	.98	.98
*	7	1.01	1.01
*	8	1.04	1.04
*	9	.95	.95
*	10	.99	.99
*	11	.98	.98
	12	.91	.92
*	13	1.00	1.00
	14	.85	.85
	15	.83	.83

	CELL NUMBER	CAPACITY	
		To 1.0V	To 0.0V
	16	.90	.91
*	17	.93	.93
*	18	.94	.95
*	19	.94	.95
	20	.65	.72
*	21	.92	.92
	22	1.08	1.08
*	23	.96	.96
*	24	1.00	1.00
*	25	.97	.97
*	26	.96	.96
*	27	.98	.98
*	28	1.01	1.01
*	29	.97	.97
*	30	.96	.96

* Cells Chosen - Most alike in capacity

TABLE II

DETERMINATION OF AVERAGE VALENCE OF HIGH VALENCE NICKEL OXIDE

SAMPLE NO.	WEIGHT NICKEL (gms)	MILLI-EQUIVALENTS NICKEL	MILLI-EQUIVALENTS $Na_2S_2O_3$ USED	$\frac{\text{MILLIEQUIVALENTS } Na_2S_2O_3}{\text{MILLI-EQUIVALENTS Ni}}$	AVERAGE VALENCE
1	0.0234	0.3986	0.4822	1.21	3.10
2	0.0263	0.4479	0.4822	1.08	3.04
Avg.	0.0249	0.4241	0.4822	1.15	3.07

TABLE III

CAPACITIES OF VARIOUS FORMED PLATES AFTER VARIOUS STANDS

FORMATION TREATMENT	CAPACITY TO 0.0 V					
	NO STAND			3 DAY STAND AT ROOM TEMP.	3 DAY STAND AT 50°C	3 DAY STAND AT 65°C
10°C-35 ma	1.11 AH	1.12 AH	.95 AH	1.04 AH	.79 AH	.55 AH
	1.11	1.10	.95	.94	.73	.55
	1.11	1.13	1.02	1.03	.78	.51
	1.07	.97	.91	.91	.68	.48
	.97	1.05	.96	.85	.69	.60
	1.04	1.08	1.00	.90	.66	.48
25°C-100ma	.87	.93	.89	.86	.66	.51
	.98	1.04	.87	.87	.72	.55
	.94	1.07	.80	.87	.51	.54
	.98	1.11	.79	.84	.61	.59
	1.10	1.11	.83	1.01	.48	.56
	.95	1.05	.89	.86	.59	.54
80°C-100ma	.87	.96	.86	.73	.62	.48
	.91	.97	.87	.78	.62	.49
	.89	.95	.80	.81	.51	.46
	.85	.86	.79	.71	.43	.42
	.87	.91	.79	.76	.48	.46
	.83	.87	.70	.74	.33	.47

TABLE IV

CYCLING DATA - PLATES WITH VARIOUS FORMATION TREATMENT

FORMATION TREATMENT	CAPACITY							
	CYCLE 1		CYCLE 2		CYCLE 3		CYCLE 4	
	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V
10°C - 35ma	.94	.96	.93	.97	.91	1.00	.87	.90
	1.01	1.08	1.00	1.09	.99	1.09	.95	1.01
	1.01	1.08	.98	1.08	.96	1.09	.91	.92
	.91	.92	.89	.92	.90	.96	.86	.91
25°C - 100ma	.98	1.05	.97	1.06	.95	1.05	.87	.91
	.97	.99	.99	1.03	.98	1.04	.87	.91
	.91	.92	.91	.98	.83	.91	Shorted	
	.96	.98	.98	.99	.83	.89	.90	.91
80°C - 100 ma	.70	.77	.71	.79	.69	.77	.65	.70
	.76	.82	.86	.94	.86	.93	.80	.82
	.60	.70	.61	.83	.67	.84	.63	.72
	.58	.69	.64	.74	.59	.73	.53	.65

TABLE V

COMPARISON OF CAPACITIES OF COBALT CONTAING VS. CONTROL PLATES AT NO STAND AND STANDS AT 65°C

PLATE NUMBER	CAPACITY					
	NO STAND		1 DAY - 65°C		7 DAYS - 65°C	
	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V
Cobalt 1	1.15 AH	1.25 AH	1.02 AH	1.03 AH	.88 AH	.92 AH
Cobalt 2	1.16	1.28	1.04	1.08	.92	.94
Cobalt 3	.98	1.07	.93	.94	.72	.77
Cobalt 4	1.00	1.07	.95	.97	.72	.81
Control 1	.94	1.07	.83	.84	.20	.23
Control 2	.95	1.07	.88	.89	.25	.28
Control 3	.91	.96	.78	.80	.48	.49
Control 4	.91	.96	.82	.83	.50	.53

TABLE VI

WEIGHT GAIN OF BERYLLIUM DOPED SINTERED NICKEL PLATES

PLATE NO.	WEIGHT GAIN
1	2.99 grams
2	3.11
3	2.99
4	3.09
5	3.04
6	3.06
7	3.00
8	2.94
9	3.07
10	2.95

TABLE VII

X-RAY DIFFRACTION LINES AND THEIR INTEGRATED INTENSITIES OBTAINED FROM PLATES STORED AT VARIOUS TEMPERATURES

FIGURE NO.	STAND TIME	STORED AS	TEMPERATURE	X-RAY "d" SPACINGS & INTENSITIES		
3	24 hrs.	Plate	10°C		Amorphous	
4	48 hrs.	Plate	10°C	4.67 (16)	---	---
5	24 hrs.	Cell	10°C	4.60 (25)	---	2.32 (8)
6	48 hrs.	Cell	10°C	4.72 (13)	2.69 (7)	2.32 (19)
7	24 hrs.	Plate	25°C	4.60, 4.72(10)	---	---
8	48 hrs.	Plate	25°C	4.67 (12)	2.71 (3)	2.34 (7)
9	24 hrs.	Cell	25°C	4.60 (6)	---	---
10	48 hrs.	Cell	25°C	4.67 (19)	2.71 (4)	2.37 (13)
11	24 hrs.	Plate	50°C	---	2.73 (12)	2.32 (11)
12	48 hrs.	Plate	50°C	4.55 (7)	2.75 (20)	2.34 (19)
13	24 hrs.	Cell	50°C	4.72 (14)	2.73 (6)	2.34 (7)
14	48 hrs.	Cell	50°C	4.55 (6)	2.71 (19)	2.32 (6)

TABLE VIII

INTEGRATED INTENSITIES OF X-RAY REFLECTIONS Vs. STATE OF CHARGE

STATE OF CHARGE %	I/I_o 001	I/I_o 100	I/I_o 101-002	I/I_o 003-γ-NiOOH
0	100	19	78	---
75	100	25	70	---
90	100	27	73	---
100	100	11	34	---
133	100	0	15 B	---
200	100	0	60 B*	24 B

γ - NiOOH

STATE OF CHARGE %	I/I_o 001	I/I_o 003	I/I_o 006	I/I_o 101-102	I/I_o 104-105
550	4	100	36	31 B	11 B

Intensities obtained by measuring the areas under the reflections with a mechanical integrator.

B = Broad

* Apparent increase in intensity of 101 reflection relative to 001 reflection due to large decrease in actual intensity of 001 reflection.


FIGURE 1

X-RAY PATTERNS vs. STATE OF CHARGE

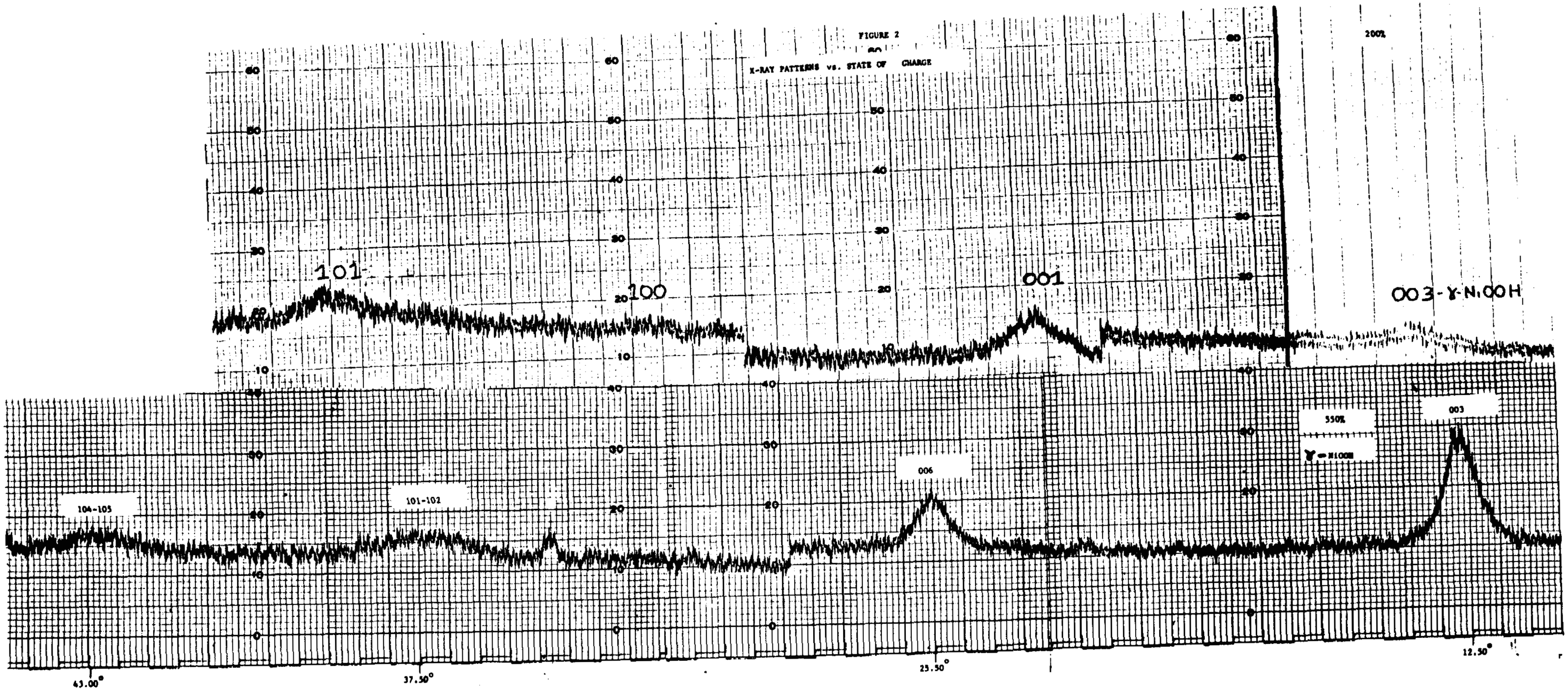


FIGURE 2

X-RAY PATTERNS vs. STATE OF CHARGE

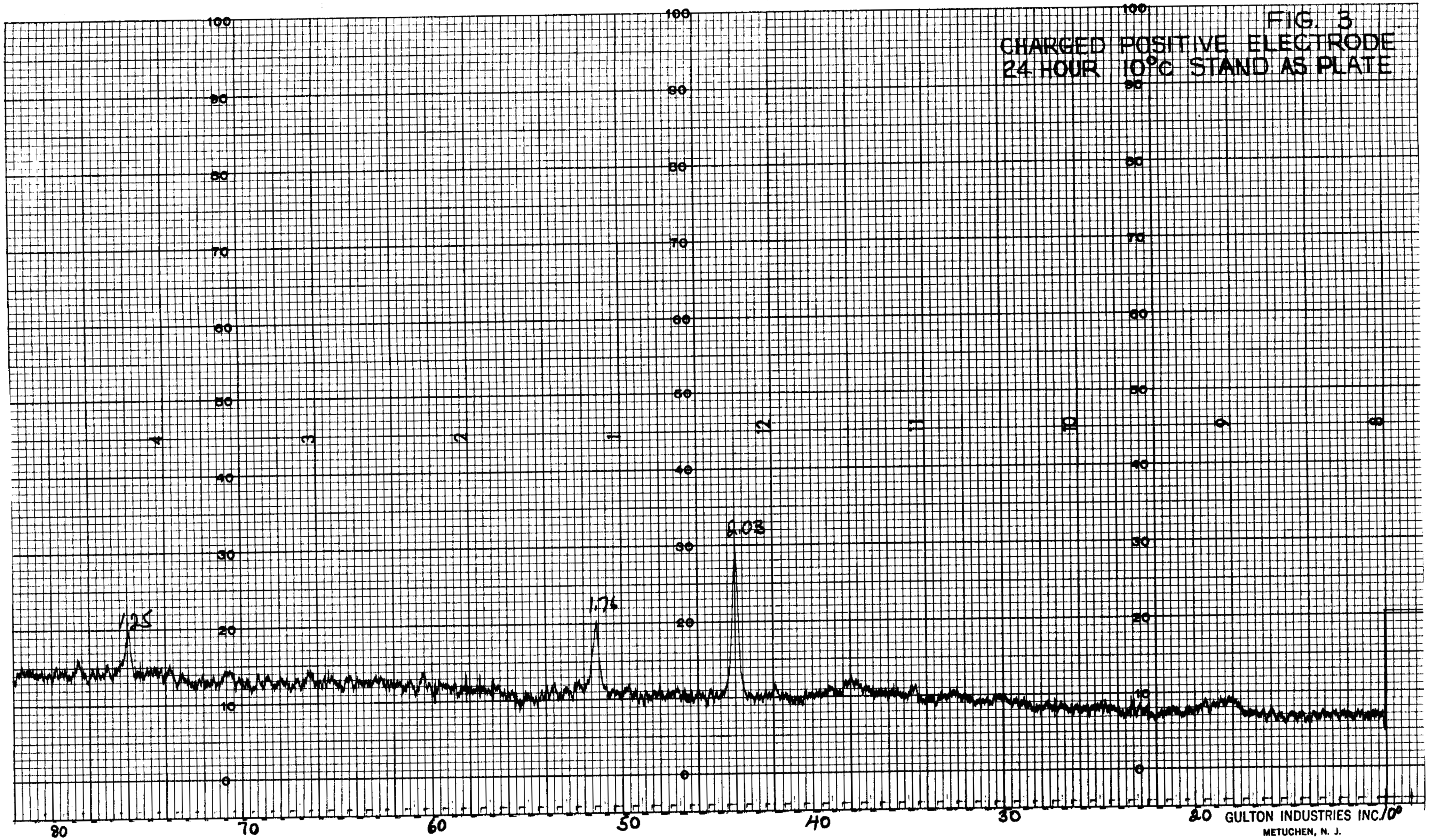


FIG. 3

CHARGED POSITIVE ELECTRODE
24 HOUR 10°C STAND AS PLATE

FIG. 4

CHARGED POSITIVE ELECTRODE
48 HOUR 10°C STAND AS PLATE

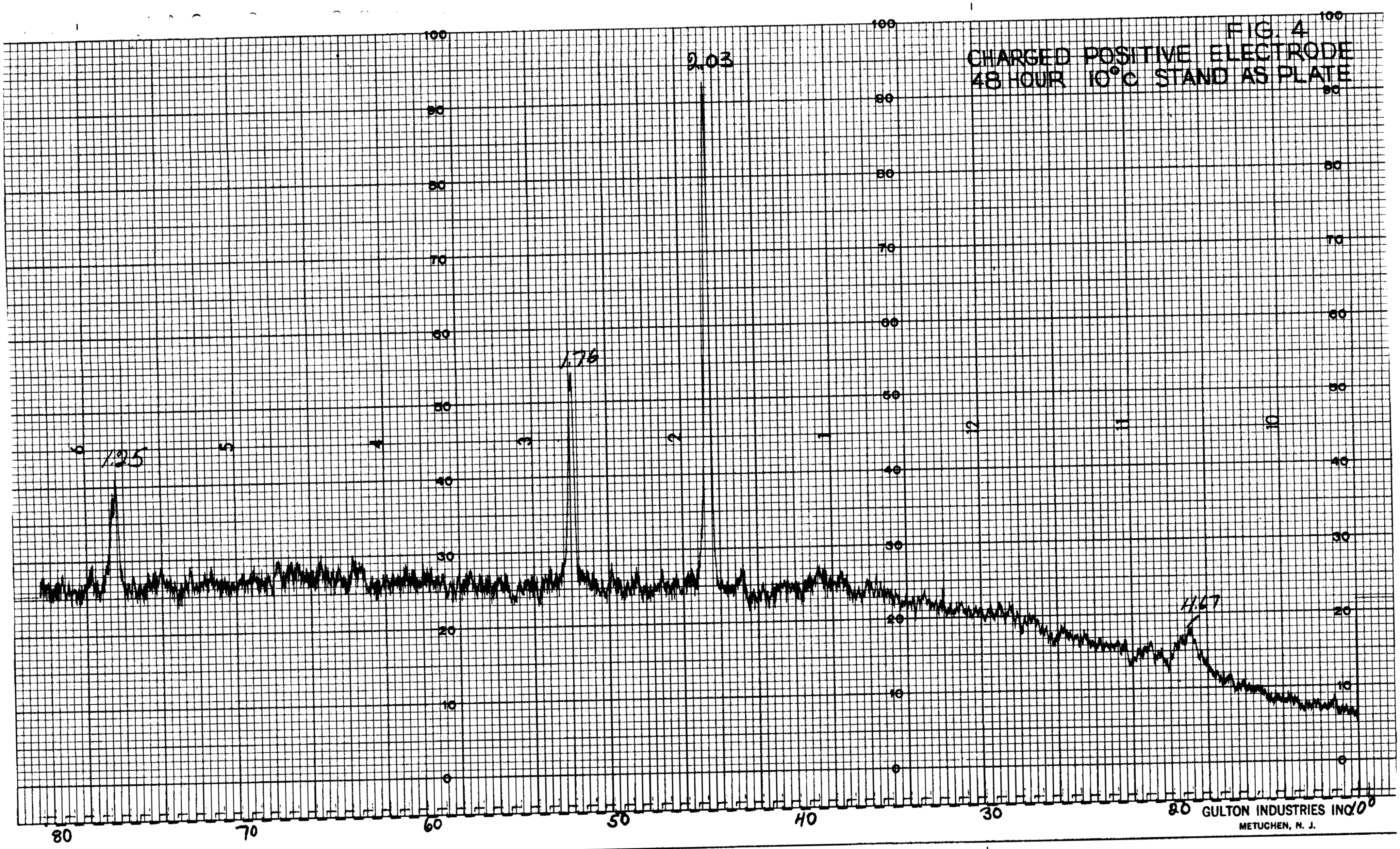
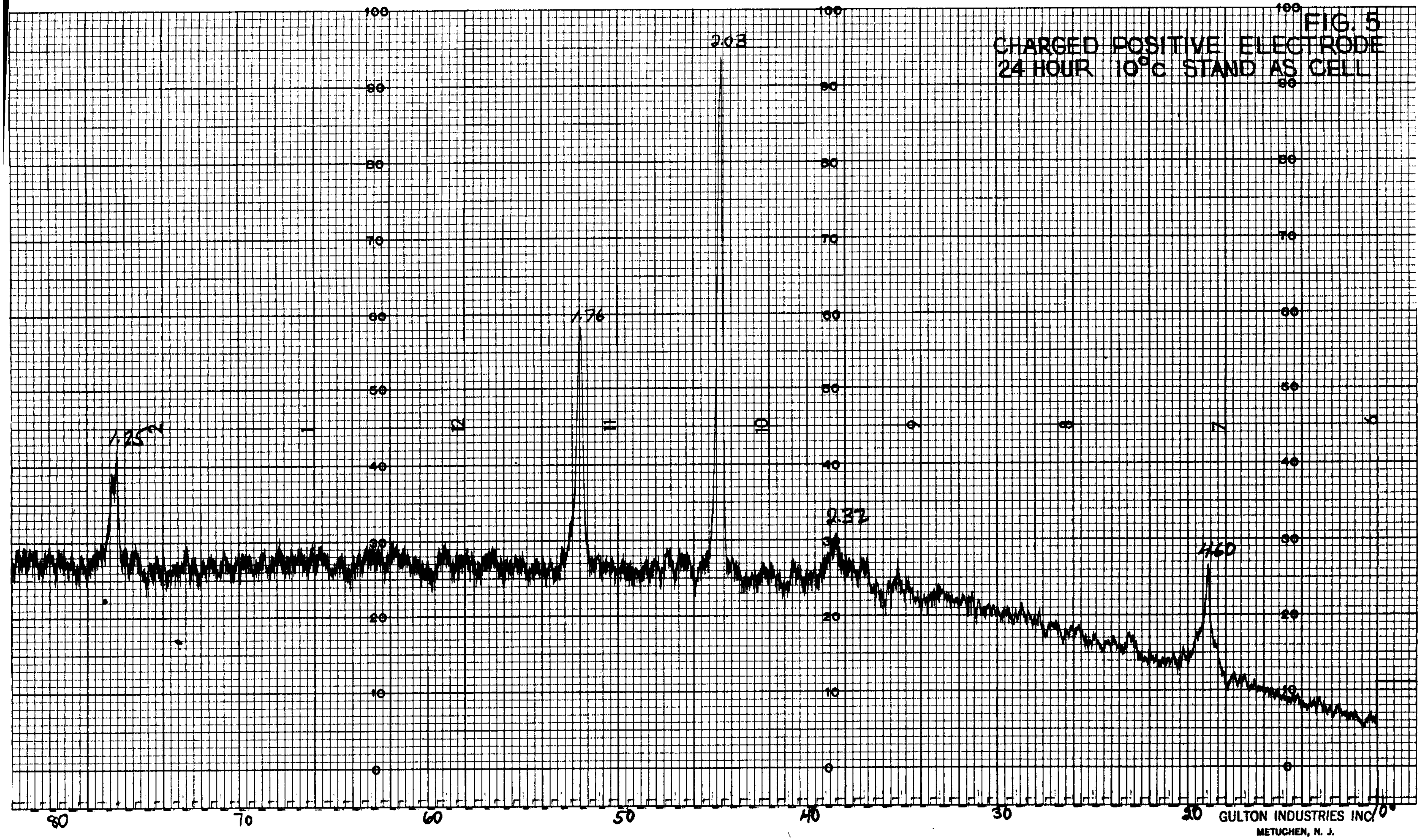


FIG. 5

CHARGED POSITIVE ELECTRODE
24 HOUR 10°C STAND AS CELL



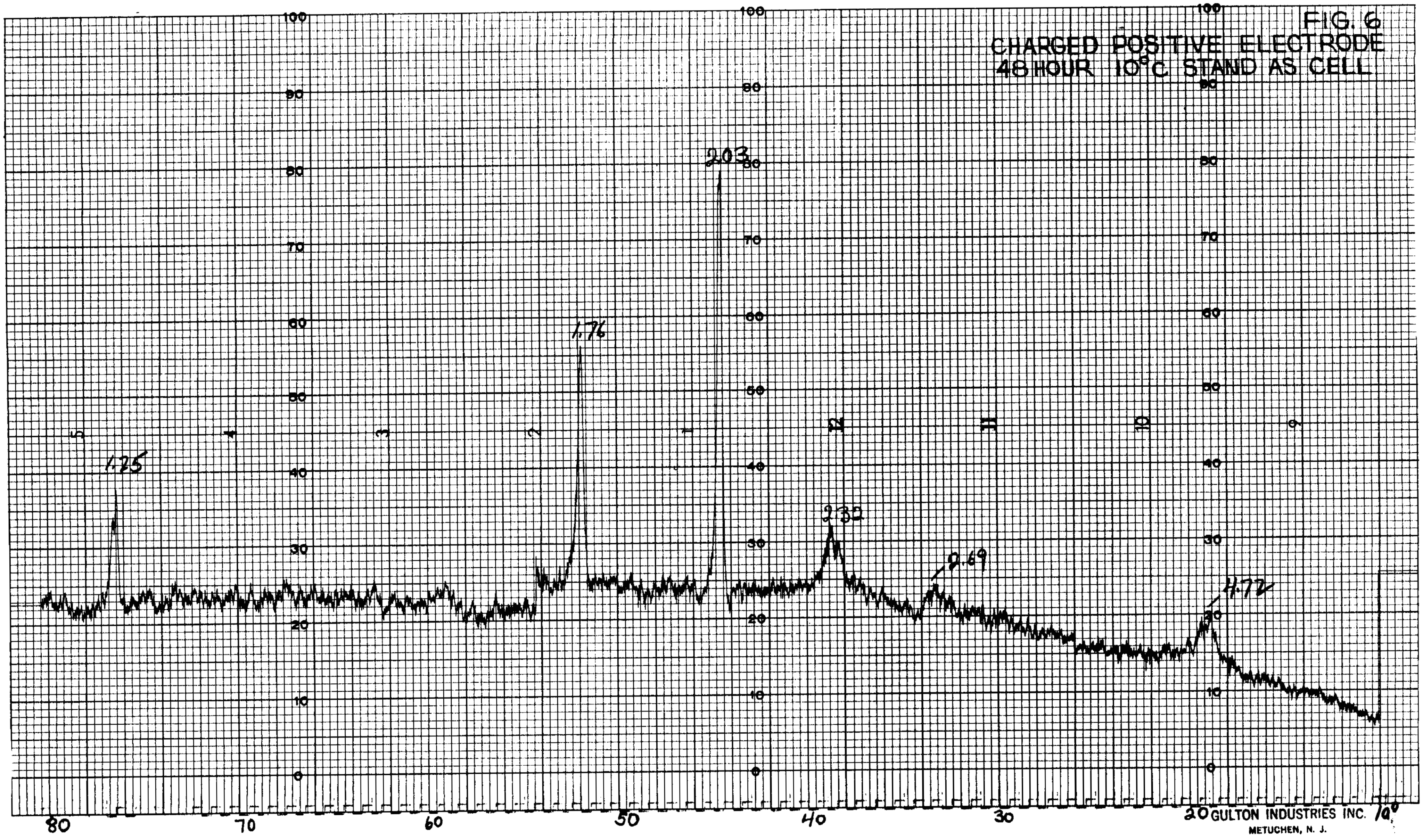


FIG. 6

CHARGED POSITIVE ELECTRODE
48 HOUR 10°C STAND AS CELL

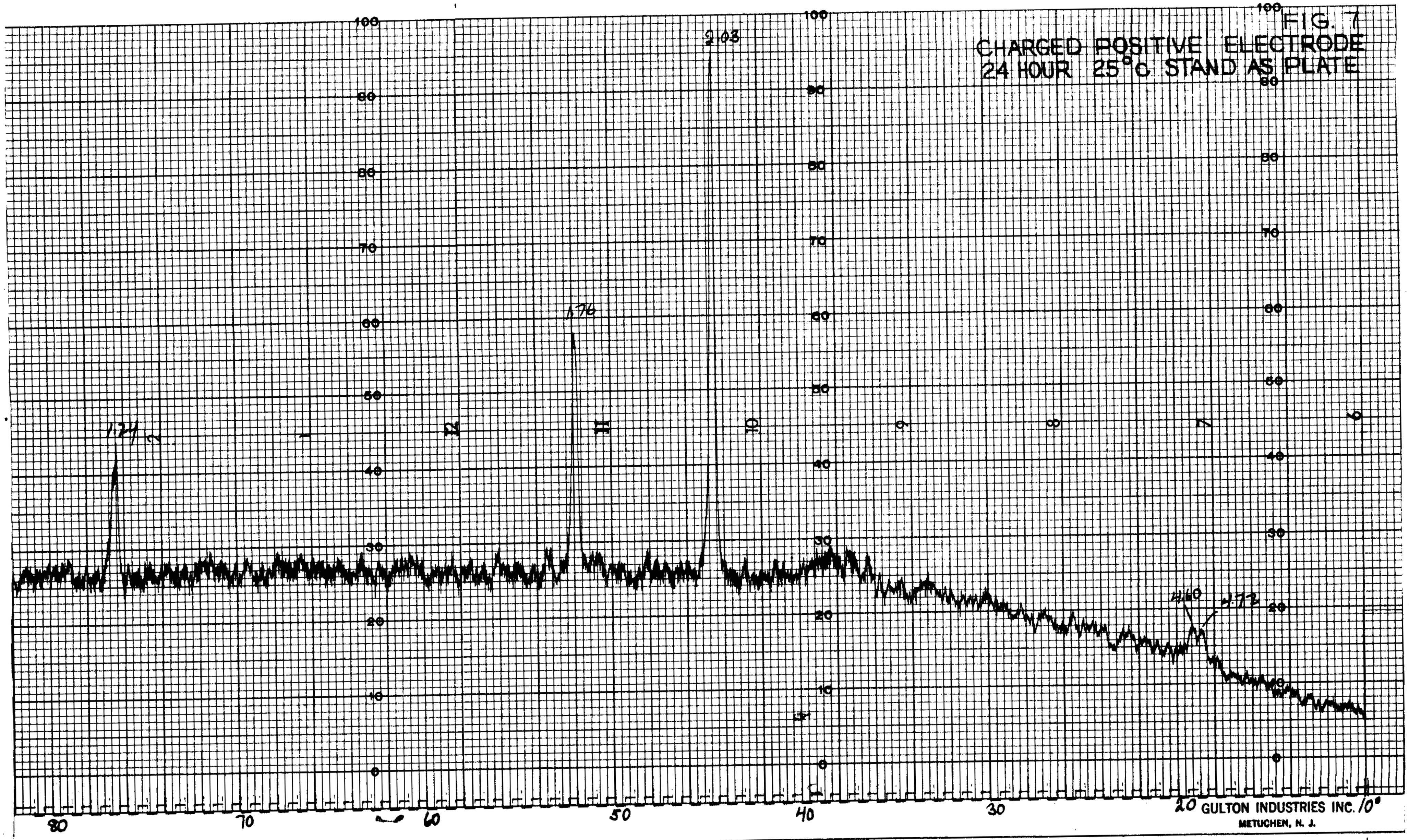


FIG. 7

CHARGED POSITIVE ELECTRODE
24 HOUR 25°C STAND AS PLATE

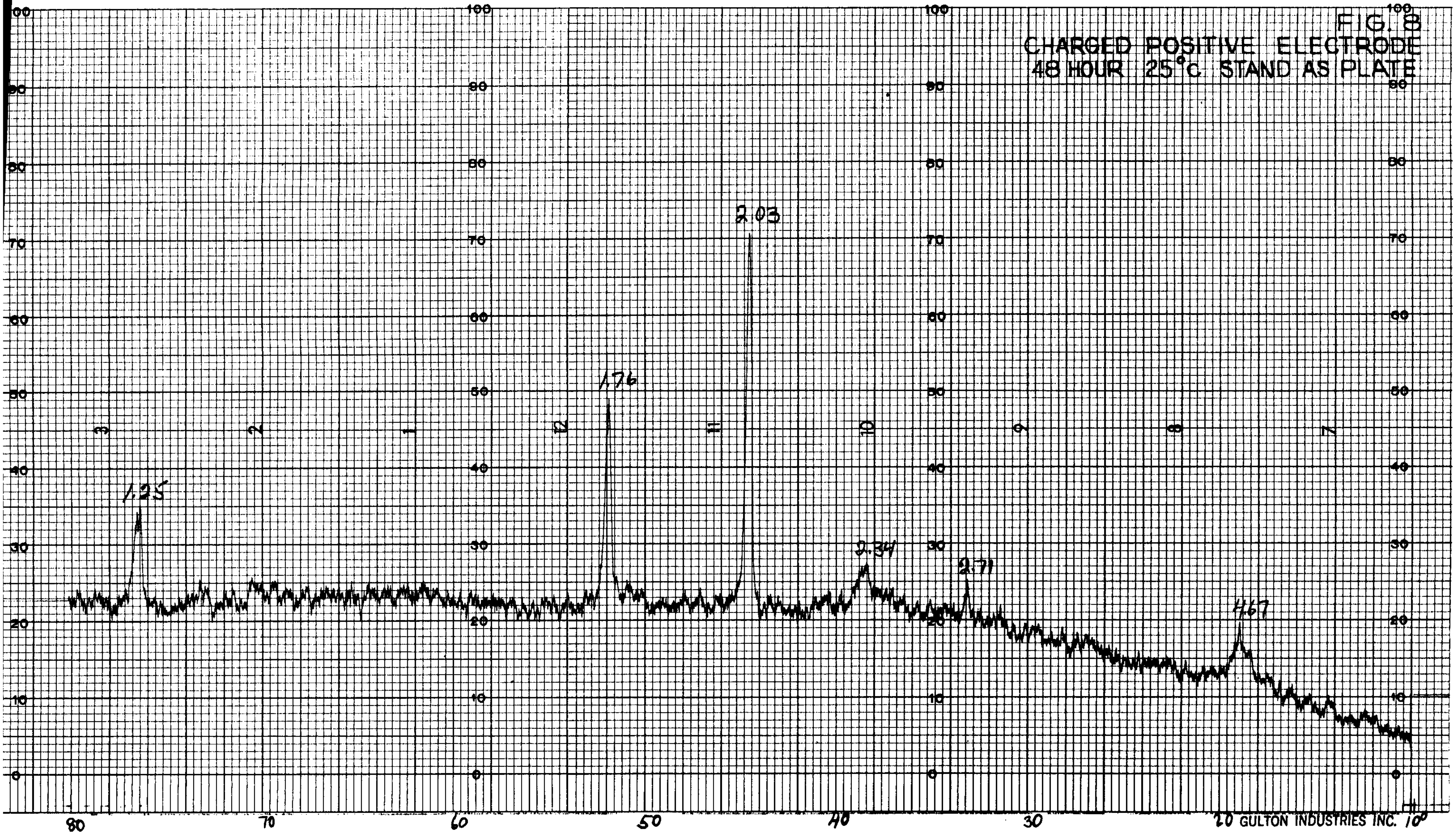
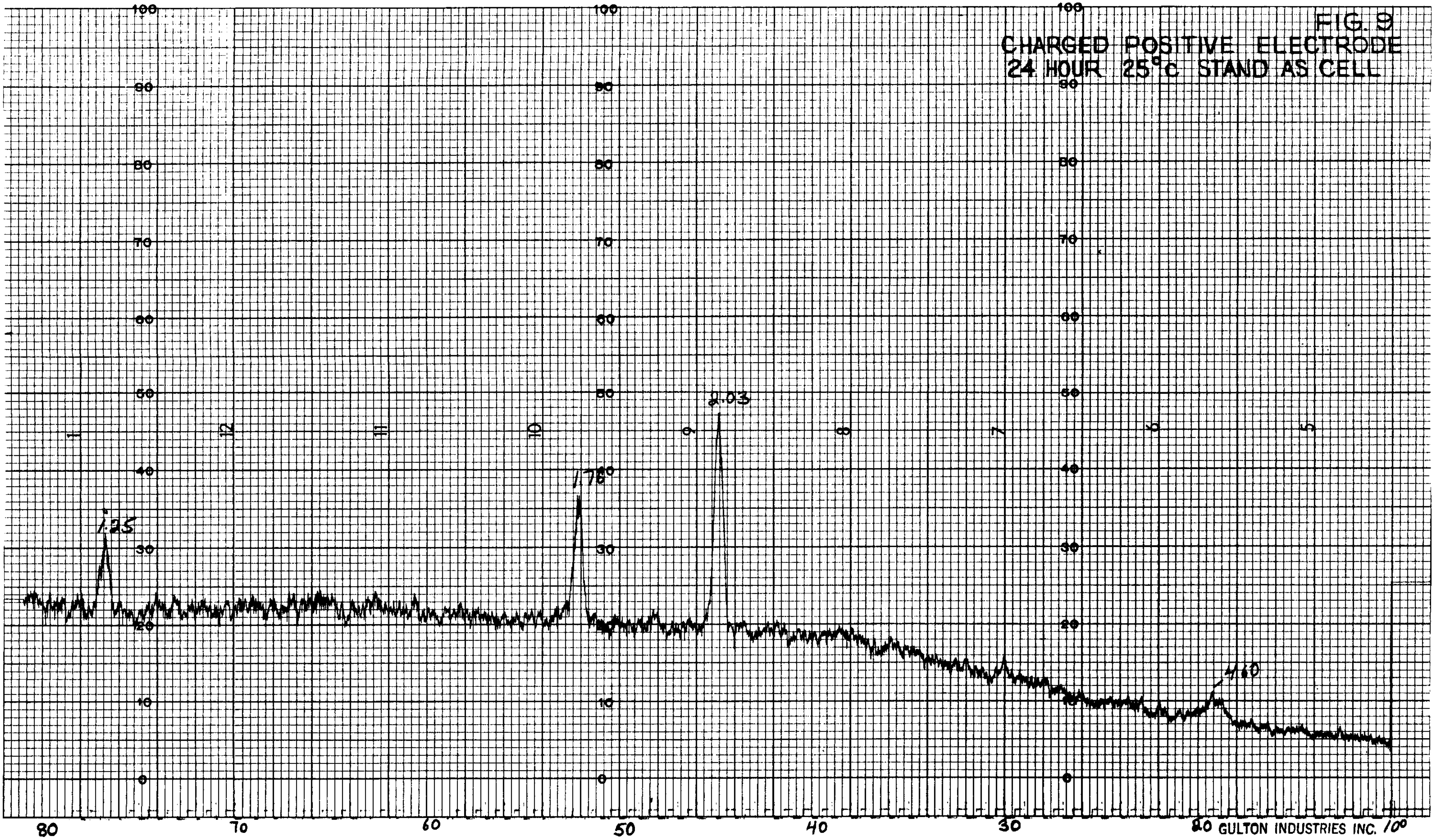


FIG. 8
CHARGED POSITIVE ELECTRODE
48 HOUR 25°C STAND AS PLATE

FIG. 9

CHARGED POSITIVE ELECTRODE
24 HOUR 25°C STAND AS CELL



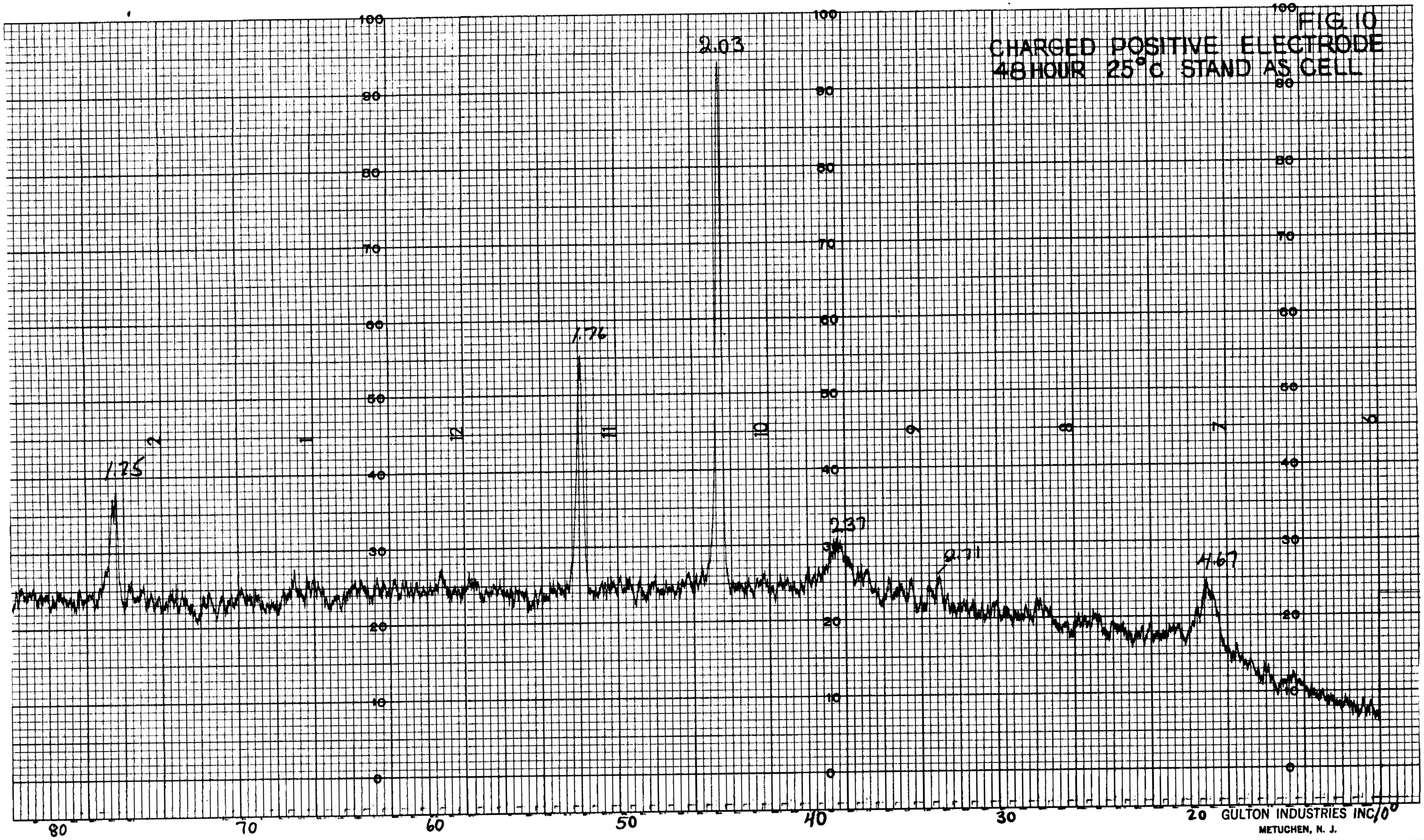


FIG. 10

CHARGED POSITIVE ELECTRODE
48 HOUR 25°C STAND AS CELL

FIG. 11

CHARGED POSITIVE ELECTRODE
24 HOUR 50°C STAND AS PLATE

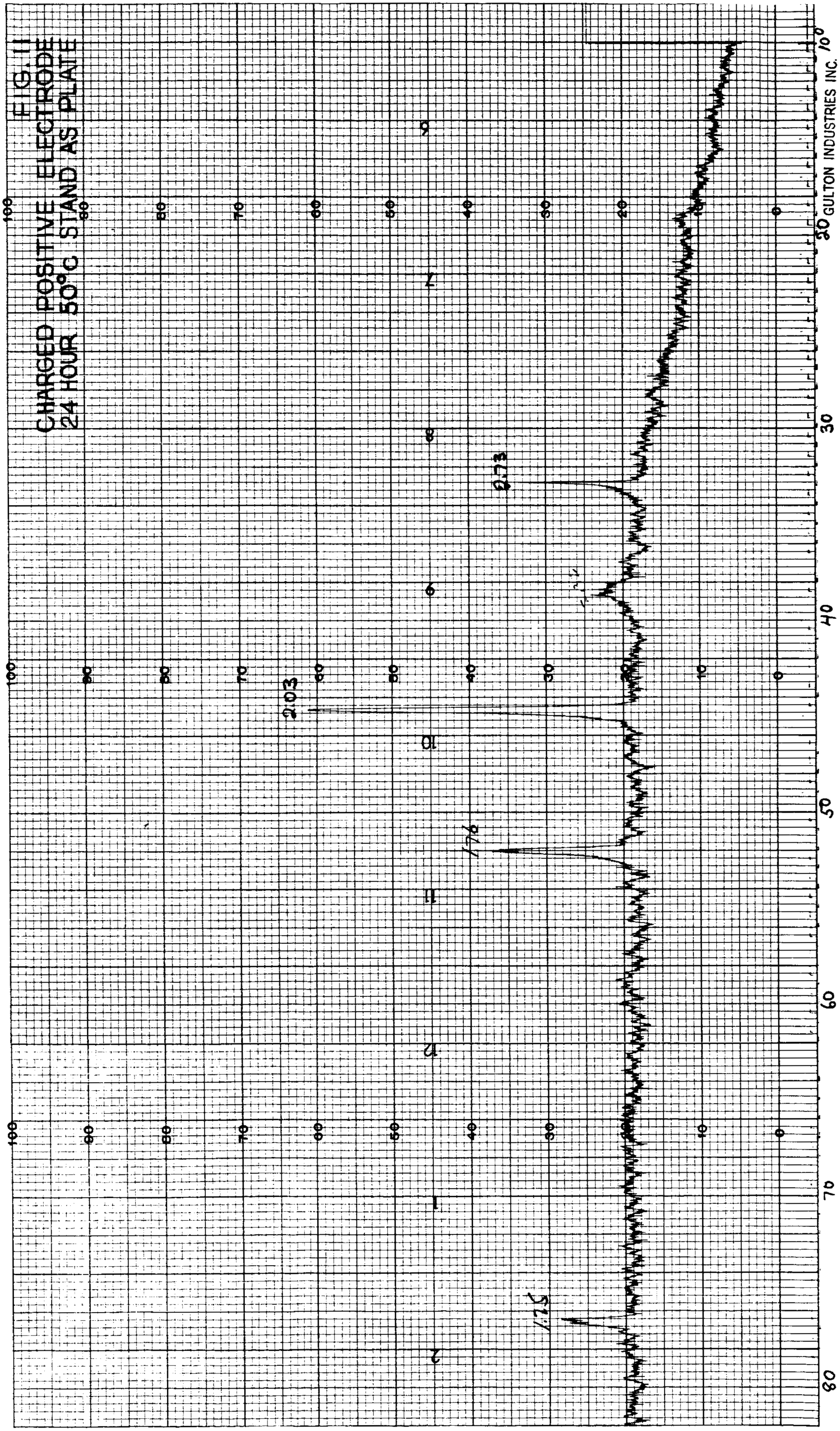
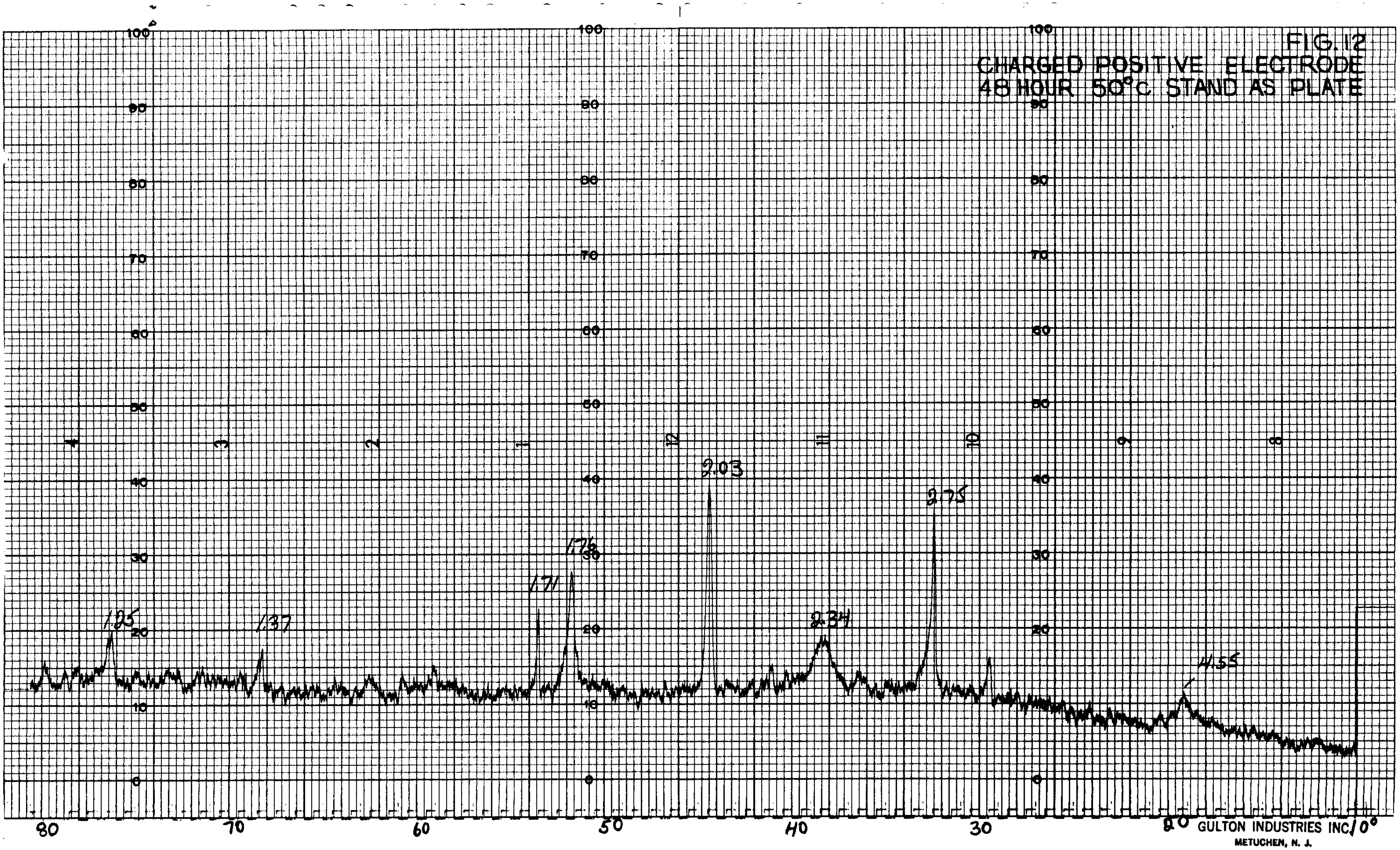


FIG. 12
CHARGED POSITIVE ELECTRODE
48 HOUR 50°C STAND AS PLATE



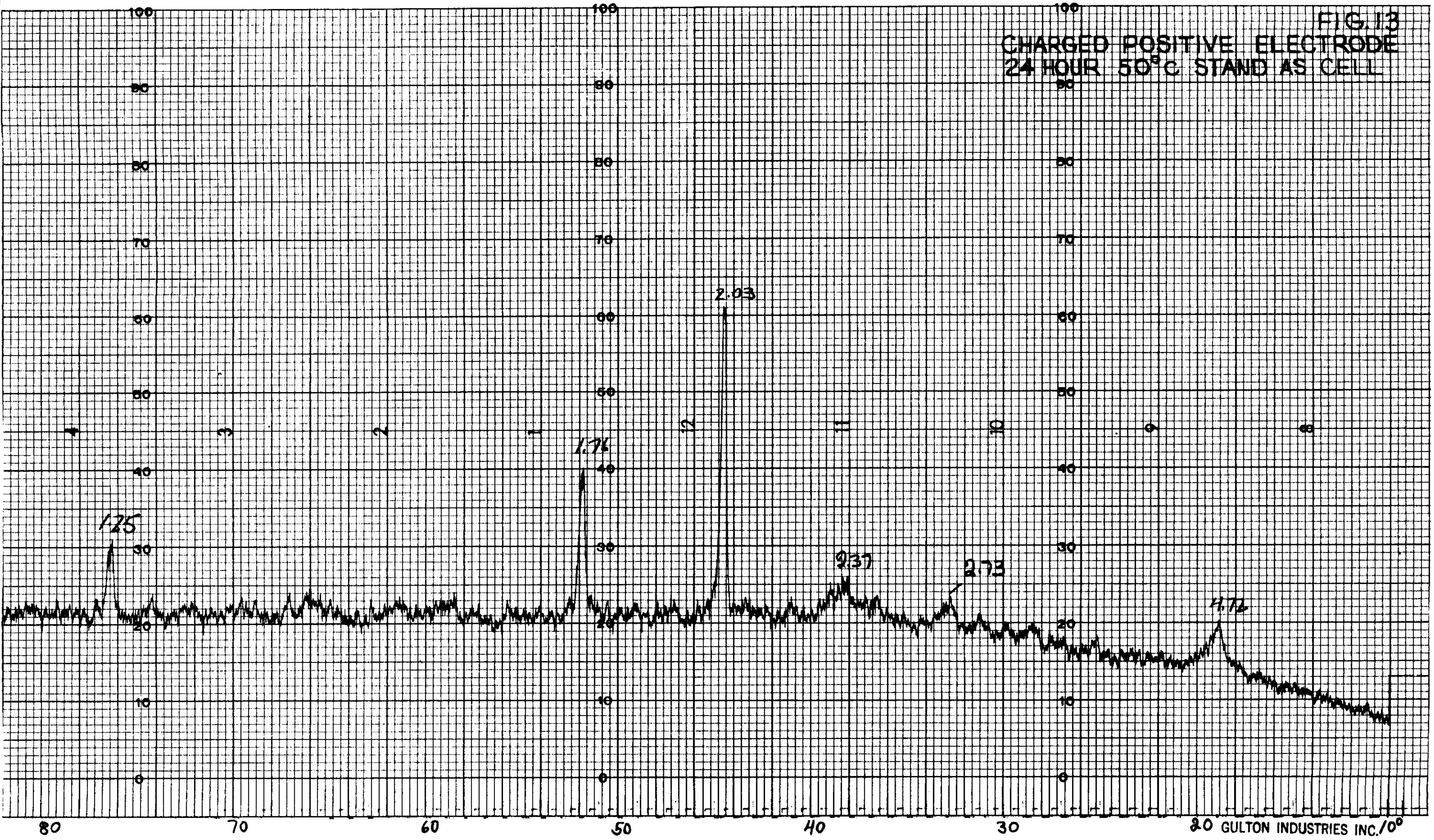


FIG. 13
CHARGED POSITIVE ELECTRODE
24 HOUR 50°C STAND AS CELL

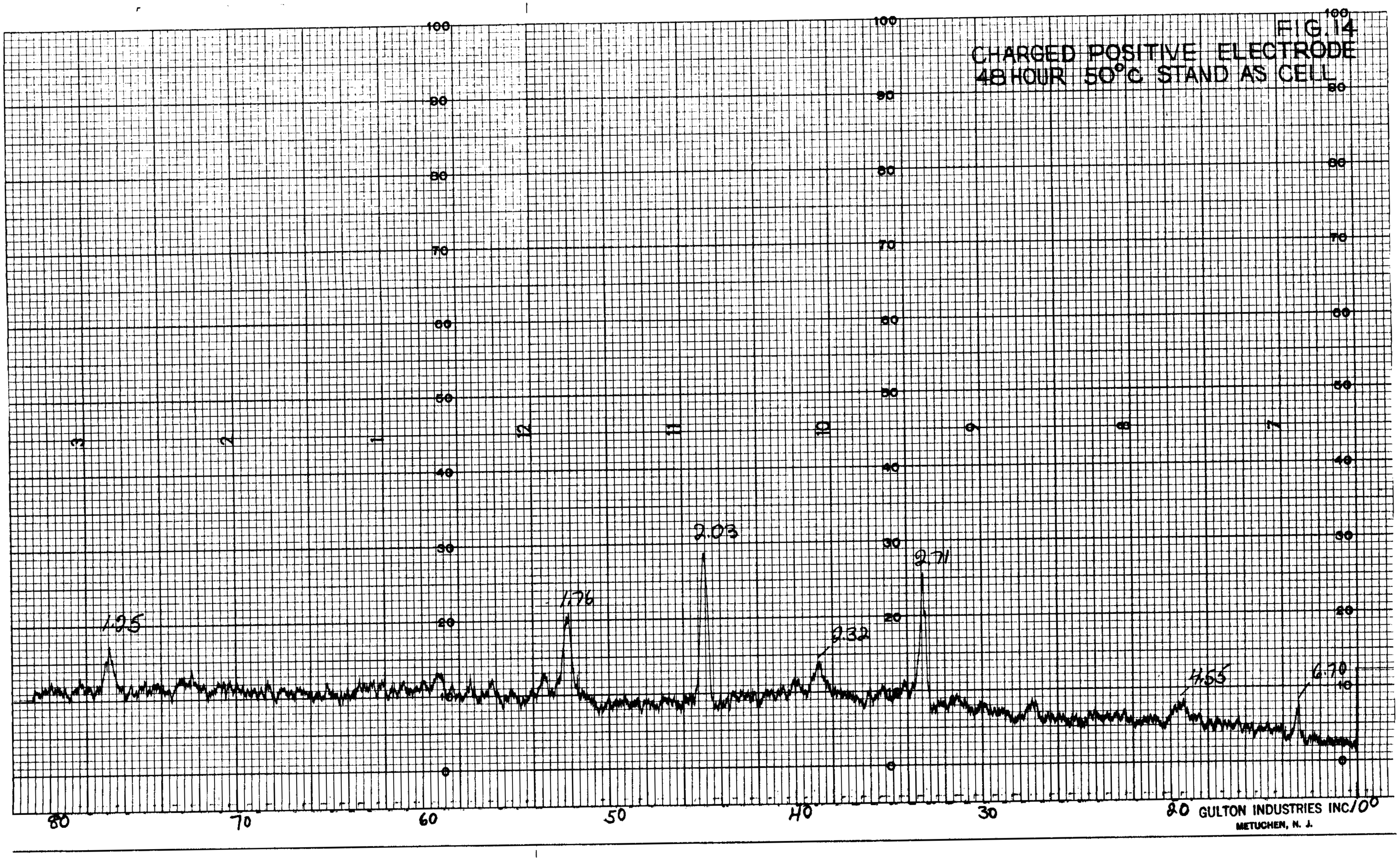
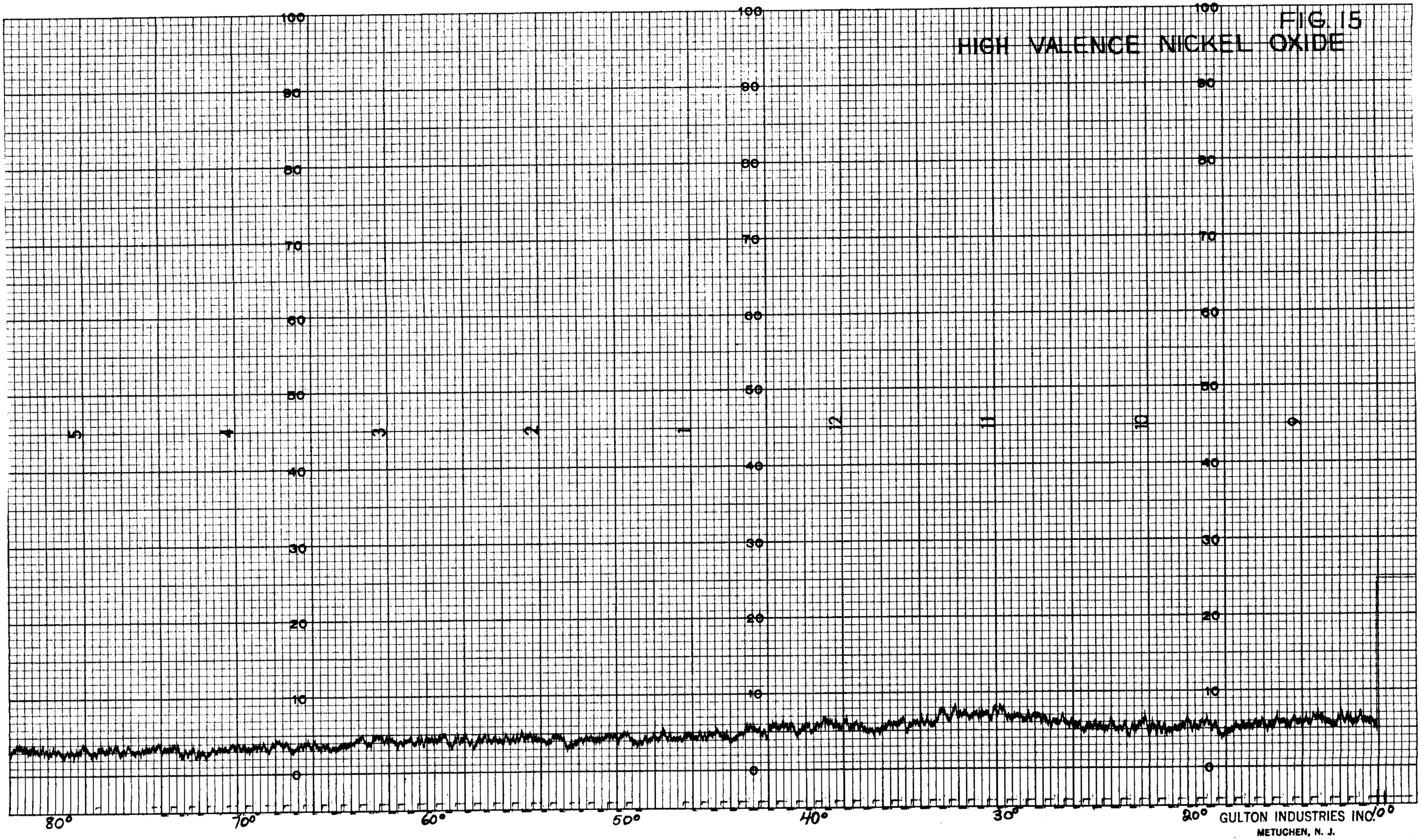


FIG. 14
CHARGED POSITIVE ELECTRODE
48 HOUR 50°C STAND AS CELL

FIG. 15

HIGH VALENCE NICKEL OXIDE



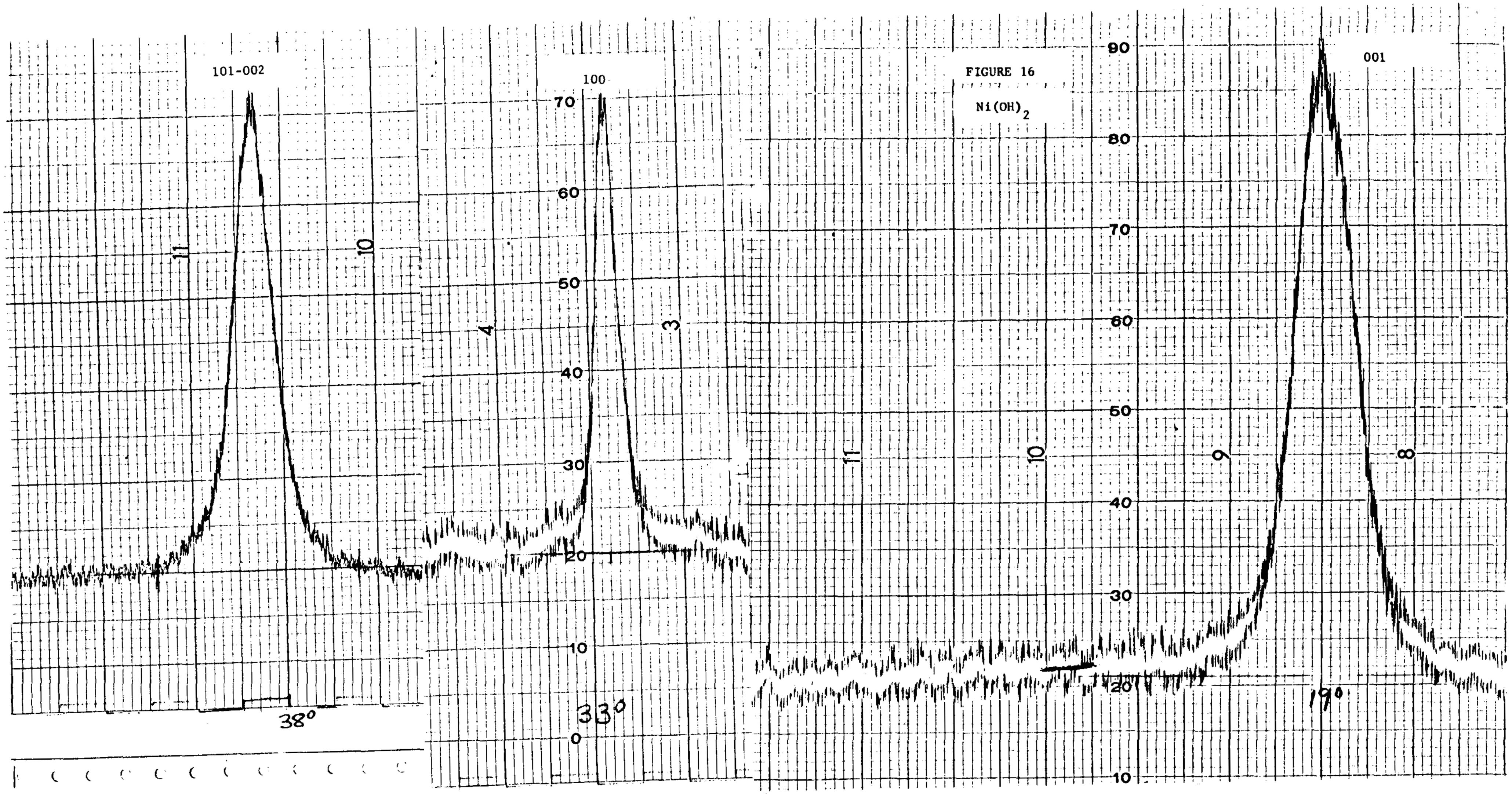


FIGURE 16

$Ni(OH)_2$

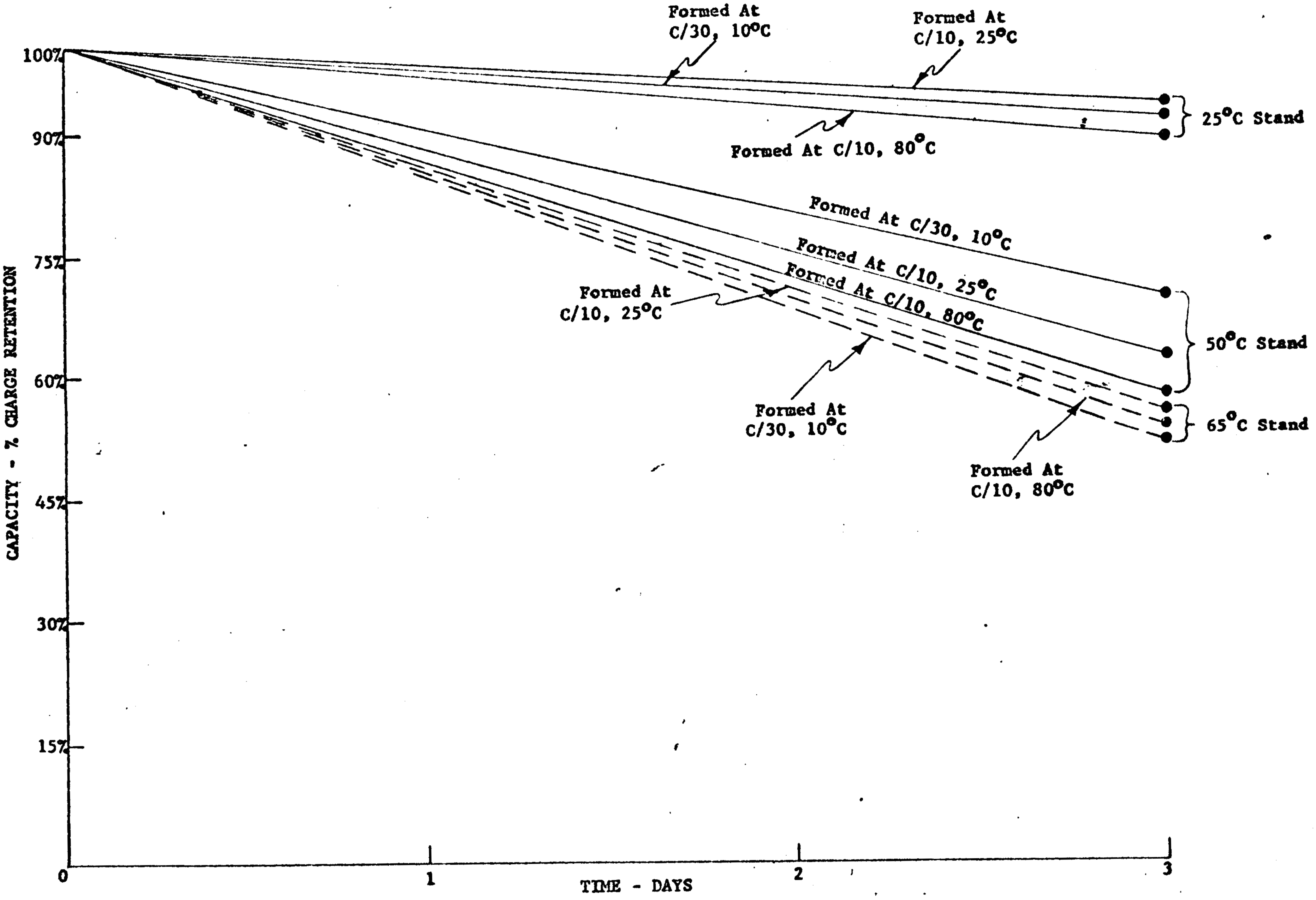


FIGURE 17. STABILITY OF POSITIVE PLATES AT VARIOUS TEMPERATURES

GULTON INDUSTRIES INC.
METUCHEN, N. J.

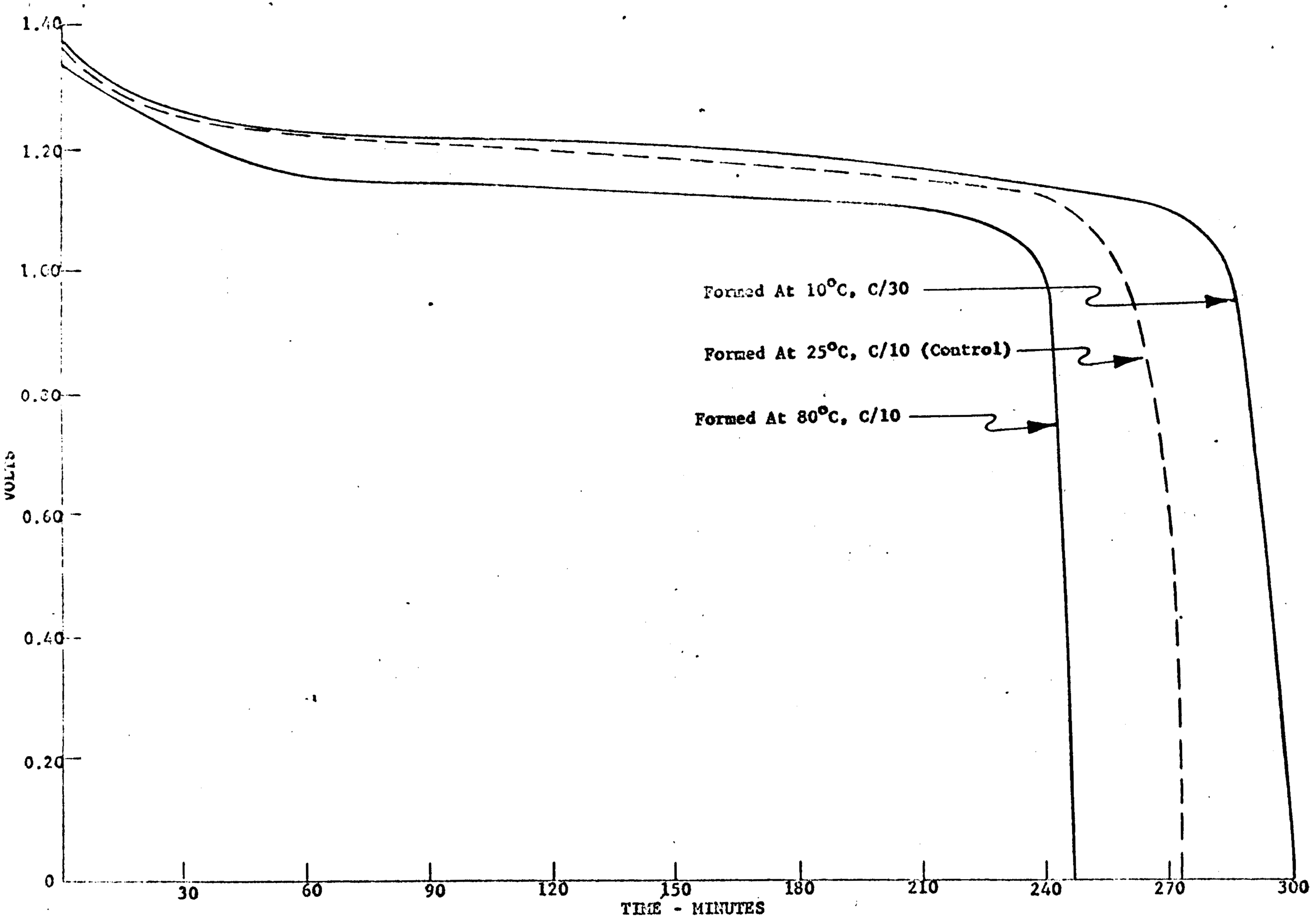


FIGURE 18. DISCHARGE CURVES OF CELLS WHOSE POSITIVES HAVE BEEN FORMED AT VARIOUS RATES & TEMPERATURES

GULTON INDUSTRIES INC.
METUCHEN, N. J.

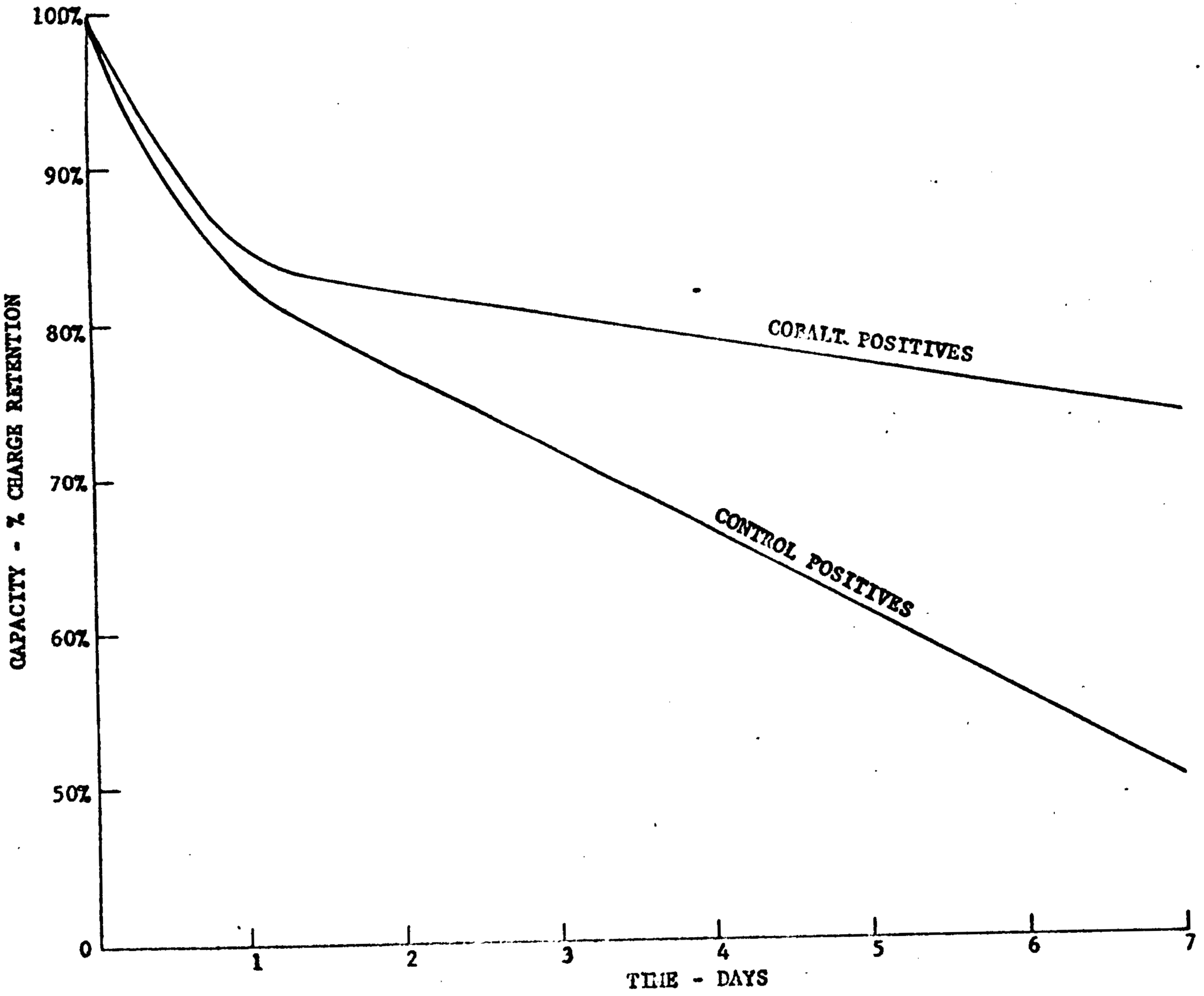


FIGURE 19. COMPARISON OF COBALT CONTAINING POSITIVES STABILITY AT 65°C WITH CONTROL POSITIVES

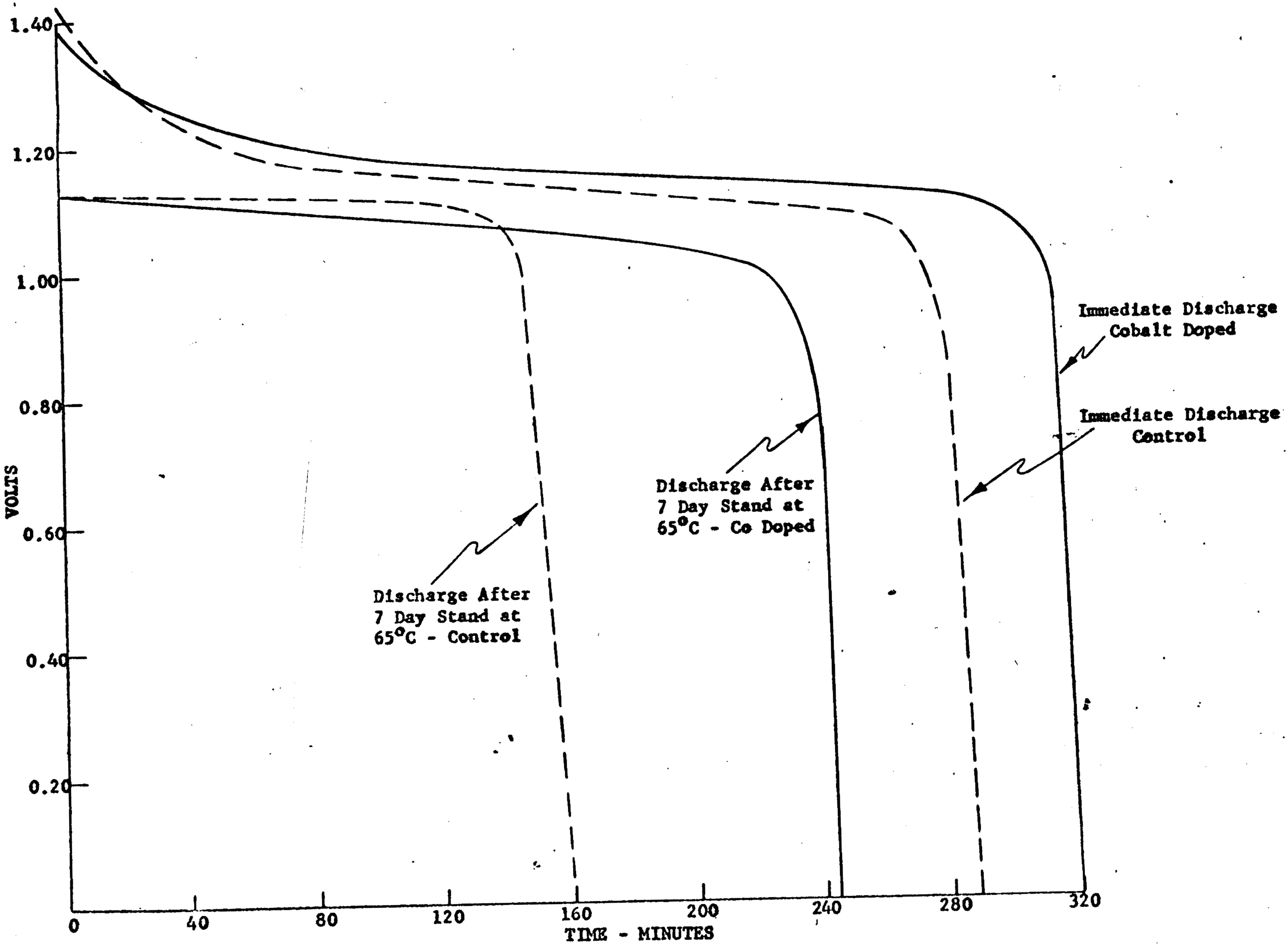


FIGURE 20. DISCHARGE CURVES OF CELLS WITH CONTROL POSITIVES AND CELLS WITH COBALT DOPED POSITIVES ON IMMEDIATE DISCHARGE AND AFTER A 7 DAY CHARGED STAND AT 65°C

GULTON INDUSTRIES INC.
METUCHEN, N. J.

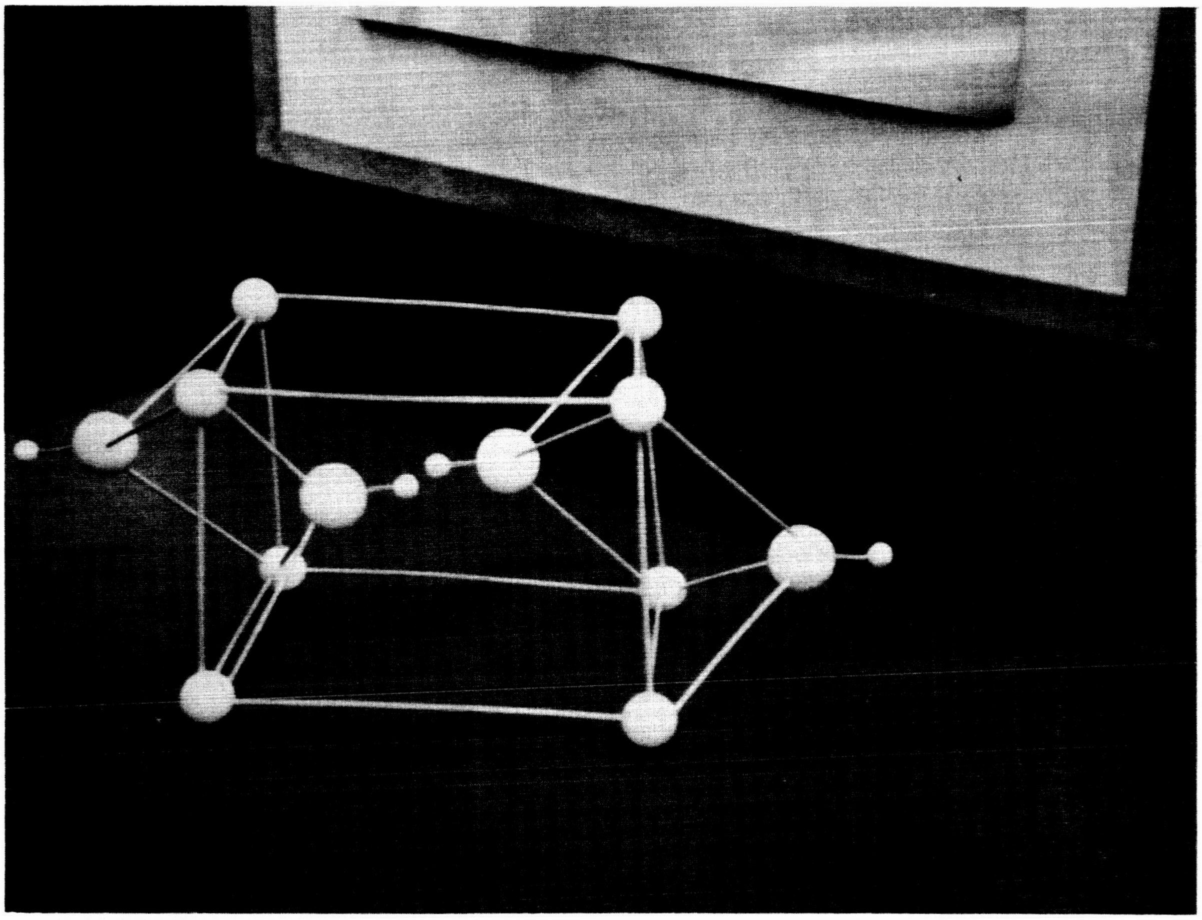


FIGURE 21. PHOTOGRAPH OF THREE DIMENSIONAL REPRESENTATION OF UNIT $Ni(OH)_2$ CELL

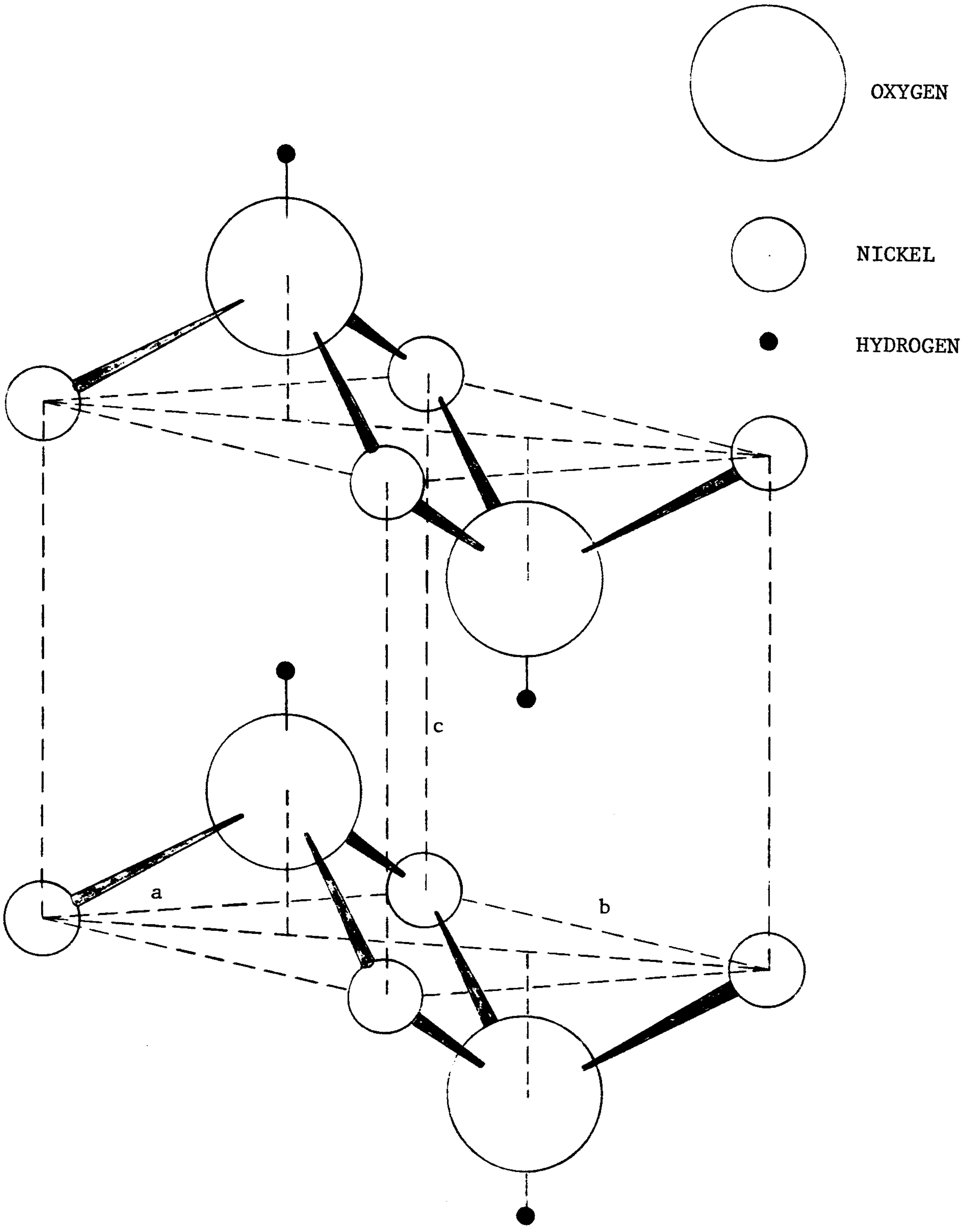


FIGURE 22. SKETCH - $Ni(OH)_2$ STRUCTURE - DISCHARGED

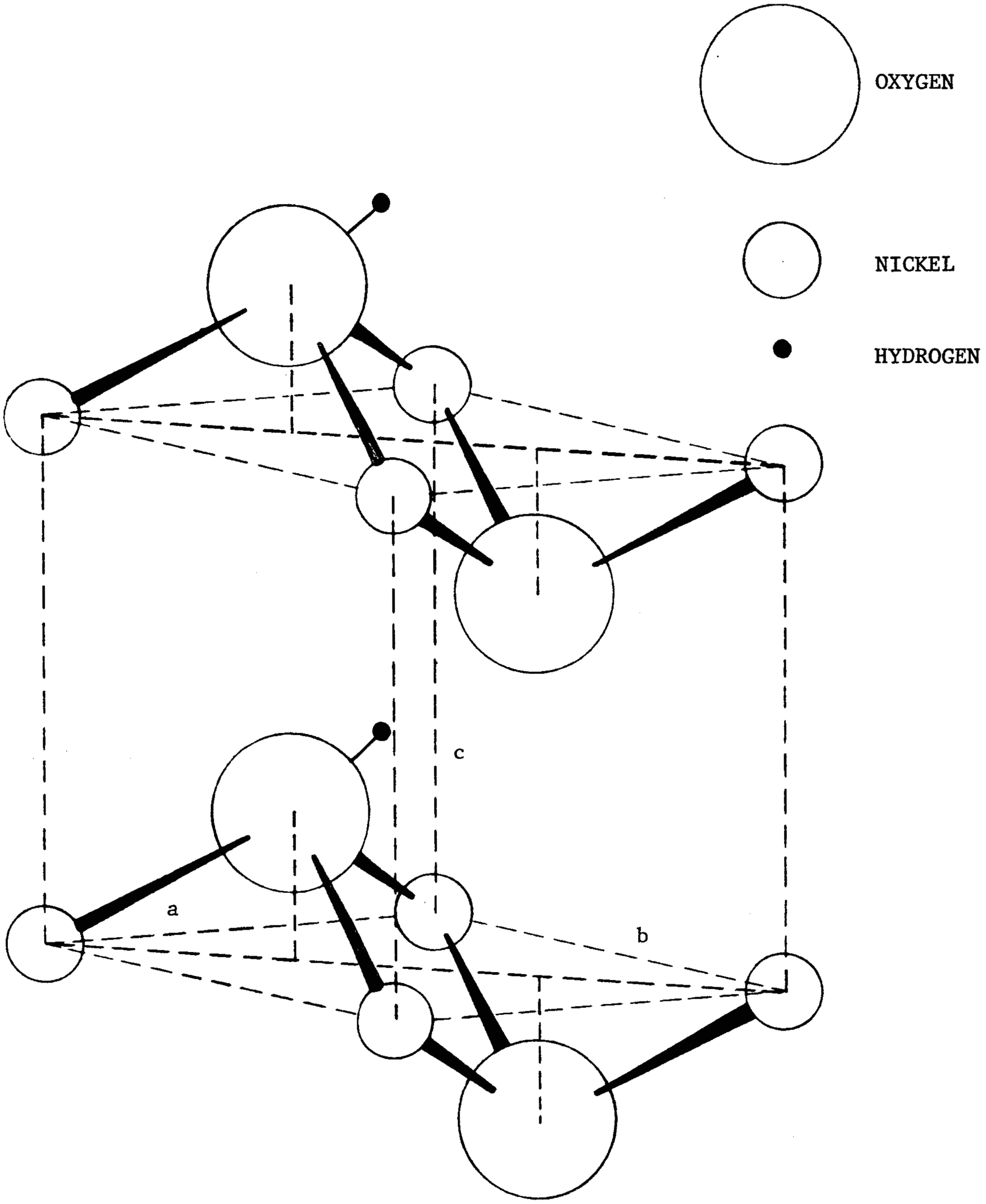


FIGURE 23. SKETCH - $Ni(OH)_2$ STRUCTURE - CHARGED