NASA CR-54832

INVESTIGATION OF BATTERY ACTIVE NICKEL OXIDES

BY

P. Ritterman and H. N. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3- 7620

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

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NASA CR-54832

FIRST QUARTERLY REPORT

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

September 12, 1965

CONTRACT NAS 3-7620

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

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SUMMARY

A study of the methods used in determining the structure of the nickel oxide electrode revealed that one could get more satisfactory results when X-raying a plate without polyethylene covering.

A possible means of determination of structure and composition, as related to state of charge, has been theorized by use of X-ray patterns of wet, uncovered plates.

Chemical methods have been developed which will make possible the determination of the formula weight of a particular state of charge of the positive electrode.

Possible superior materials, with respect to capacity and charge retention, by formation at 10°C-35 ma and 80°C-100 ma, have been produced.

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ABSTRACT

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X-ray patterns are presented indicating the interference of polyethylene covering. The removal of such a cover yields patterns which are more meaningful, with respect to their relation to state of charge.

Chemical methods have been developed which will make possible the determination of the formula weight of a particular state of charge of the positive electrode.

Superior materials, with respect to capacity and charge retention, by formation at 10°C-35 ma and 80°C-100 ma, have been produced.

author

I. INTRODUCTION

A. PURPOSE

The investigation performed under this contract will include the following: (1) continuation of identification and characterization of nickel electrode materials; (2) intensive studies of stabilization of positive electrode material at elevated temperatures; and (3) studies of the utilization, efficiency, voltage and cycling characteristics of those positives stabilized by the most effective method.

B. MEETINGS

On July 28, 1965, a meeting was held with Mr. W. Nagle of NASA/Lewis. Dr. H. N. Seiger, P. Ritterman, and R. Michaels represented Gulton Industries. The meeting took place at Gulton Industries, Metuchen, N. J. The final report of Contract NAS 3-4178 was discussed, as well as the work plan for the current contract.

It was decided that in addition to the work plan, the following special tests should be conducted.

1. The rate of heating of the metal block under the conditions of the D.T.A. experiments would be determined.
2. A sheet of nickel would be anodized in KOH and then its X-ray diffraction pattern determined.
3. Thermogravimetric analysis as a means to determine the composition of the sintered plate electrode will be investigated.

II. OUTLINE OF PROGRAM

The program is divided into two major parts. The first involves the continued investigation of the nature and amount of materials found in the sintered nickel oxide electrode. These studies will be made at various stages of charge, current densities, and temperatures. A study of the effect of open circuit stand of charged nickel oxide electrodes, both in the presence and isolated from their counter electrode material, the Cd/Cd$(OH)_2$, will be made. The second part will concern itself with methods of stabilizing nickel oxides and hydroxides. The methods will include (1) doping (the inclusion of foreign materials within the structure of nickel oxide crystals); (2) formation at various currents and temperatures; and (3) any other means of nickel oxide electrode stabilization deemed feasible will be presented for the approval of the NASAp project manager.

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

1. Construction of Test Cells

a. Plates

Gulton positive plates will be used, all of which were impregnated at the same time with $Ni(NO_3)_2$ and then converted chemically to $Ni(OH)_2$.

b. Stacks

Single positive plates will be surrounded by excess negative capacity in the form of 2 sintered cadmium electrodes with two layers of non-woven nylon serving as separator and 34% KOH as electrolyte.

2. Formation Treatment

Thirty cores will be constructed and cycled using the following regime:

a. Charged at C/10 for 16 hours.
b. Discharged to 0 volts at C/3.
c. Shorted for 2 hours.

This will be repeated 3 times. Twenty cells most alike in capacity will be chosen for further testing.

3. Effect of State of Charge and Rate of Charge.

a. After the third formation cycle is completed, 12 cells will be discharged at C/2 for 4 hours.

b. Two cells will be discharged at C/2 for 1 hour.

c. Two cells will be discharged at C/2 to 1.0 V.

d. Two cells will be discharged at C/2 for ½ hour.

e. Two cells will retain their fully charged state.

f. Two cells will be charged to the gassing point.

After a 24 hour stand on open circuit, the cells will be taken apart and the positive plate analyzed by various means which will be described in a later portion of this section. The same will be done at the C/10 rate.

4. Stand time at Various Temperatures

After preparing 24 cells as in (2.) above, they will receive the following treatment.

a. 24 cells will be charged at C/10 for 20 hours at room temperature.

b. 8 cells will be placed in an oven at 50°C.

c. 8 cells will be placed in a cold box at 10°C.

d. 8 cells will remain at 25°C in oil bath.

Four cells will be disassembled immediately upon storage at each temperature and the positive placed in a beaker of 34% KOH. After 24 hours, two positives will be analyzed which were in a beaker and two positives which were part of a cell. The other positives and cells will stand at their respective temperatures for 3 months and then be analyzed.

5. Methods of Analysis

The plates will be analyzed by chemical means, X-ray diffraction, and differential thermal analysis.

a. Chemical Means

Emphasis will be placed on chemical analysis for quantitative determination of Ni, H, and O in the active part of the plate.

(1) Nickel

In a sintered plate, the interference of pure nickel must be eliminated. Total nickel can be determined by electroplating or precipitation in alkaline solution as nickel dimethylgloxime.

Methods for separating Ni^o from the divalent, trivalent, or tetravalent nickel oxides will be explored. Determination of the amount of Ni^o present in an impregnated sintered plaque will also be explored.

(2) Hydrogen

A washed and dried sample will be mixed with K_2CrO_4 and $PbCrO_4$ and heated to 600°. The water vapor then produced will be captured in a weighed drying tube.

(3) Ni^{+2}/Ni^{+3}

Methods will be sought to determine the amount of Ni^{+2}/Ni^{+3} present in a particular sample.

(4) Oxygen

Oxygen can best be determined by difference, with respect to the total nickel and hydrogen determined.

b. X-ray Diffraction

As was stated in the Final Report,(2) the possibility of X-raying a wet positive without polyethylene covering will be further examined. The plate will be kept in polyethylene until just before mounting it into the goniometer. The plate will be wet with KOH and, in essence, be identical with the plate within the cell. 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.

c. Differential Thermal Analysis

The plate sample will be ground into a powder and placed in a stainless steel block containing 3 thermocouples. Another hole in the block contains powdered alumina. The thermocouples are so arranged that there is a response to any reaction or transitional change of the sample. The question of obtaining standards besides $Ni(OH)_2$ remains the difficulty.

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(2) See References, Page 22

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation at Various Temperatures and Rates

Cells will be constructed using one unformed sintered positive surrounded by two negative plates. As described in previous sections, formation will be performed at the C/2, C/10, and C/30 rates and at temperatures of 10°, 25°, and 80° for each rate. Three cells will be 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, and Mn. These elements are near nickel in the periodic table. Alkali and alkaline earths will include Li, Mg, Na, Be, and Ca. These will be incorporated by use as the salt of the nitrate ion. A control solution of pure nickel nitrate will also be used.

For each quantity and additive type, 10 plates will be impregnated. These will be formed by standard methods or by the procedure found to yield optimum results.

3. Other Techniques of Stabilization

Other means besides the vacuum 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 solutions of nickel salts.

The impregnation method with which we are familiar, by previous experience, involves the impregnation of a sintered nickel plaque made cathodic in a solution of dilute nickel nitrate. It has been found that nickel-cadmium cells made from plates of this type have performed very well at elevated temperatures.

C. PRELIMINARY EVALUATION

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

1. Storage and Evaluation

Three cells of each group will be constructed and charged at the C rate for 2 hours, and then immediately discharged at C/5. This will determine initial capacity at room temperature. The charge will be repeated, and after a stand time of one day, the cell will again be discharged at C/5. This will be done at 50°C as well. The stand on open circuit will be extended to 3 days. The same kind of test will be conducted at 65°C. A check of capacity on immediate discharge at room temperature will be made before each stand test. Thus, the effect of cycling on the stabilized material can also be evaluated.

D. EVALUATION OF IMPROVED MATERIAL

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

1. Decomposition of Charged Positive

Using 15 cells consisting of the superior material, with respect to stabilization, the following tests will be performed.

Cells will be allowed to stand at temperatures of 20°, 40°, 60°, 80°, and 95°C and after a passage of 1 day, removed, discharged at the C/10 rate to a 1.0 V end point at room temperature. The capacity of all cells will be determined immediately after charge at the C rate. This will be repeated by charging the same cells at the C rate and extending the stand time to 3 days. The test will be repeated allowing just the charged positive plates to be immersed in electrolyte at the various temperatures, the capacity of which, again, will have been previously determined. These plates will then be surrounded by negatives and discharged to 1.0 V at the C/10 rate. This, too, will be repeated extending the charged stand time if significant differences are noted between the 1 and 3 day stand.

2. Investigation of Sintered Plate paramaters

After establishing a loading factor which meets the approval of the NASA project manager, the following investigation will be made.

a. Establishment of Optimum Formation Technique.

The optimum formation shall be considered to be the one which produces a plate which, when incorporated into cells, yields the highest voltage level on discharge, the greatest capacity per unit weight and volume, optimum charge efficiency, and most consistent reproducibility of the aforementioned results.

A statistical experiment involving rate, amount of overcharge, and number of cycles will be used to establish optimum conditions. Before such an experiment is begun, past experience tells us that an initial low rate charge and discharge cycle at the C/10 rate or less should be used.

b. Establishment of Charge Acceptance as a Function of Charge Rate, and Determination of Point of Oxygen Evolution at Various Rates.

The characteristics of positive plates can be established with one experiment. A positive plate is contained in a sealed chamber of known volume together with an oxygen consuming electrode. Both the oxygen electrode and the positive plate have external connections allowing for charge. The sealed chamber is filled with pure oxygen and a pressure gauge records oxygen pressure. As current is passed to charge the positive plate and cause oxygen reduction at the appropriate electrode, the rate of oxygen pressure decay should be in direct proportion to the charging current provided that no oxygen is produced at the positive. The deviation from the theoretical slope will not only establish the charge acceptance, but will also indicate the point at which oxygen evolution begins. This can be established for the one, two, five, and ten hour rates.

c. Determination of Utilization Factors at Various Rates of Discharge.

The three plate cells, consisting of 1 positive and 2 negative electrodes, will again be employed here. All charges will be done at the 1 hour rate. Discharges will be performed at the 10 minute, 1 hour, two hour, 5 hour, and 10 hour rates. Capacities will be determined to 1.0 V and also the point just before the graphitic level.

d. Determination of Utilization Factors for Depth of Discharge at 25%, 35%, 50%, 75%, and 100%.

A group of three plate cells will be charged at the C rate. After the initial charge, the cell will be discharged for 15 minutes at the C rate. It will then be charged for 15 minutes at the C rate and finally discharged to 1.0 V at the C rate. This will be repeated for a 21 minute discharge, a 30 minute discharge, and similarly to obtain the other stated depths of discharge. A comparison will be made of the capacities obtained when discharging to 1.0 V versus the various depths of discharge. This will be done for other charge rates as well.

III. EXPERIMENTAL PROCEDURES & RESULTS

A. DETERMINATION OF BATTERY ACTIVE MATERIALS EXISTING IN THE SINTERED PLATE NICKEL OXIDE ELECTRODE

1. Chemical Means

Various methods were attempted to determine quantitatively the amounts of active nickel, oxygen, and hydrogen present on the sintered plate.

a. Nickel, Ni^{+2}, Ni^{+3}

An attempt was made to analyze a positive plate for the three valence states of nickel, namely; Ni^{o}, Ni^{+2}, and Ni^{+3} by allowing the plate to react with nitric acid. The Ni^{o} was expected to react so as to yield hydrogen gas which could then be collected. From the amount of gas, the quantity of Ni^{o} would be determined. Total nickel could then be determined by dimethylgloxime precipitation or electroplating. When a plate was dissolved in nitric acid, it yielded a mixture of gases. It was found, however, when trying to dissolve Ni powder by itself in nitric acid that this did not occur due to passivation both in dilute and concentrated solution. When a piece of platinum was added to the plate, dissolution occurred, but the gas liberated contained oxides of nitrogen rather than H_2. This was due to the decomposition of the nitric acid.

Both Ni_2O_3 and NiO did not react with nitric acid. Ni_2O_3 was reported to be soluble in HCl with the evolution of chlorine gas. This was not found to be the case for 1:1 HCl at room temperature and elevated temperatures.

A freshly charged positive was cut into several parts. One part, while still charged, was reacted with As_2O_3. Another part was discharged and then reacted with As_2O_3. After allowing for size, there was no significant difference in consumption of As_2O_3.

A third part of this charged plate was X-rayed. The pattern obtained is shown in Figure 1. This pattern, particularly with the peak at 6.79Å, is indicative of a fully charged plate and containing some unstable oxide yet. Thus, it is concluded that the As_2O_3 technique as employed for higher oxide detection is unsuitable under the particular experimental conditions involving a sintered plate.

b. Analysis of Hydrogen

The amount of hydrogen in a sample of pure $Ni(OH)_2$ was determined by means of oxidation of the hydrogen by K_2CrO4 and $PbCrO_4$. The details of the analysis are given below.

A combustion tube was set up in the following manner. At the exit end was one inch of copper gauze, then 12 inches of lead chromate, followed by 4 inches of copper gauze. The sample crucible was placed in next, followed by another four inches of copper gauze. The section of the combustion tube was heated first to 300°C while dry air passed through the system. When all moisture had been removed, the section under the sample crucible was heated to 700°C. The exiting steam was caught in a drying tube containing Drierite. The flow of air was adjusted to 2 ml/sec. The amount of hydrogen in an impregnated plate was also determined. A source of error, such as condensation of water vapor near the exit of the drying tube, was overcome by use of a hot air blower. The results of the hydrogen analysis for pure $Ni(OH)_2$ powder yielded .0438 gram H for a 2.0175 gram sample. The result of the hydrogen analysis for the impregnated plate was .0666 gram H for a plate that showed a gain of 2.8313 grams of active material during impregnation.

c. Determination of Conversion of Ni^o to Active Nickel as a Result of Impregnation

One of the difficulties which occurs when trying to deduce a formula weight from a sintered plate is the weight of inert nickel that has been converted to active nickel. An impregnated plate whose weight had been previously determined was reacted with a mixture of NH_4OH and $(NH_4)_2S_2O_8$ (ammonium persulfate). After two hours in solution, the plate was removed, washed with deionized water, then dried and weighed. The plate originally weighed 5.6203 grams. After impregnation and this treatment, the residue was 5.4269 grams. Thus, approximately 190 mg of the nickel sinter was activated by processing. This corresponds to about 3.4%. The active material gained by the plate was 2.963 grams.

d. Determination of Active Nickel in a Sintered Plate

The solution obtained from (c.) above was electroplated on to a preweighed platinum grid. The electroplating involved taking an aliquot of the solution, 100 ml out of 1500 ml, adding excess ammonia and then passing a current at 3.0 V between the platinum anode wire and the cathode grid. The plating was considered complete by the cleanliness of the solution. The clean solution was tested for nickel by dimethylgloxime and yielded no red precipitate. The weight gain of the platinum grid was .1289 gram of nickel.

e. Impregnation of Sintered Nickel Plates

Sintered nickel plates were impregnated with active material in the following manner.

(1) The plates were weighed blank.

(2) They were then placed in a vacuum chamber while in a beaker. The chamber was then evacuated, and a solution of $Ni(NO_3)2$ was admitted into the beaker.

(3) After 5 minutes, the vacuum was broken, the plates were removed, and the excess solution was allowed to drain off.

(4) The plates were then dried in a circulating air oven.

(5) They were placed into a beaker of 25% KOH at 70°C for 10 minutes.

(6) The plates were removed from the beaker. They were washed with a stream of deionized water until neutral to litmus paper.

(7) The plates were again dried in a circulating air oven and then weighed to determine the weight gain.

(8) This procedure was repeated until plates had gained about 3 grams of active material. The weight gains of the plates are listed below.

Plate No.	Final Weight	Initial Weight	Weight Gain
1	8.6208	5.6962	2.9246
2	8.6407	5.6381	3.0026
3	8.5800	5.6203	2.9597
4	8.5947	5.6678	2.9269
5	8.5986	5.6636	2.9350
6	8.6126	5.6322	2.9804
7	8.6708	5.6416	3.0292
8	8.7568	5.7417	3.0151
9	8.6327	5.6477	2.9850
10	8.7351	5.6917	3.0434

These plates will be used for mass balance experiments involving the determination of hydrogen and nickel at various states of charge of the plate. From this, it will be possible to determine the formula weight at various states of charge.

f. Evaluation of Results of Chemical Analysis

The difficulties of obtaining positive results with respect to separation and determination of Ni^{+++} were discussed with several chemists at Inco Research Laboratories, and they were of the opinion that Ni^{+++} is unstable in aqueous solution. Thus, any solution method for the higher valence state of nickel would not be feasible.

By separating oxidized nickel from elemental nickel and determining hydrogen, a formula can be written. Such a formula will, naturally, be the equivalent of all the oxides of nickel oxide present. Without a direct measure of the ratio $(Ni^{+2})/(Ni^{+3})$, such a formula will be most useful.

(1) Hydrogen Assay

The analytical procedure for determination of hydrogen was tested by analyzing some $Ni(OH)_2$ freshly prepared from $Ni(NO_3)_2 \cdot 6H_2O$ in this laboratory. The analytical result was 2.17% hydrogen in the sample, which compares favorably with the theoretical value of 2.14%.

(2) Formula Weight

(a) % Hydrogen in Impregnated Plate

Using the conversion factor in 1.c., the active material on the plate used to determine hydrogen has increased by .190 gram. Since the weight of the active material without the correction factor was 2.8313 grams, and the weight of hydrogen collected equal to .0666 grams,

$$\% H = \frac{.0666}{2.8313 + .190} = 2.3\%$$

(b) % Ni^{+n} in Impregnated Plates

The amount of active nickel is given by (from 1.d.) (15 x .1289) = 1.934 grams. The total active material equals

$$2.9631 + .190 = 3.1531 \text{ grams}$$

Thus

$$\% \text{ nickel is equal to } \frac{1.934}{3.1531} = 61\%$$

(c) % Oxygen

Oxygen is determined by difference, thus $100\% - (61\% + 2.3\%) = 36.7\%$

By dividing these per cents by the atomic weight of the material, we obtain

$$\frac{2.3\%}{H} = 2.3 \qquad \frac{61\%}{Ni} = 1.04 \qquad \frac{36.7\%}{O} = 2.3$$

$$H = 1 \qquad Ni = 58.7 \qquad O = 16$$

On this basis, the active material impregnated onto the sintered nickel plate has the formula weight of $Ni(OH)_{2.2}$

2. X-ray Diffraction Patterns

To eliminate any possible interactions due to polyethylene, a group of plates in the discharged, charged, and freshly charged state were X-rayed uncovered and wet with KOH. This was done early in the quarter. The patterns obtained seemed alike and apparently independent of state-of-charge. The structure appeared to be that of $Ni(OH)_2$. To check on these results, an even more carefully run experiment was carried out. This involved determining the X-ray patterns of positive plates which were first covered with polyethylene and then with the polyethylene removed. This latter experiment is described in detail below.

a. Effect of Polyethylene Covering at Various States of Charge

Several unformed impregnated plates were given three formation cycles against excess negative capacity. The formation consisted of a charge at 1.0 ampere for 2 hours, a discharge at 500 ma to 0 volts, followed by a short-circuit for 1 hour. The capacity of the plates did not change from cycle to cycle and were all equal to 1.1 ampere hours.

After formation, two of these positive plates were left in the discharged state; two were charged at 1.0 ampere for 2 hours, and then discharged at 500 ma for 1 hour. Two cells were charged at 1.0 ampere for 2 hours. All plates were X-rayed first covered with polyethylene, then with polyethylene removed. The scan was made between $2\theta = 10^\circ$ to 80°. The X-ray patterns are shown in Figures 2 through 13. Figures 2, 4, 6, 8, 10, and 12 represent the patterns obtained from the various plates when they were covered with polyethylene. Figures 3, 5, 7, 9, 11, and 13 represent patterns obtained from the same plates, respectively, without polyethylene covering. The states of charge of the plates were: fully charged Figures 2, 3, 4, 5; half charged Figures 6, 7, 8, 9 and; discharged Figures 10, 11, 12, 13. Another plate of this group was charged at 1 ampere for 1 hour. This avoids overcharge. The positive of the cell was X-rayed covered and uncovered with polyethylene. The patterns obtained are shown in Fig. 14 and 15 respectively. The patterns obtained at the various states of charge have a common difference, due to the polyethylene covering. There is also a masking effect of peaks at 1.53 and 1.47. In all cases, peaks at 3.70 and 2.47 angstroms were found due to the polyethylene in addition to the well established peaks at 4.08. It was found that an intensification of the peak at d = 4.5-4.7 Å resulted from the polyethylene covering. With respect to state of charge, a difference exists when the plate was uncovered, as shown in Table I.

With the exception of a small peak at 4.7 Å, the fully charged, uncovered plates appear amorphous. This, however, could be contributed to by the relatively short stand time before X-ray (2 hours). The half discharged plates have some of the peaks associated with $Ni(OH)_2$. The completely discharged plates have all the peaks associated with $Ni(OH)_2$.

The plate charged to the gassing point (1 hour) has a larger peak at 4.7 than the overcharged plates.

b. Plates X-rayed Without Polyethylene Covering.

Another group of plates of the same size were first formed by charging at 100 ma for 16 hours, followed by discharging at 500 ma to 0.0 volts. The plates were again charged at 100 ma for 16 hours. One plate was discharged against excess negative capacity to 0.0 volt. The plate was removed from the cell and X-rayed wet with KOH and uncovered. The patterns obtained were that of $Ni(OH)_2$, as shown in Figure 16. The plate was returned to its negative, thus remaking the cell which was then charged for 2 hours at 500 ma. The plate was removed from its cell and again X-rayed in its wet, uncovered condition. The pattern is shown in Figure 17. Figure 18 shows the diffraction pattern obtained from a fully charged plate at 100 ma for 16 hours which was X-rayed in the wet, uncovered condition. Figure 19 shows the pattern obtained from the same plate after a 5 day stand. Figure 20 shows a diffraction pattern of a plate which, after being charged for 16 hours at 100 ma, was discharged for 1 hour at 500 ma (the plate is half charged). The "d" spacings and their intensities are shown in Table II.

From these results, it would seem that differences exist between the charged and discharged states which are clearly shown by X-ray patterns obtained from plates wet with KOH. The variation of results, with respect to the fully charged plates in Tables I and II, in comparing the peak at 4.6-4.7 angstroms, may be due to variation of formation treatment and/or variation of charge rate. It will be noticed that, even though there was a variation in charge rate from Figure 17 to Figure 18, this did not affect the peak at 4.6-4.7 angstroms.

Although peak heights are given as indication of intensity, it is actually the area under a particular peak region which is identified with quantity of material (state of charge).

The change occurring in a plate first X-rayed discharged and then charged is an indication of the disappearance of lines due to a more random structure (Fig. 16 vs. Fig. 17).

B. STABILIZATION STUDIES

1. Formation

27 positive plates which were formed at 10°C, 25°C, and 80°C, at rates of 500, 100, and 35 ma, during the previous quarter, were evaluated for their charge retention properties as well as cycling durability as cells. Capacities were determined immediately after charge and then after stand at room temperature and 50°C. All charges were conducted for 2 hours at 1 ampere, discharges at 200 ma to 0.0 volt. The nominal positive capacity was 1.0 ampere.

Three test positives, as cells, comprised a group representing formation at each temperature and rate. The tests consisted of a charge at room temperature followed by either open circuit stand or immediate discharge, depending on the test. Following the test, discharged cells were shorted for at least 16 hours.

Due to flucuation in line current during the first 3 cycles, these data were not considered precise enough for presentation. The cycle sequence after the first three cycles was as follows:

(1) Immediate discharge
(2) Immediate discharge
(3) Open circuit for 24 hours after charge, then discharge
(4) Open circuit for 24 hours at 50°C, then discharge
(5) Open circuit for 3 days, then discharge
(6) Immediate discharge
(7) Open circuit for 3 days at 50°C, then discharge

The capacities obtained from these plates are compared in Table III with respect to average discharge capacities to 1.0 V and 0.0 V after the above tests.

The results indicated that the greatest capacity loss during the 24 hour stand comes from the groups formed at room temperature, while the groups formed at 10°C showed the least capacity loss. At this point, the formation rate had no effect on the loss of capacity as a result of stand. This was found to hold true for both room temperature and 50°C and for capacities to 1.0 V and 0.0 V. As for capacity itself, "immediate discharge" positives formed at 10°C and 35 ma, and those formed at 80°C and 100 ma yielded the best results.

The results of the stand at room and 50°C temperatures for a three day stand are compared in Table IV.

A comparison of capacity on immediate discharge obtained from Table III with that obtained from Table IV indicates an effect due to cycling. Cells formed at room temperature are most seriously affected. Cells formed at 80°C-100 ma, in general, were not so affected. The group which indicated the best results, however, with respect to charge retention and cycling, was the one formed at 35 ma and 10°C. Another formation will be run consisting of the standard 100 ma-room temperature type and the 35 ma-10°C and the 100 ma-80°C. These will be evaluated as will be outlined in a later section.

2. Additives

Solutions of nickel nitrate containing 5, 10, and 20 metal atom % of Co and Mg have been prepared. These solutions will be used to impregnate sintered nickel plates by the method previously described.

C. SPECIAL TESTS

1. Determination of Rate of Heating of the Metal Block Used in D.T.A. Experiments

The rate of heating of the metal block in the oven, when the heating element was connected to the 110 V line (the condition used in obtaining thermograms) was determined. This was done using a chromel-alumel thermocouple. The average rate of heating was found to be 42.5°F per minute from room temperature to 1800°F. Figure 21 shows the plot of two runs made of rate of heating versus time.

2. Anodization of Nickel Sheet

A piece of pure nickel 2" x 1" sheet was anodized in 34% KOH at a current of 3 amperes for 3 hours. A black layer formed on the foil which, when X-rayed without polyethylene cover, yielded only nickel lines and, thus, seemed amorphous. The experiment was repeated and the same X-ray pattern was obtained. In each case, upon the completion of X-ray, the black layer had disappeared. The X-rays did not strike all of the sample, so that a spontaneous decomposition is speculated upon rather than a reaction induced by X irradiation.

The method of anodization was changed. A 2" x 1" nickel foil sheet was anodized at 1 ampere for 24 hours. A yellowish material appeared and remained. The X-ray pattern obtained is shown in Figure 22. The pattern seems to be that of γ NiOOH(1) although a strong line 2.70 Å of $Ni(OH)_2$ is also present.

X-rays were taken within 2-3 hours of completion of charge.

3. Thermogravimetric Analysis

Contacts were made with Fisher Scientific, Perkin Elmer and almost all the analytical research laboratories within the area. It seems that none of them are set up to do thermogravimetric analysis as a service.

IV. DISCUSSION

Although specific methods for determining the various oxidation states of nickel could not be found nor developed, the analytical approach is fruitful. Firstly, the oxides of nickel are soluble in a mixture of ammonium hydroxide and ammonium persulfate. By grinding, then cone and quartering plates, representative samples may be obtained. Separation of elemental from oxidized nickel by dissolution of the latter yields one piece of requisite information. Secondly, determination of soluble nickel by electro-deposition yields a second piece of information. Hydrogen is then determined directly by the chromate oxidation method. Having all this, oxygen is determined by difference and the percentage composition of the nickel oxides are thusly determined.

The accuracy of this method depends strongly on the homogeniety of the samples withdrawn for analysis and the suitability of the nickel determination. Electro-deposition methods are well-known for their accuracy. Fortunately, the hydrogen is present in small amounts so that the oxygen (from the difference) cannot be in great error. For the hydrogen itself, a weakness exists. Hydrogen, being the lightest element, will have to be determined with great accuracy. Since the composition is expressed in moles, a small error in weight will be magnified when converted to a mole basis.

This, then, is the method for determining the composition of nickel oxides for the remainder of the contract.

The structure of the oxides of nickel must come from other physical methods. Because of the lack of standards, it appears that X-ray diffraction will be most useful.

It has been determined that the use of polyethylene as an evaporation retardant has interfered with the diffraction patterns. This has been definitely established in Figures 2 to 15 of this report. All future work will be done with plates that are wet with aqueous potassium hydroxide (this was established in a very early report in this series -- in the Second Quarterly Report under Contract NAS 3-4178).

These figures also show that the charged state is nearly amorphous. This is speculatively due to a disorder in the crystal structure of the higher oxide. As the electrodes are discharged, additional lines develop. Ultimately, upon complete discharge, the diffraction patterns are similar to those of impregnated but unformed plates. This, in spite of the fact that the formed plates are black and the unformed are still green.

During formation of a discharged nickel oxide, or during charging, two stages of normal oxidation occur; (1) stage of normal plateau charging with small liberation of oxygen and; (2) stage of overage with considerable evolution of oxygen. During the first stage, there is little change in the diffraction pattern of the oxide phase which almost everyone agrees is hexagonal $Ni(OH)_2$ in the completely uncharged state. During high rate overcharge, changes occur in the diffraction pattern. The most marked change occurs with the appearance of a prominent line with a "d" spacing of about 6.95 at high rates of charge. During the first plateau range of charging, the crystal structure of $Ni(OH)_2$ is based on hexagonal closest packing of oxygen. The Ni^{++} ions are placed in actahedral interstices in alternate layers between the O layers. The location of the hydrogen is not known but they are likely to be involved in hydrogen bonds between pairs of O layers which do not contain Ni^{++} between them. The oxidation (charging) process might then involve (1) an electron jump from an Ni^{++} ion to the adjacent Ni metal to form Ni^{+++}, (2) removal of a proton from the structure by OH^- in the electrolyte, and (3) charge migration in the $Ni(OH)_2$ by electron jumps between Ni^{++} and Ni^{+++} and/or proton jumps from proton positions to holes.

This description is consistent with the observation that charging occurs with relatively little structural changes. The disappearance or shrinkage of lines, rather than growth of new lines, is referred to as a small structural change.

The structural changes involve a type of disordering of closest packed O layers. This might well be caused by weakening of the interlayer due to loss of protons.

The anodized nickel sheet yielded peculiar behavior and diffraction patterns. The high rate (3 hour) anodization gave a black material which yielded no pattern and disappeared while being studied. The lower rate and longer (24 hour) anodization gave a yellowish deposit. This deposit apparently contained γ NiOOH. In both instances, the results of the anodization were different from the usual diffraction patterns obtained from impregnated sintered plates.

The stabilization experiments dealing with formation rates and temperatures appear to have shown a condition where the nickel oxide was stable on a one day stand. This was, particularly, formation at 10°C. Although 9 cells were involved in this portion of the work, greater confidence can be placed on these results if they can be reproduced. A fading of capacity occurred which confounded the results of stand for 3 days. This intensifies the need for repetition of parts of the experiment. To this end, formations will be carried out at 10°C and 35 ma and 80°C and 100 ma. As a control, a formation group at 25°C and 100 ma will be used. This latter approximates the usual formation treatment.

V. CONCLUSIONS

1. Chemical analysis has yielded the formula $Ni(OH)_{2.2}$ for an unformed nickel oxide electrode. This led to certain considerations for improvement of accuracy which are now being used.

2. Diffraction patterns are best obtained without the polyethylene as an evaporative barrier.

3. Changes in the diffraction patterns as a function of state-of-charge has led to a hypothesis on the order of the crystal structure.

4. Preliminary and tentative evidence has been found indicating that oxides of nickel formed at certain experimental conditions are more stable than the usual industrial conditions.

5. Two kinds of deposits were found on anodized Ni foil. One, black, was amorphous and disappeared. The other was yellowish and apparently is γNiOOH. In either case, there is no resemblance to the usual electrode.

VI. FUTURE WORK

A. Additives - Impregnation of 1-7/8" x 2-1/8" sintered plates will be done.

B. Formation - The two superior groups, 10°C-35 ma and 80°C-100 ma, will be formed using 25°C-100 ma as a control.

C. X-ray Diffraction - Slow speed scanning at various peak heights will be used as a means of discerning state of charge from the X-ray diffraction patterns of various positive plates.

D. Method of Evaluation of Improved Material - The means of evaluation will be changed to involve tests of plates by capacity loss as well as cycling properties. This will be done by electrochemical, X-ray, or chemical means, depending on the development of the latter two.

REFERENCES

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

2. Final Report NASA CR-54654, Investigation of Battery Active Nickel Oxides, Ritterman and Seiger, Contract NAS 3-4178, June 11, 1965.

TABLE I

STATE OF CHARGE AND EFFECT OF POLYETHYLENE COVERING

FIG. NO.	STATE OF CHARGE	"d" SPACINGS AND INTENSITIES *						
2	Fully Charged (Covered with Polyethylene)	4.66(20)	3.77(5)		2.45(8)			
3	Fully Charged (Uncovered)	4.83(3)						
4	Fully Charged (Covered with Polyethylene)	4.65(17)	3.77(4)		2.45(8)			
5	Fully Charged (Uncovered)	4.66(3)						
6	50% Charged (Covered with Polyethylene)	4.71(25)	3.77(5)	2.73(8)	2.44(10)	2.34(10)		
7	50% Charged (Uncovered)	4.66(14)		2.72(8)		2.33(10)		
8	50% Charged (Covered with Polyethylene)	4.59(15)	3.77(7)	2.72(5)	2.47(8)	2.35(8)		
9	50% Charged (Uncovered)	4.68(10)		2.72(5)		2.35(10)		
10	Discharged (Covered with Polyethylene)	4.54(15)	3.77(7)		2.47(10)	2.36(5)		
11	Discharged (Uncovered)	4.73(10)		2.73(10)		2.34(10)	1.57(6)	1.48(6)
12	Discharged (Covered with Polyethylene)	4.66(12)	3.70(5)	2.71(7)	2.47(10)	2.36(5)	1.56(5)	1.49(5)
13	Discharged (Uncovered)	4.66(7)		2.71(6)		2.35(5)	1.56(5)	1.49(5)
14	Charged 1 Hr. to Gassing Point (Covered with Polyethylene)	4.56(12)	3.77(5)		2.43(8)			
15	Charged 1 Hr. to Gassing Point (Uncovered)	4.73(8)				2.36(5)		

* "d" Spacings in Angstroms, relative intensities are indicated in brackets, nickel lines omitted.

TABLE II

UNCOVERED PLATES X-RAYED AT VARIOUS CURRENT DENSITIES

FIGURE NO.	STATE OF CHARGE	"d" SPACINGS AND INTENSITIES				
16	Discharged	4.66(13)	2.71(8)	2.33(12)	1.56(8)	
17	Charged - 1.0 Amp Input	4.63(13)		2.41(5)		
18	Overcharged	4.61(13)				
19	Overcharged - 5 Day Stand	4.66(20)		2.35(5)		
20	Half Charged	4.66(13)	2.69(5)	2.31(12)	1.55(3)	1.47(3)

TABLE III

COMPARISON OF CHARGE RETENTION - 24 HR. STAND

TEST CONDITION	FORMATION RATE								
	500 ma			100 ma			35 ma		
	FORMATION TEMPERATURE								
	10°C	25°C	80°C	10°C	25°C	80°C	10°C	25°C	80°C
Discharge Room Temperature									
1.00 V	257	247	242	241	255	273	322	266	253
0 V	262	253	253	253	262	302	336	267	268
Discharge After 24 Hr. Stand-R.T.									
1.00 V	247	205	212	228	210	253	304	215	230
0 V	253	208	221	230	213	271	313	218	242
Discharge After 24 Hr. Stand-50°C									
1.00 V	247	158	213	241	172	250	291	191	229
0 V	255	166	223	248	178	265	298	200	235

NOTE: Capacity in minutes
Average of 3 cells

TABLE IV

COMPARISON OF CHARGE RETENTION
72 HOUR STAND

TEST CONDITION	FORMATION RATE								
	500 ma			100 ma			35 ma		
	FORMATION TEMPERATURE								
	10°C	25°C	80°C	10°C	25°C	80°C	10°C	25°C	80°C
Discharge-Room Temperature									
1.00 V	210	125	195	218	130	236	293	143	249
0.0 V	219	126	207	233	141	252	296	157	263
Discharge After 3 Day Stand-R.T.									
1.00 V	215	63	223	215	105	265	300	156	224
0.0 V	219	65	231	225	110	273	303	160	235
Discharge After 3 Day Stand-50°C									
1.00 V	155	70	186	138	86	232	261	113	206
0.0 V	164	81	197	183	94	238	266	120	207

NOTE: Time in Minutes
Average of 3 cells

FIG. 1

OVERCHARGED POSITIVE XRAYED
WITHOUT POLYETHYLENE COVER

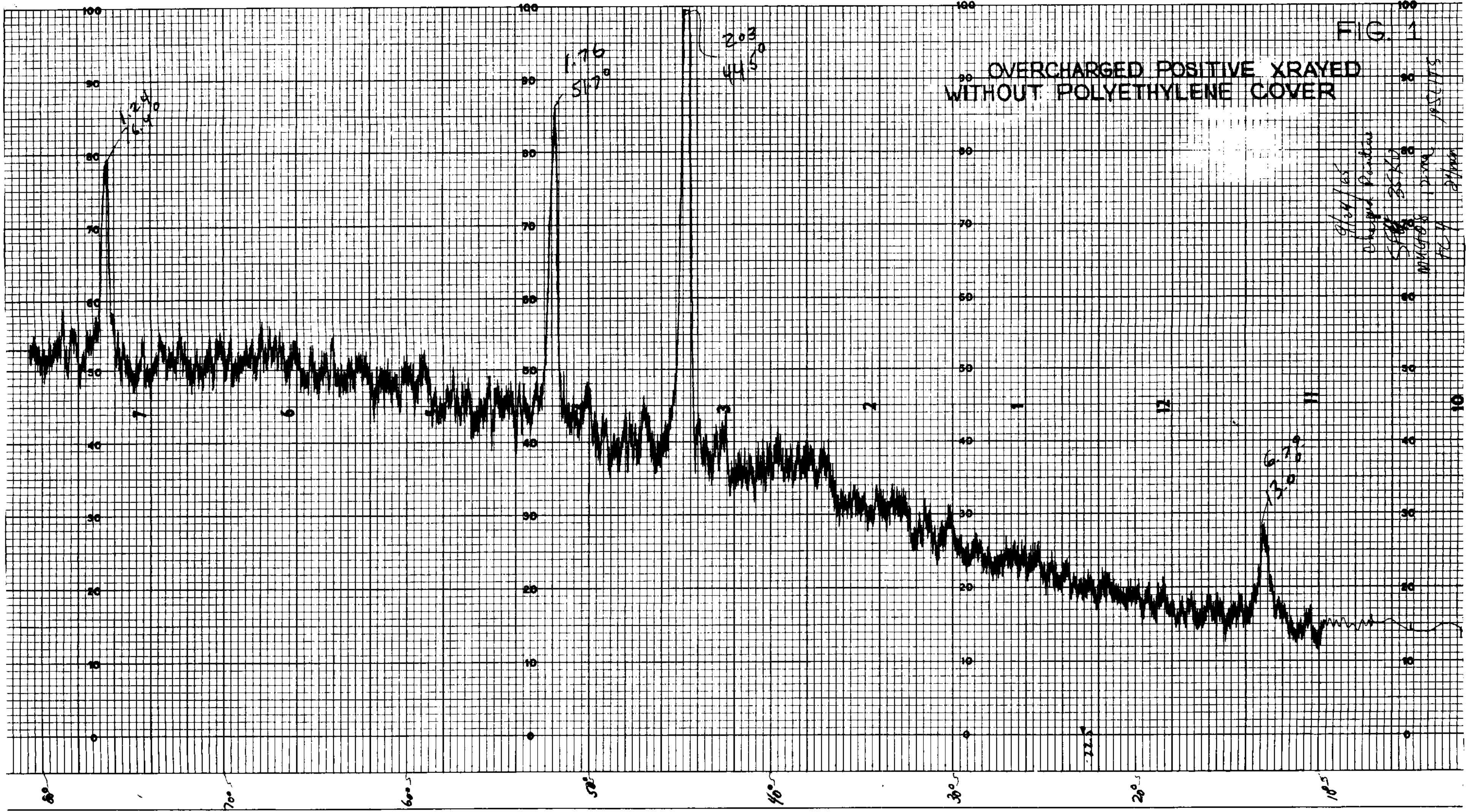
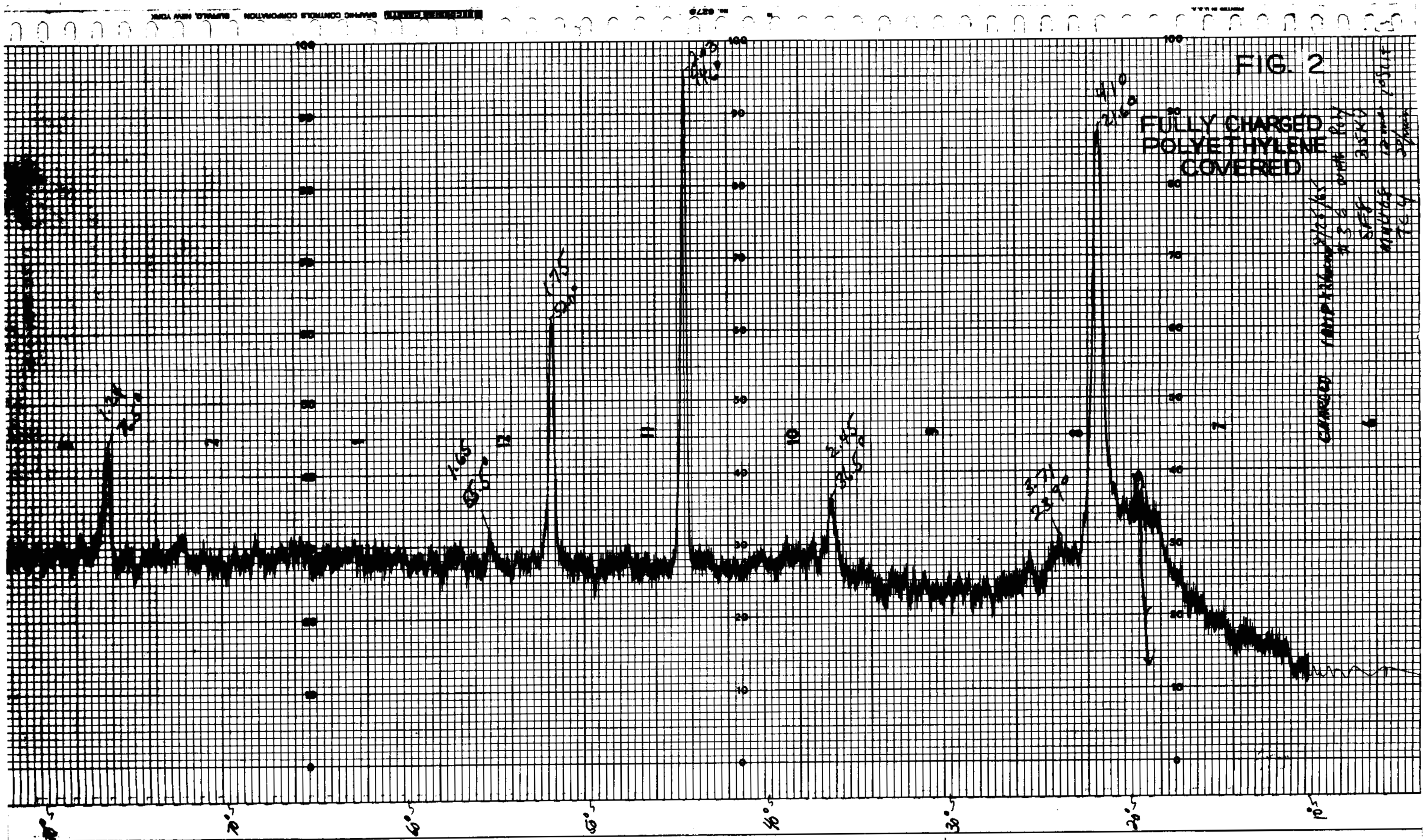


FIG. 2



FULLY CHARGED POLYETHYLENE COVERED

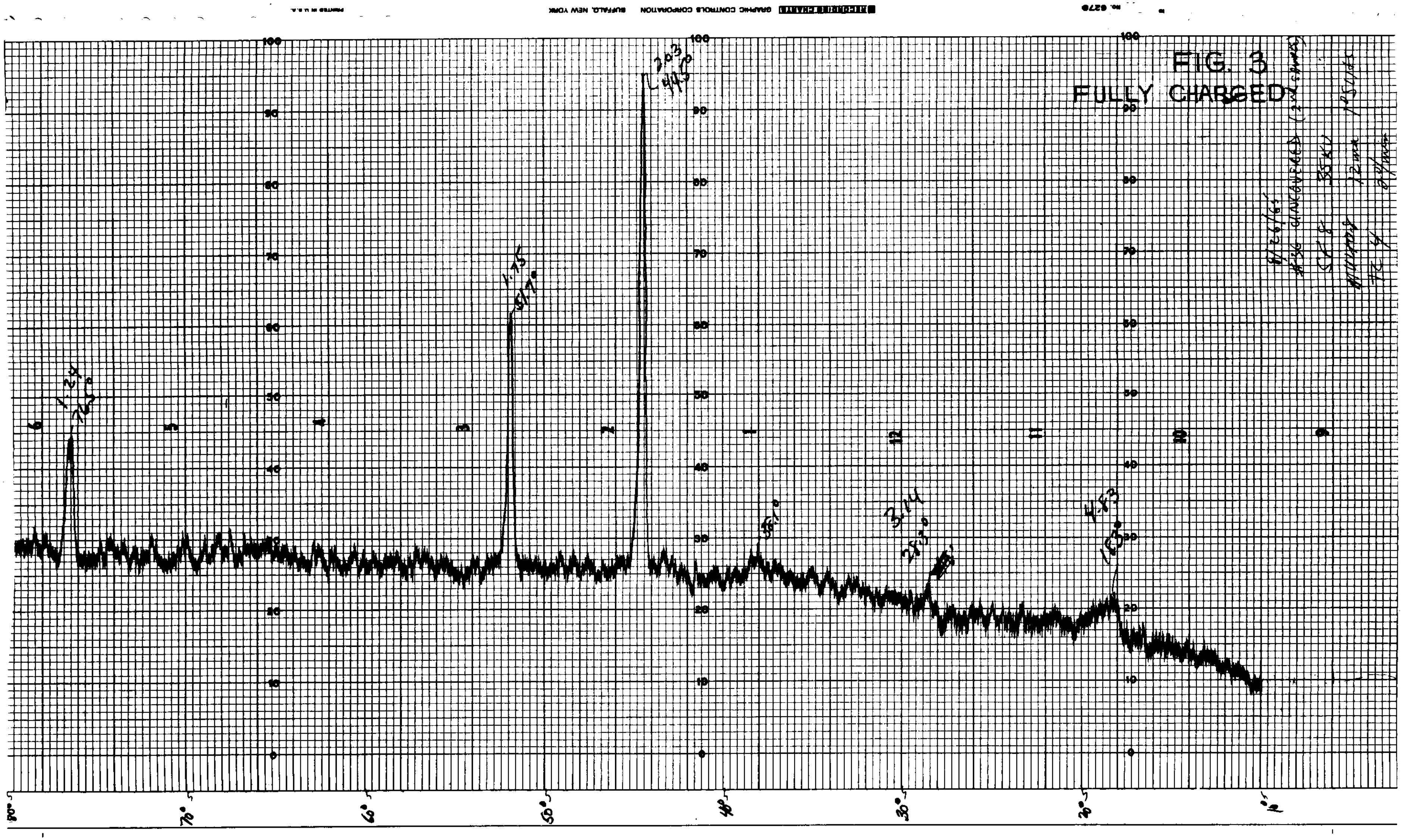
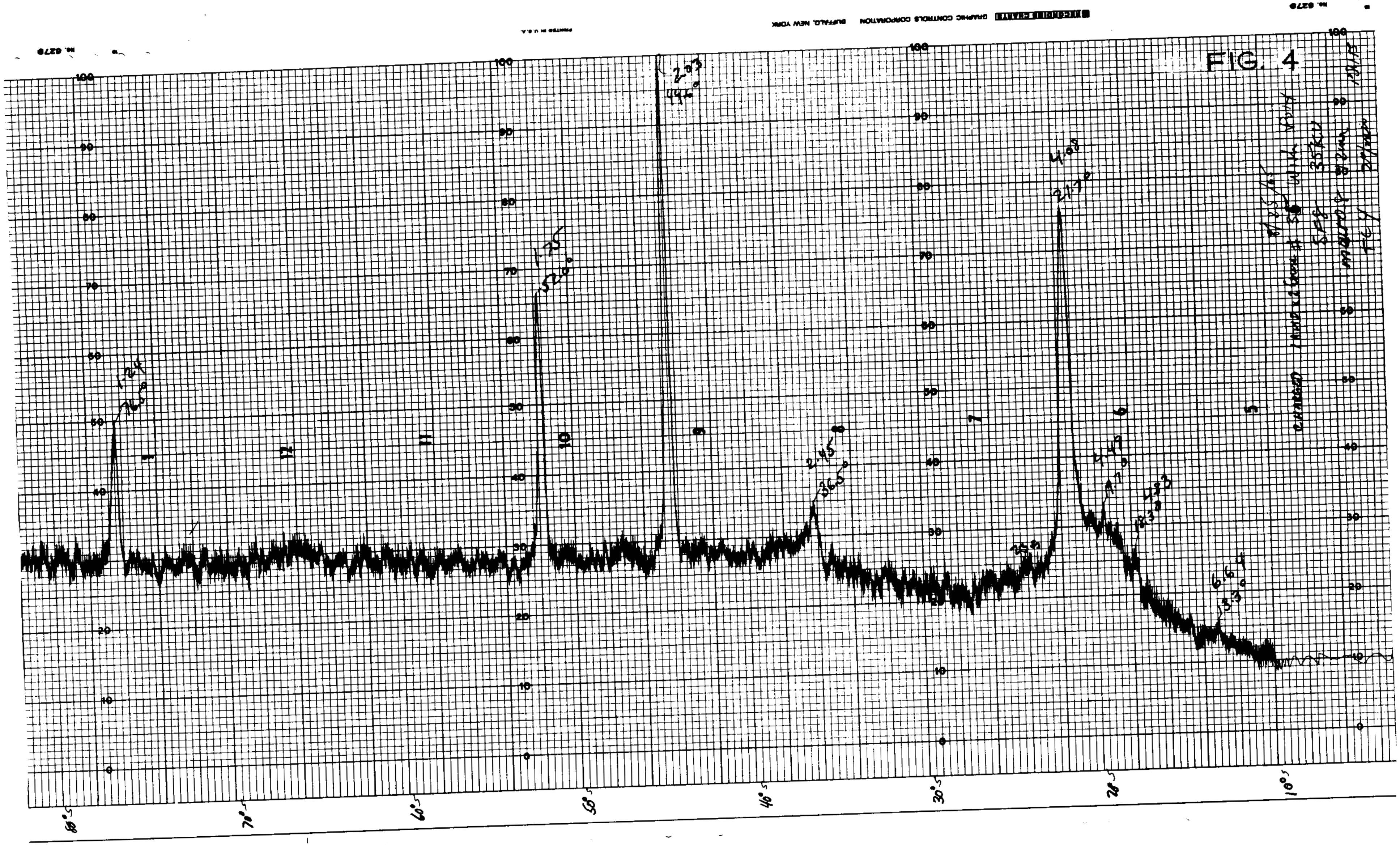


FIG. 3
FULLY CHARGED

FIG. 4



CHARGED [illegible] # 56 with [illegible]
SFS 35KV
FCY 2°/min
1.24
76.6°
1.75
52.0°
2.03
44.6°
2.45
36.5°
4.08
21.7°
4.47
19.7°
4.83
18.3°
6.64
13.3°
10°
20°
30°
40°
50°
60°
70°
80°
0
10
20
30
40
50
60
70
80
90
100
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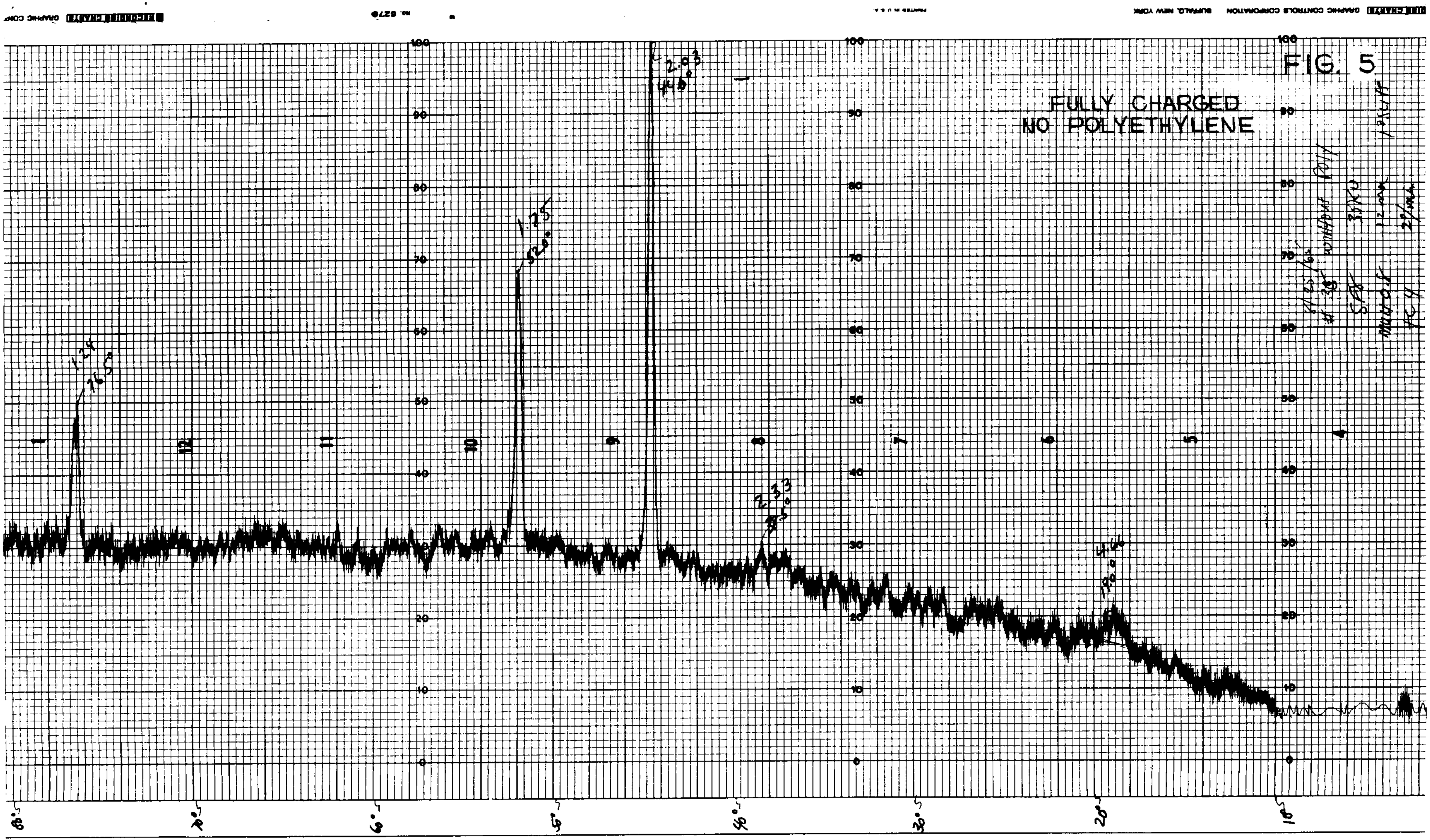
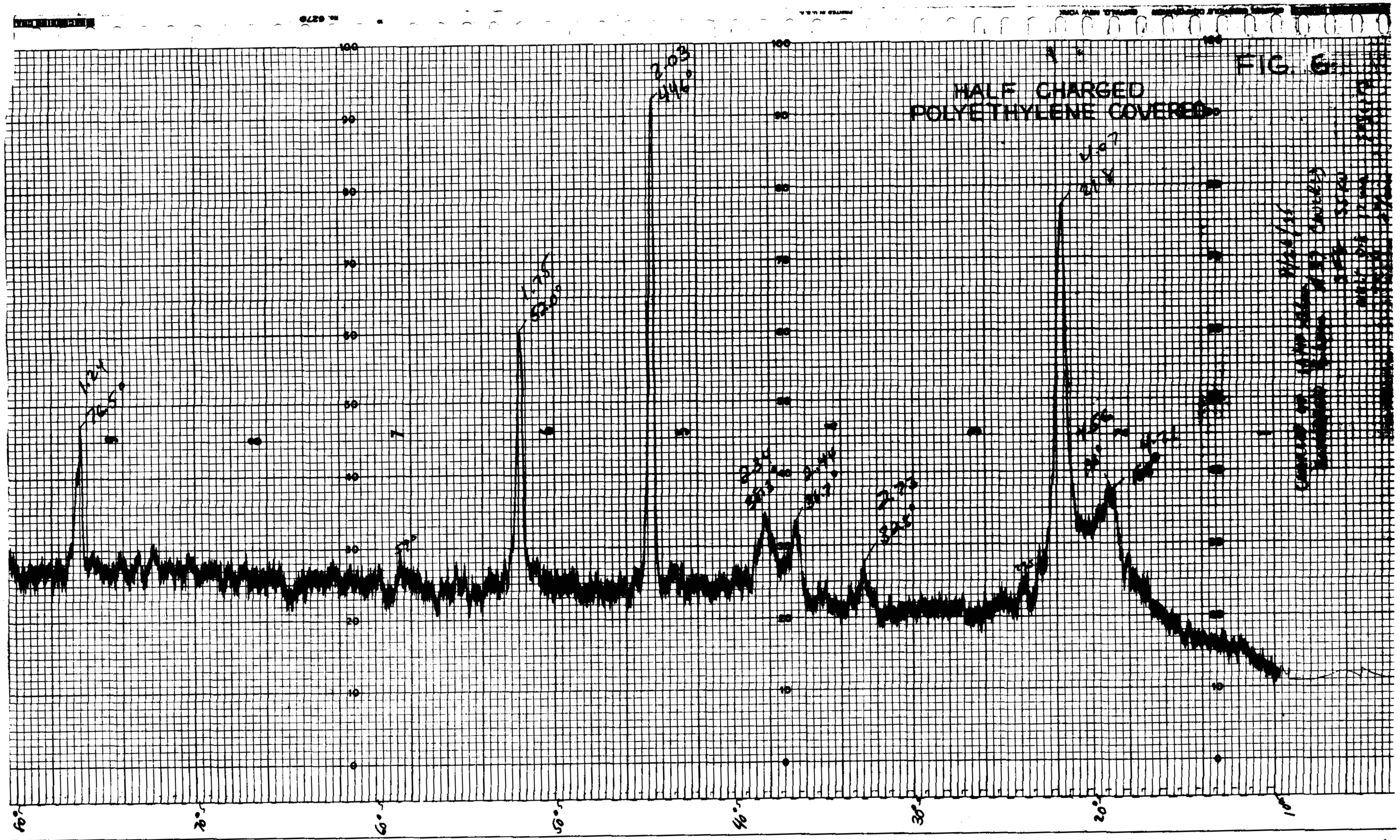
FIG. 5



FULLY CHARGED
NO POLYETHYLENE

FIG. 6


HALF CHARGED POLYETHYLENE COVERED

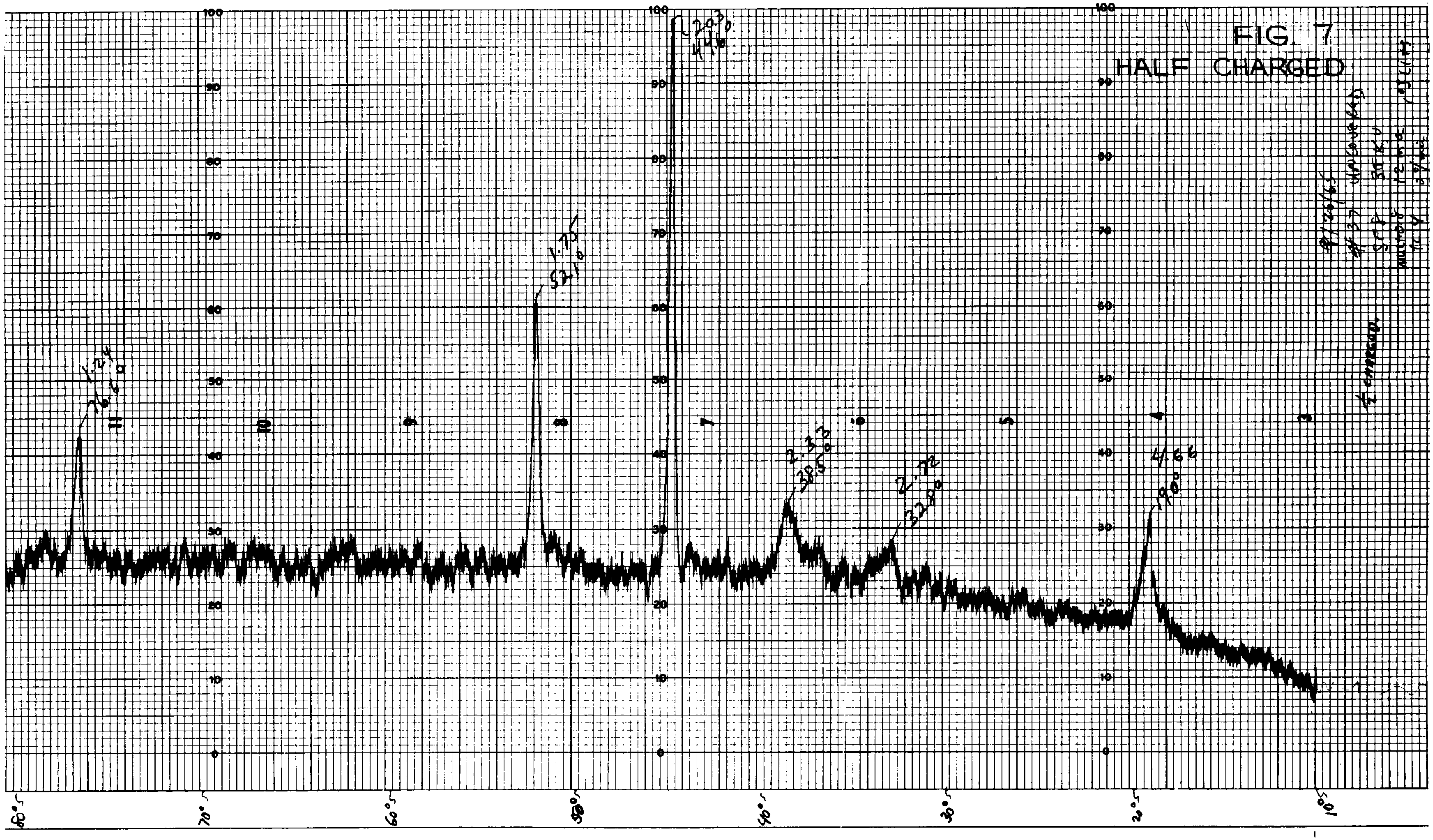


FIG. 7

HALF CHARGED

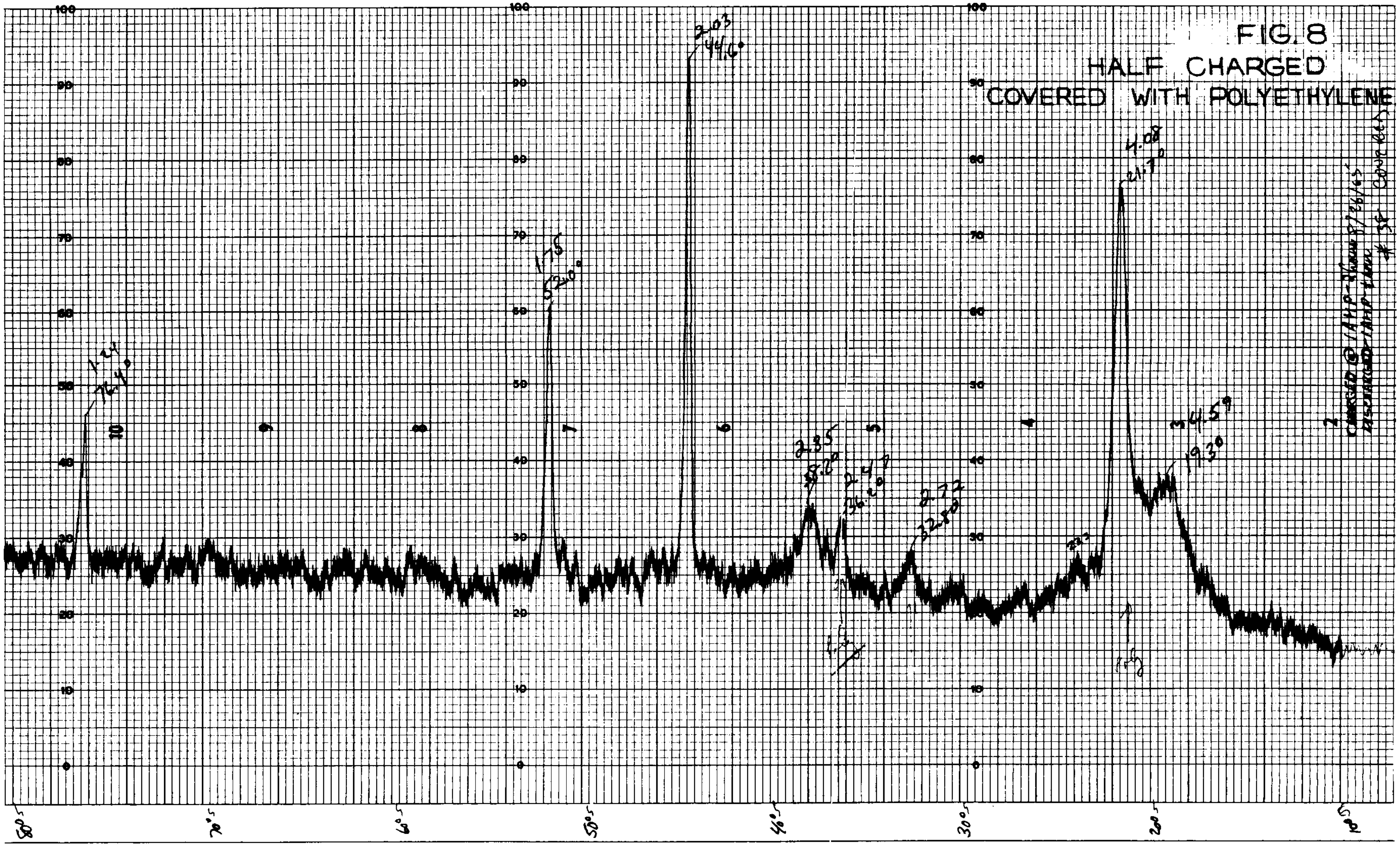
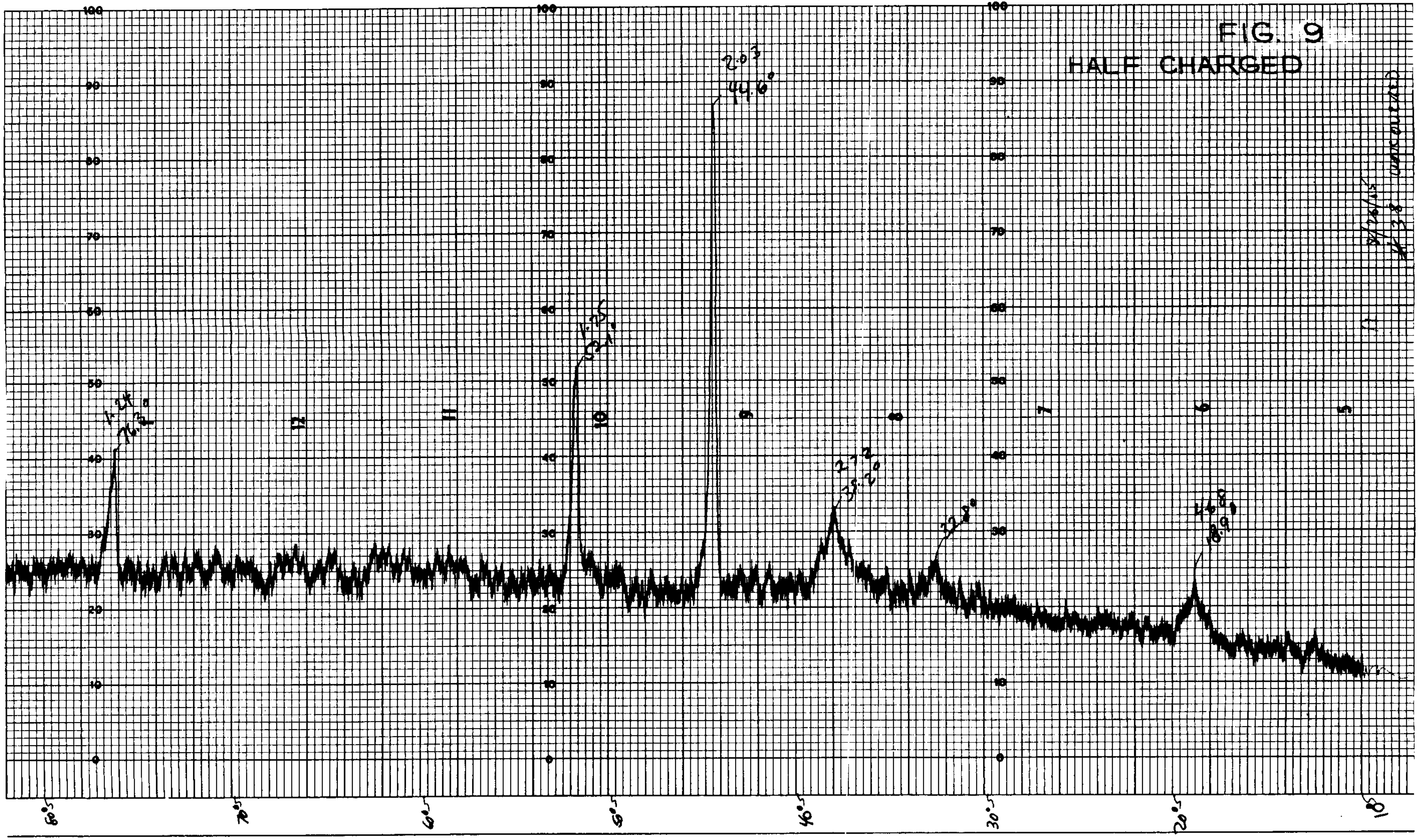


FIG. 8

HALF CHARGED
COVERED WITH POLYETHYLENE

FIG. 9

HALF CHARGED



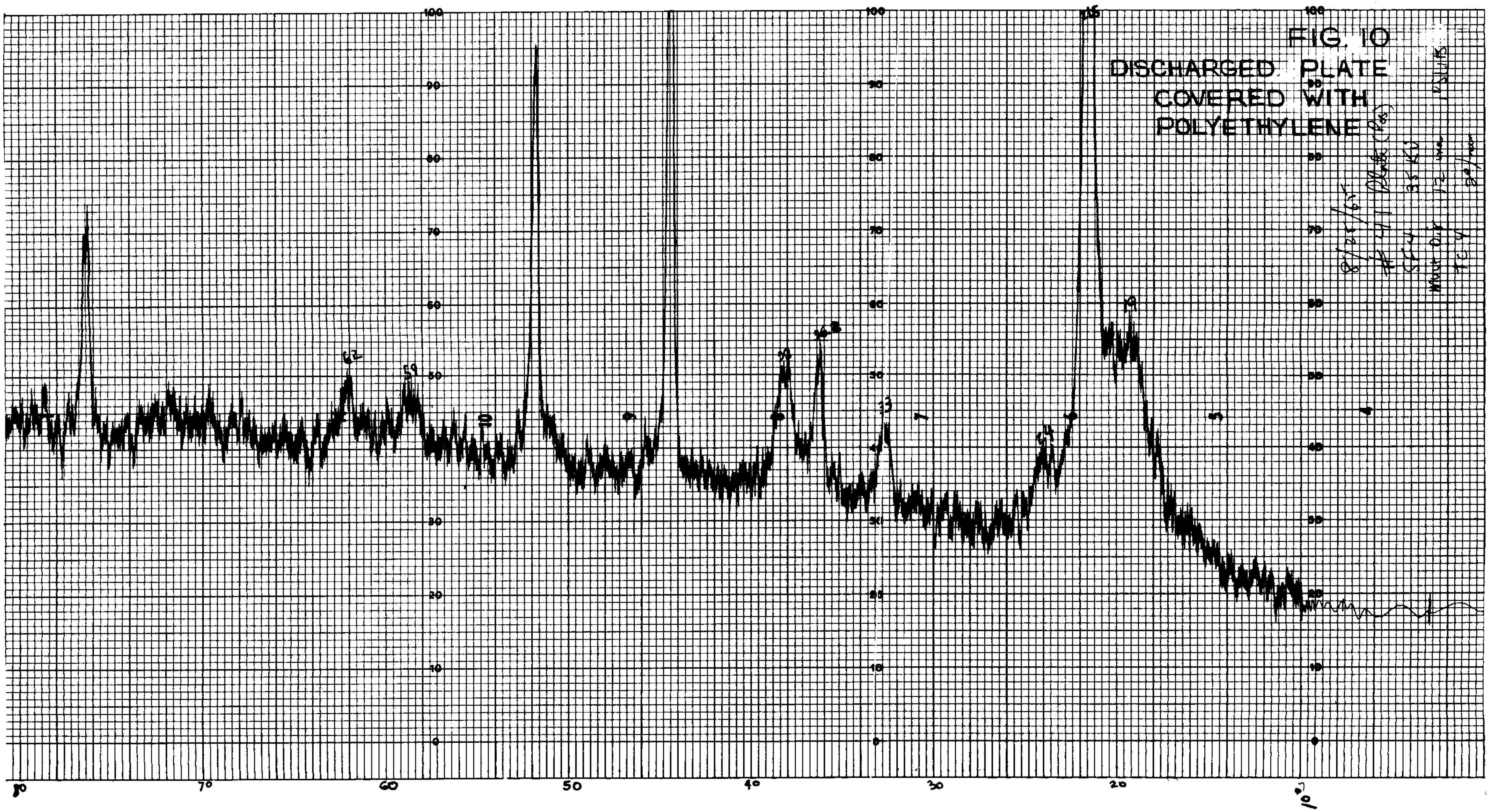


FIG. 10

DISCHARGED PLATE COVERED WITH POLYETHYLENE

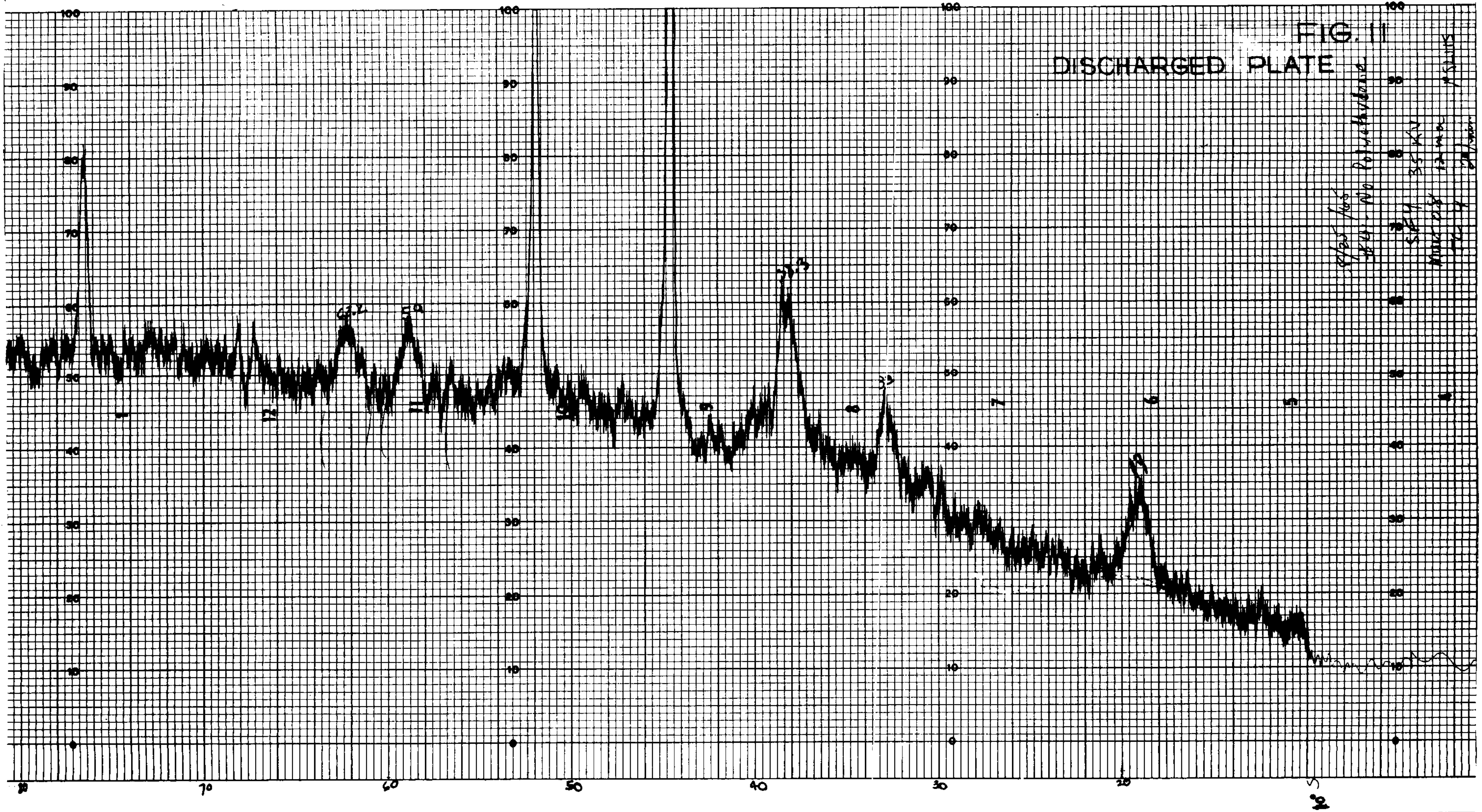
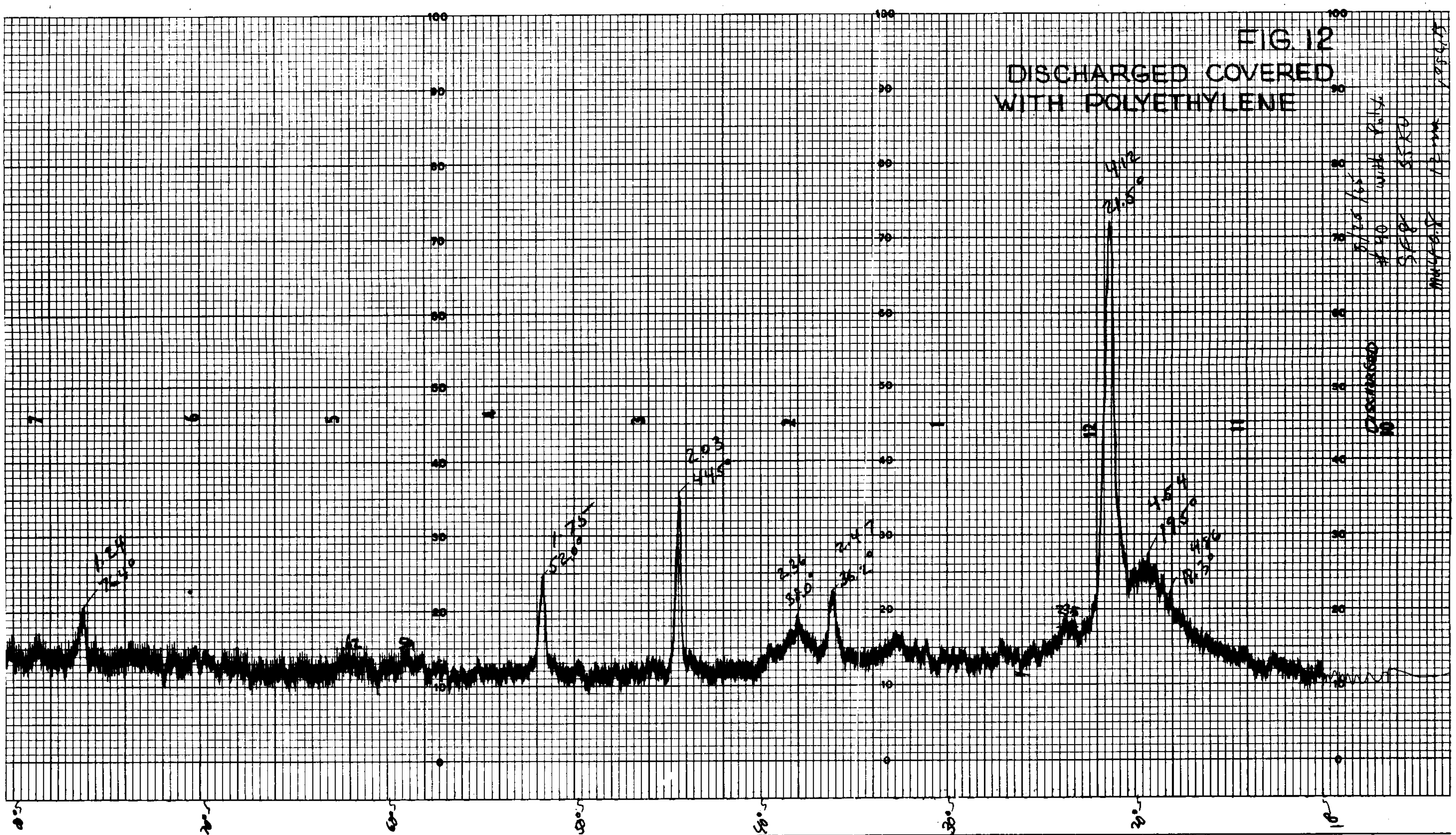


FIG. 11

DISCHARGED PLATE

FIG. 12
DISCHARGED COVERED
WITH POLYETHYLENE
8/26/64
#40 with Poly
5KV 85KV
MoKα 17 ma [illegible]
10584
Discharged
4.12
21.5°
4.54
19.5°
4.76
18.7°
2.47
36.2°
2.36
38.0°
2.03
44.5°
1.75
52.0°
1.24
76.4°
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
10
11
12
No. 627B
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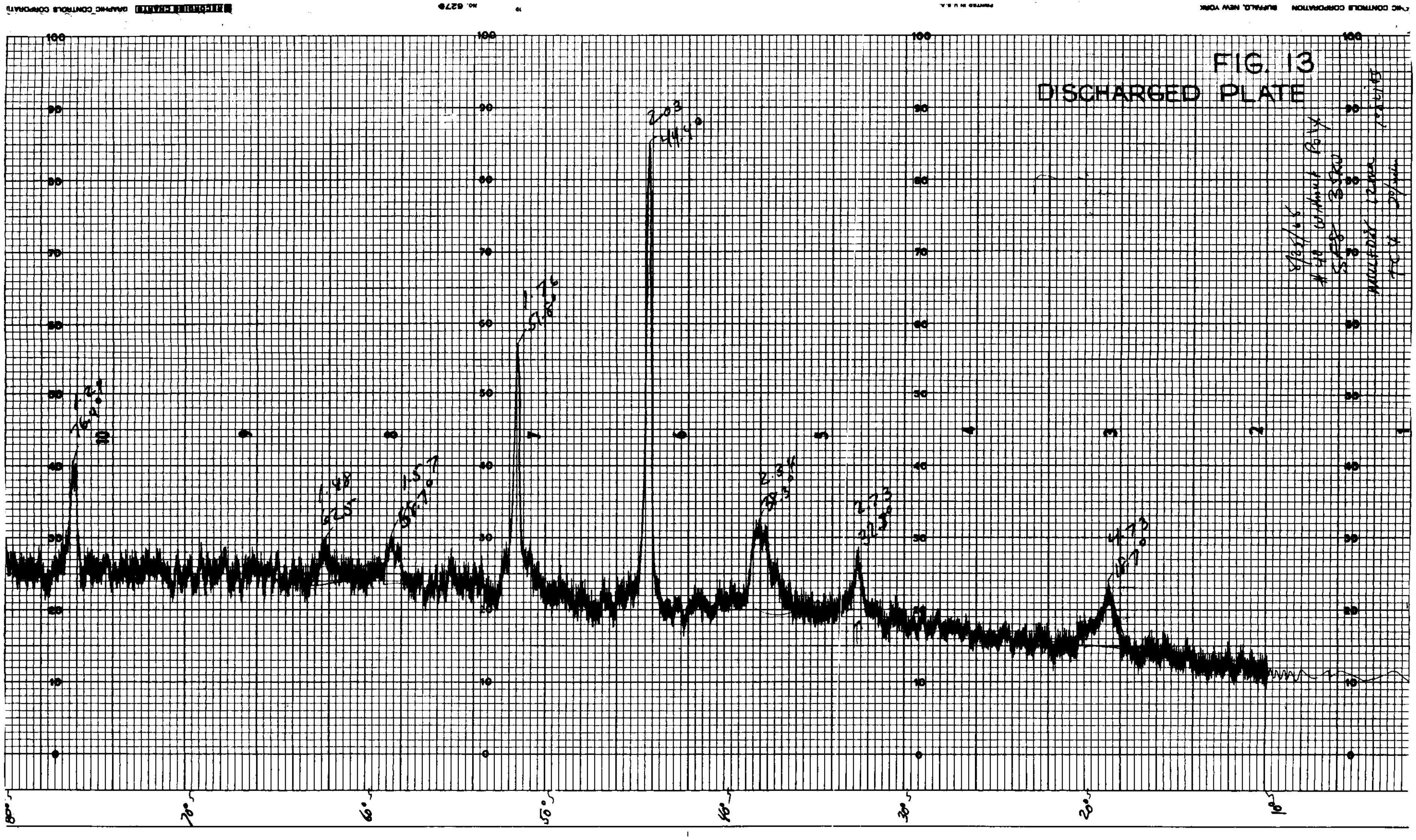
FIG. 13
DISCHARGED PLATE
8/23/65
#48 without Poly
SF38 35KV
WALLFDAY 12mA
TC 4 20/min
2.03
44.4°
1.76
51.8°
2.38
38.3°
2.73
32.8°
4.73
18.7°
1.48
62.5°
1.57
58.7°
1.24
76.4°
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
80°
70°
60°
50°
40°
30°
20°
10°
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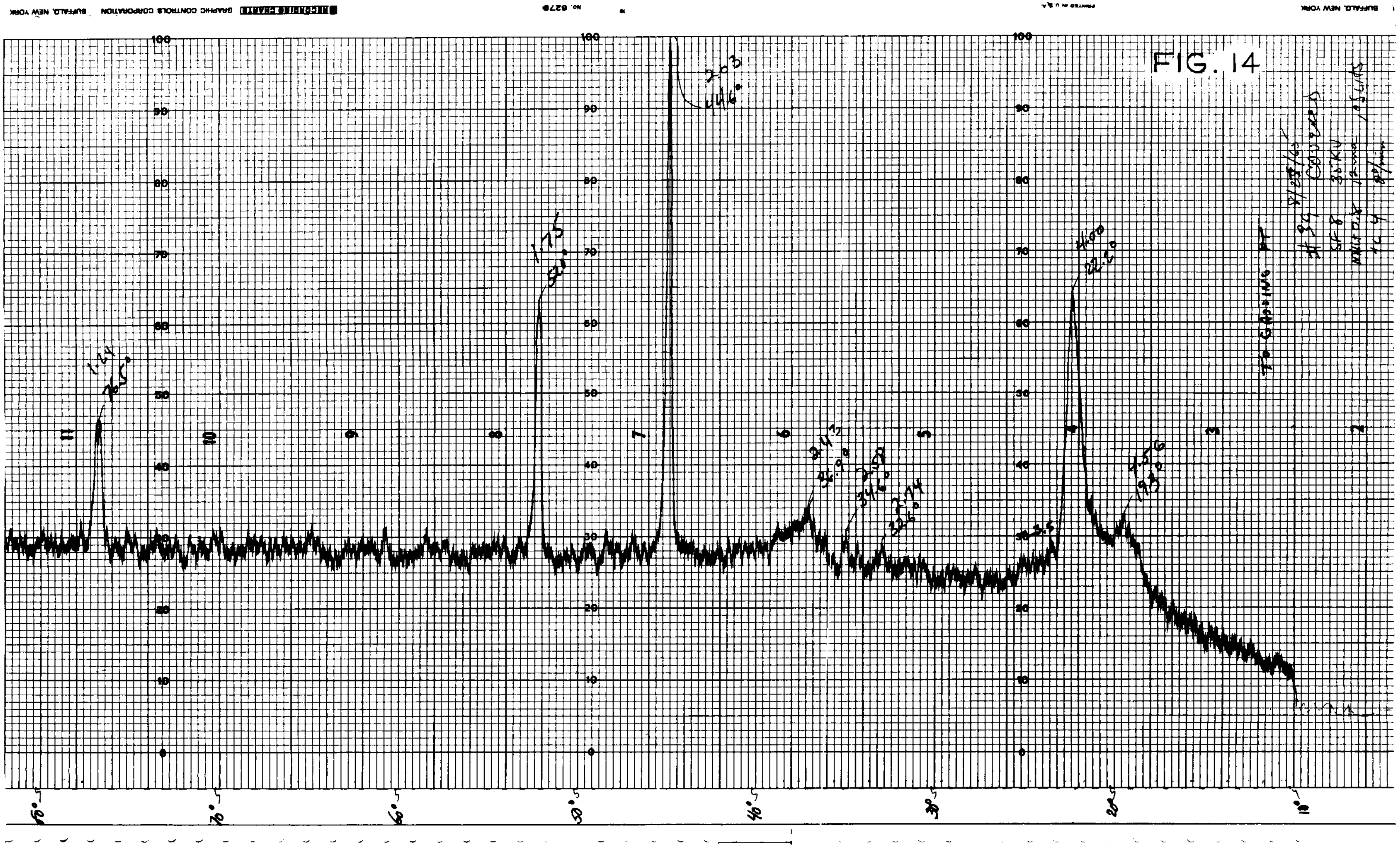
NO. 6270
RECORDING CHARTS



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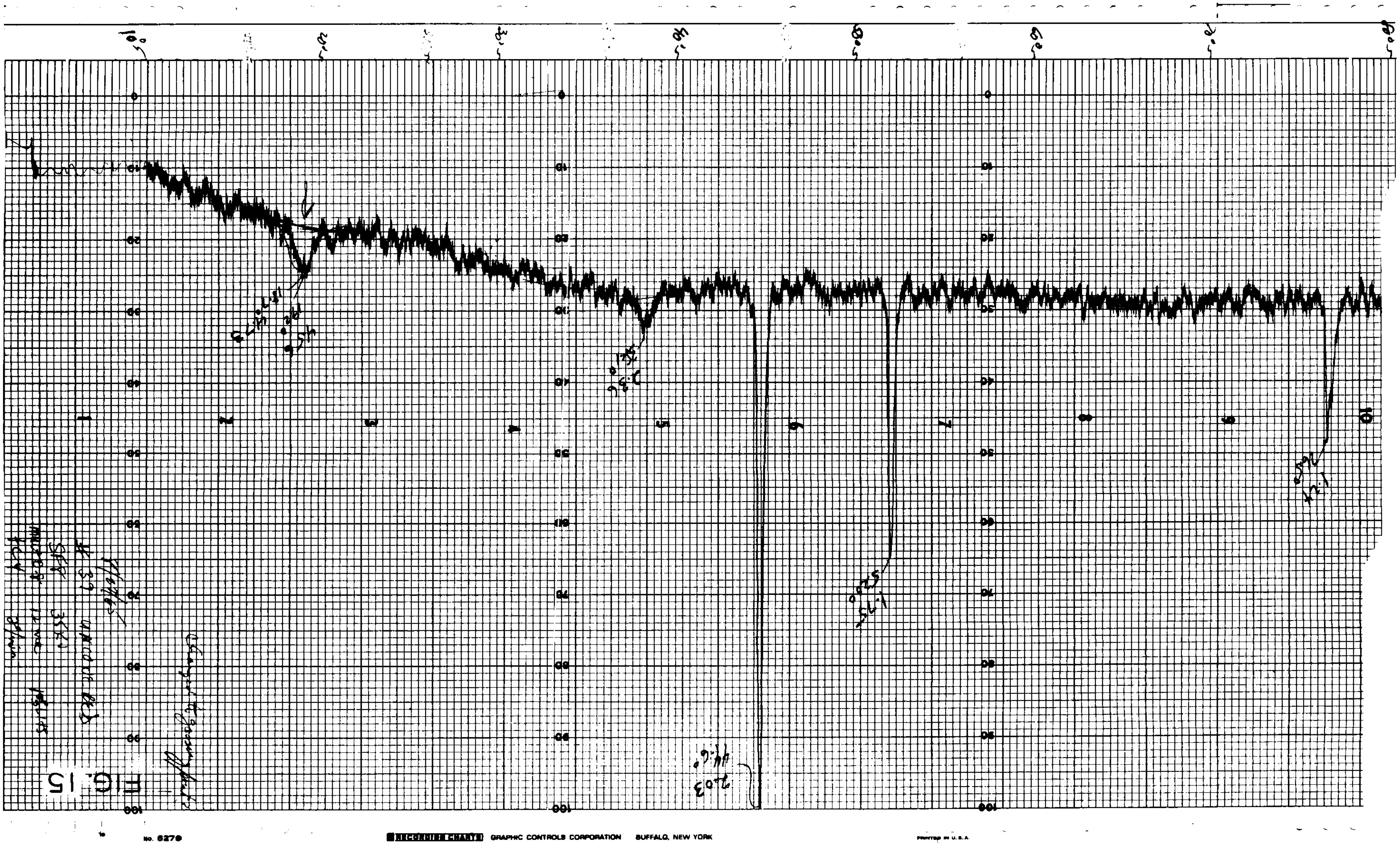
NO. 827B
RECORDER CHARTS GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK
To Casting PT
#34 8/23/65
SF 8 35KV
MILLIAMP 12 ma 10 sec/45
TC 4 8°/min
2.03
44.6°
1.75
52.0°
1.24
76.5°
4.00
22.2°
4.56
19.3°
2.42
37.0°
2.58
34.6°
2.74
32.6°
3.5
100
90
80
70
60
50
40
30
20
10
0
11
10
9
8
7
6
5
4
3
2
80°
70°
60°
50°
40°
30°
20°
10°

FIG. 14



0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
8
9
10
2.03
44.6°
1.15
52.0°
SFF 35KV
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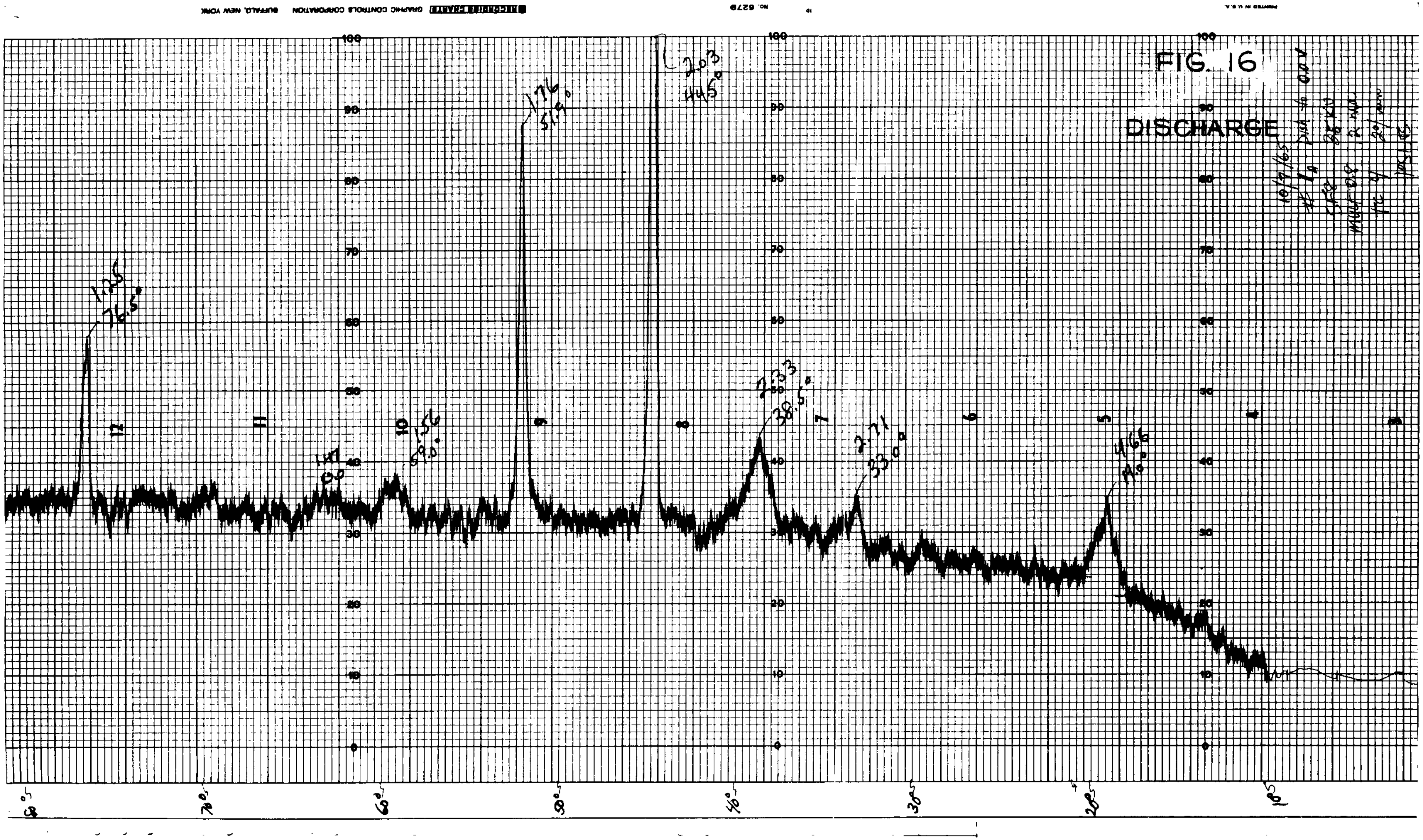
FIG. 15

FIG. 16

DISCHARGE



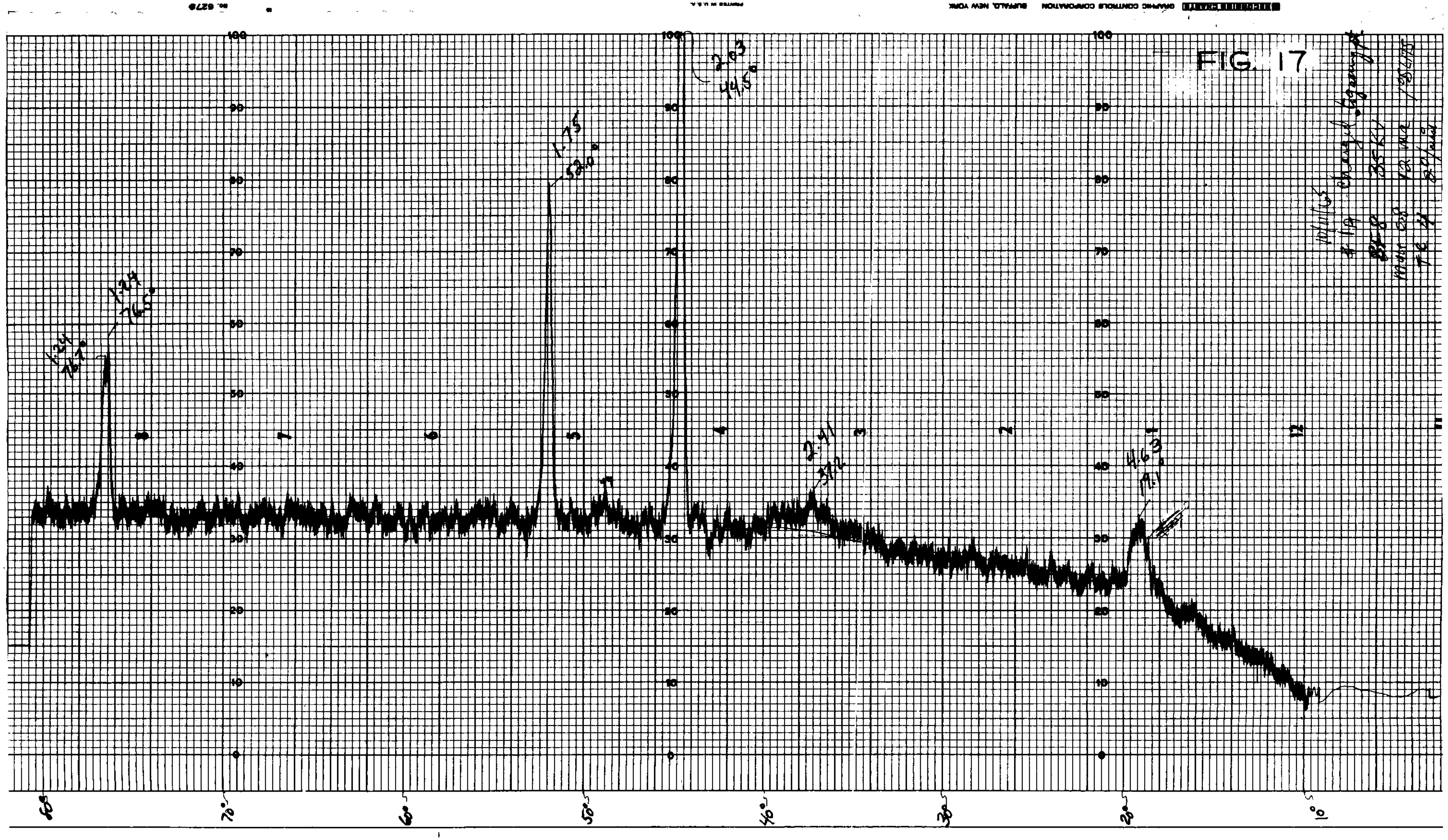
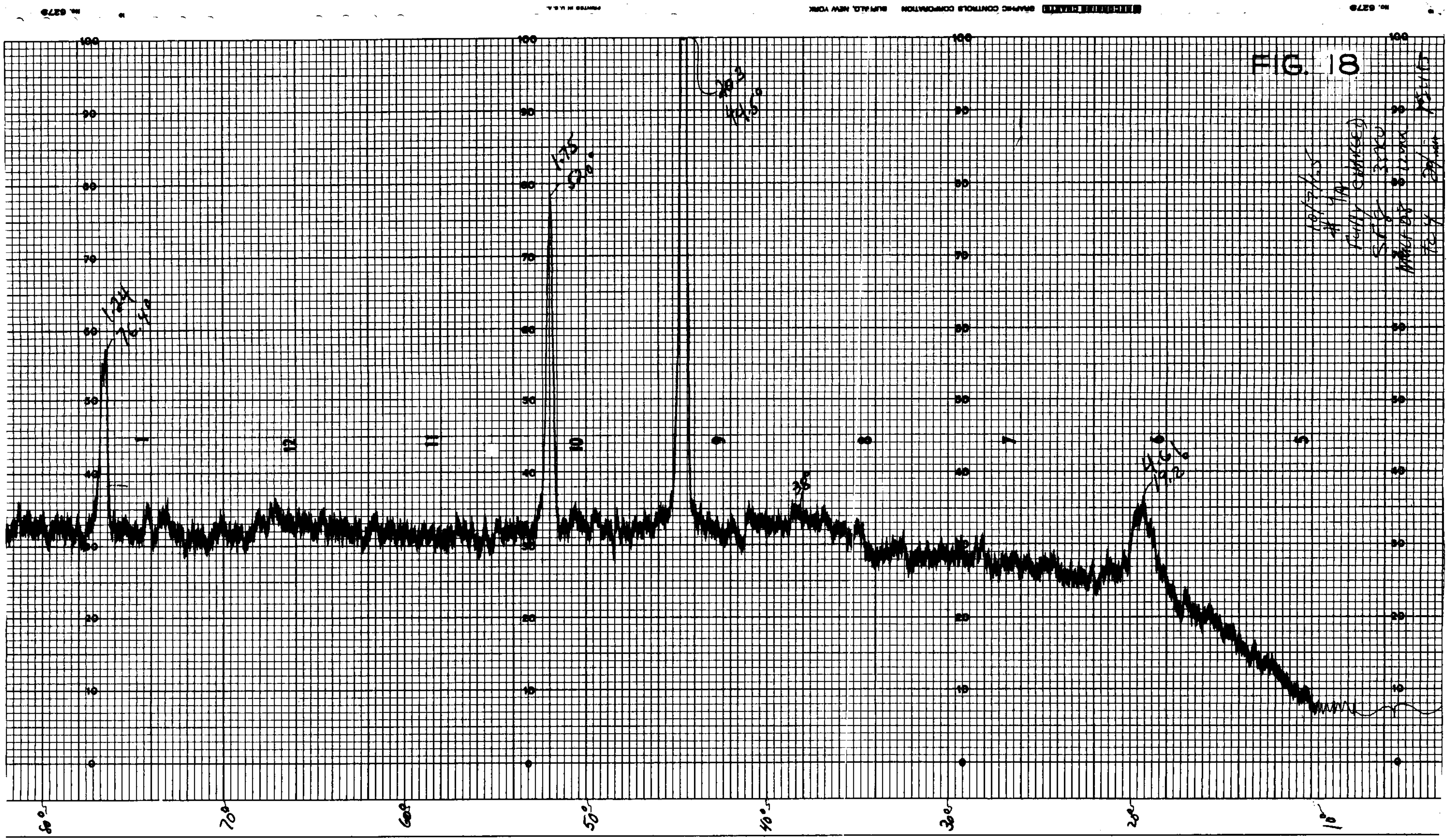


FIG. 17

10/11/65
#1A charged Lagging
BE-8 35 KV
Mode 0.8 12 MA 1°/[illegible]
TC 4 2°/min

FIG. 18


10/7/65
#4A
Fully oxidized
SF6 3KV
Max d.g. 1.2mA
Tc 4 2°/min
4.6
19.2°
38°
2.03
44.5°
1.75
52.0°
1.24
76.4°
10°
20°
30°
40°
50°
60°
70°
80°
0
10
20
30
40
50
60
70
80
90
100
5
6
7
8
9
10
11
12
1
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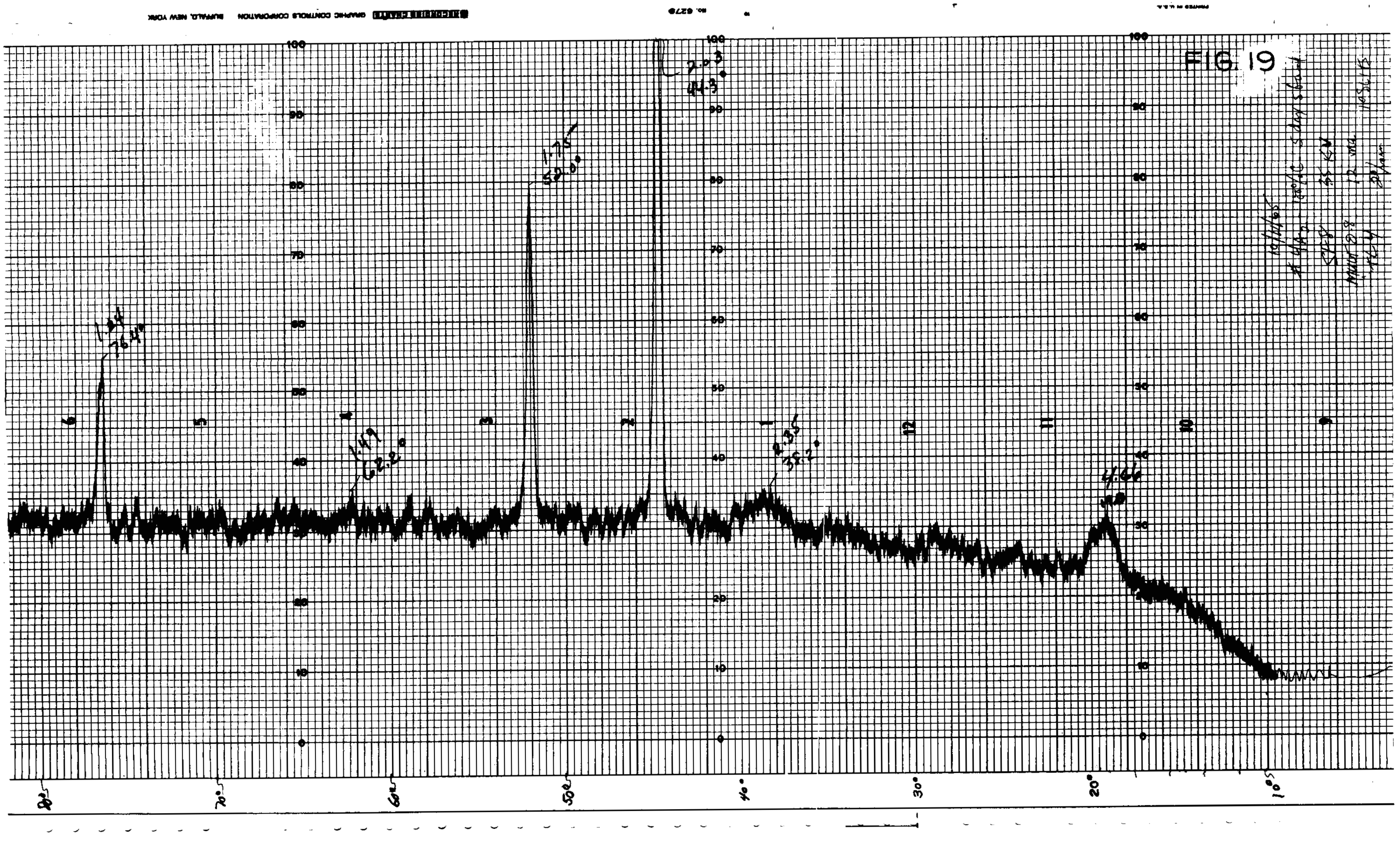
10/11/65
4A2 180°C 5 day soak
STP 35 KV
Mult 0.8 12 ma
TC 4 2°/min
105C45
1.24
76.4°
1.49
62.2°
1.75
52.0°
2.03
44.3°
2.55
35.2°
4.46
80°
70°
60°
50°
40°
30°
20°
10°
0
10
20
30
40
50
60
70
80
90
100
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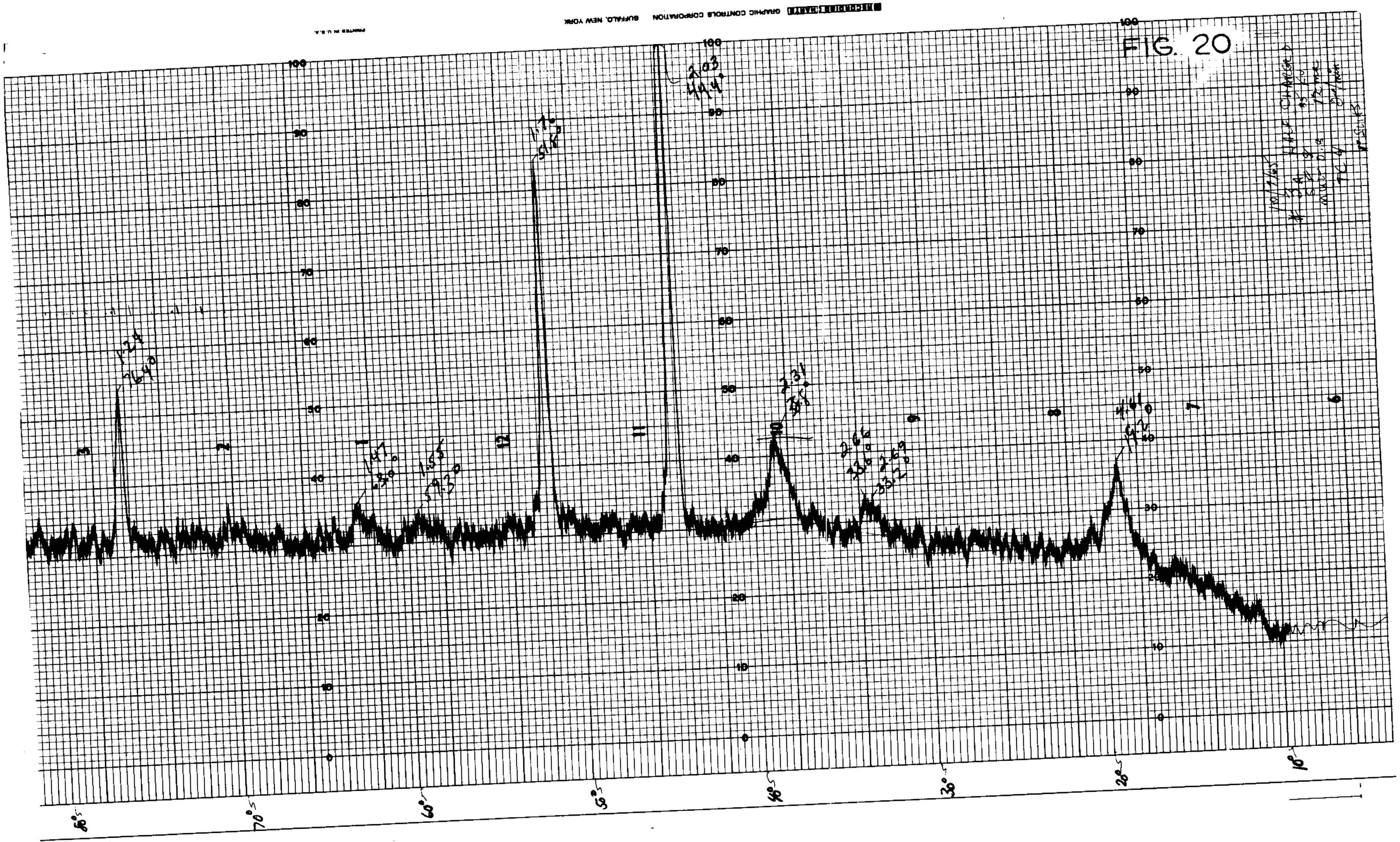
FIG. 19

FIG. 20



10/7/65
3A HALF CHARGED
SF 3 35 KV
MULT 0.8 12 MA
TC 4 2°/min
Ni Slits
1.24
76.4°
1.47Å
63.0°
1.55
59.3°
1.76
51.8°
2.03
44.4°
2.31
38.8°
2.66
33.6°
2.69
33.2°
4.41
19.2
80°
70°
60°
50°
40°
30°
20°
10°
100
90
80
70
60
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0
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FIG. 21

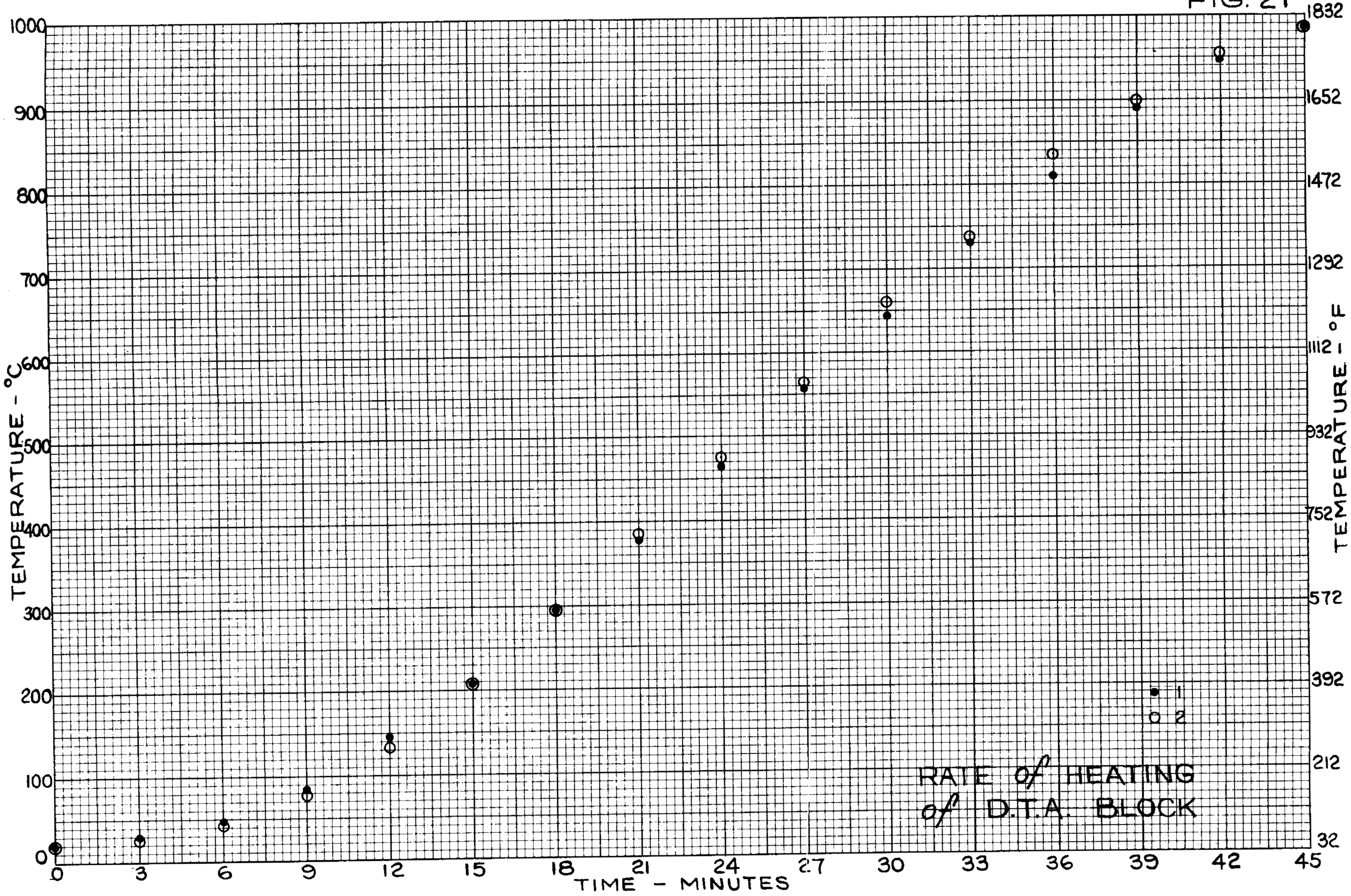
RATE of HEATING
of D.T.A. BLOCK
● 1
○ 2
TEMPERATURE - °C
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE - °F
32
212
392
572
752
932
1112
1292
1472
1652
1832
TIME - MINUTES
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45

FIG. 22

ANODIZED NICKEL SHEET