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ULTRASONICS APPLIED TO ELECTRODE REACTIONS

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OBJECT OF THE RESEARCH

The problem is the use of ultrasonics produced by magnetostriction as a means of studying phenomena at the interface between electrode and electrolyte.

EXPERIMENTAL WORK

During this period, work was continued on the effect of magnetostriction on the cathode potential at a series of charging currents extending from a few microamperes to values well above that corresponding to the decomposition potential; most of the readings, however, were made in the range of lower current densities, below the decomposition potential, where the effects are more pronounced.

Since the effect in which we are interested represents a rather small difference between two relatively large potentials, it is evident that a high degree of reproducibility must be secured. Therefore, series of experiments were run under various controlled conditions in an attempt to discover the factors influencing the reproducibility of the results.

In order to avoid the difficulty previously experienced with stripping of the plated silver from the nickel base, a solid silver cap was screwed to the end of the magnetostriction tube, the nickel portion being shielded from the solution by a rubber diaphragm.

A continued study of the difficulty due to the temperature effect indicates that it increases with time of exposure to the vibrations; for the most part, therefore, readings were restricted to the first minute after exposure to the ultrasonic vibrations. It was found that when the vibrations were applied only long enough to permit a single potential reading with a potentiometer, the values for the differences in potential with and without magnetostriction checked to ± 0.6 millivolt. Along this line, the exciting current for the magnetostriction rapidly raises the temperature of the tube, so, as was expected, the effect is greater for the shorter tube.

Since previous work indicated that the potential values for zero current showed considerable variation, it might be thought desirable to use a fresh cathode for each series of experiments; however, due to the complexity of the apparatus this is not feasible. Improved results were, however, obtained by bringing the charging current to zero after a potential reading had been taken at each current value. Typical results are shown in Fig. 1. In this figure the current flowing between the electrodes is plotted against the decrease in cathode potential (ΔE_c) which results from the effect of magnetostriction.

It might also be considered that the cathode could be brought to a standard value by shorting it against a pure silver wire. However, due to the instability of the silver wire in this system, the potential values proved to be not sufficiently steady. To remedy this the silver wire was stabilized by previously using it as an anode in sulfuric acid solution. Typical curves obtained using this procedure are shown in Fig. 2.

Another possible factor involved is the length of time during which the electrode is subjected to ultrasonic vibration. This factor must clearly be standardized in each series. For the curves of Fig. 1, the duration of vibration was about 1-1/4 minute, while for the curves of Fig. 2 the vibrations were supplied only during a uniform interval of 1/4 minute.

While the magnitude of the ΔE_c values for a given current density varies somewhat with the conditions of experiment, the general shape of the curves under suitably controlled conditions is the same. The most striking characteristic is the pronounced effect at about 25 microamperes.

Some instances were observed in which much larger ΔE_c values occurred, amounting to several hundred millivolts and in one case exceeding 500 millivolts. In general, these very large effects occurred either (1) when the electrode had been allowed to charge at a given (relatively low) current density for several hours, or (2) when the electrode, having previously been charged cathodically at a higher current density, was reduced in potential by application of a lower current density. It should be noted that in all cases the selected charging current was allowed to flow for at least 1/2 hour before ultrasonic vibrations were applied.

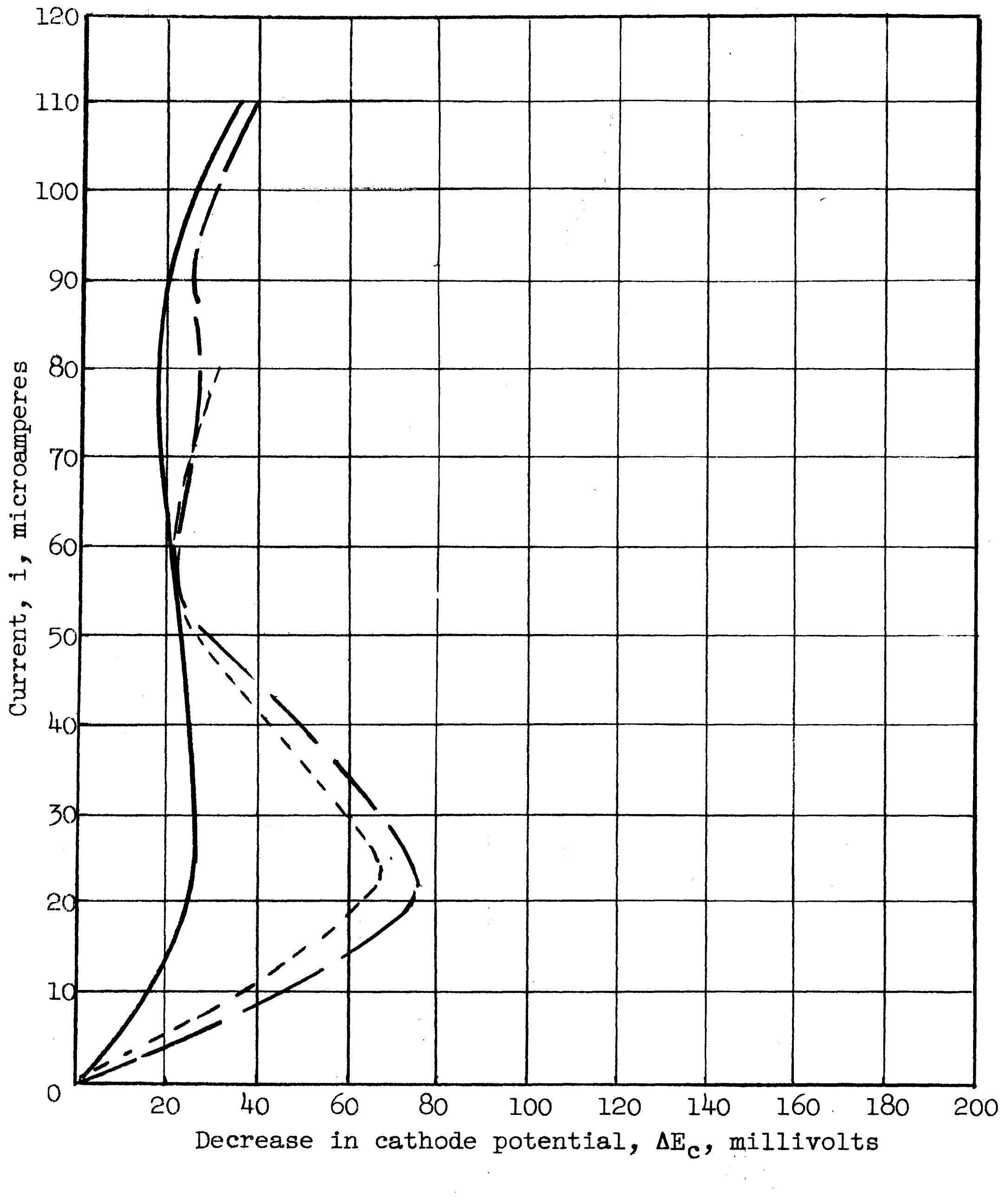

Fig. 1. Effect of Magnetostriction on Cathode Potential.
Current reduced to zero after each observation;
silver cathode; 9.5 kc.

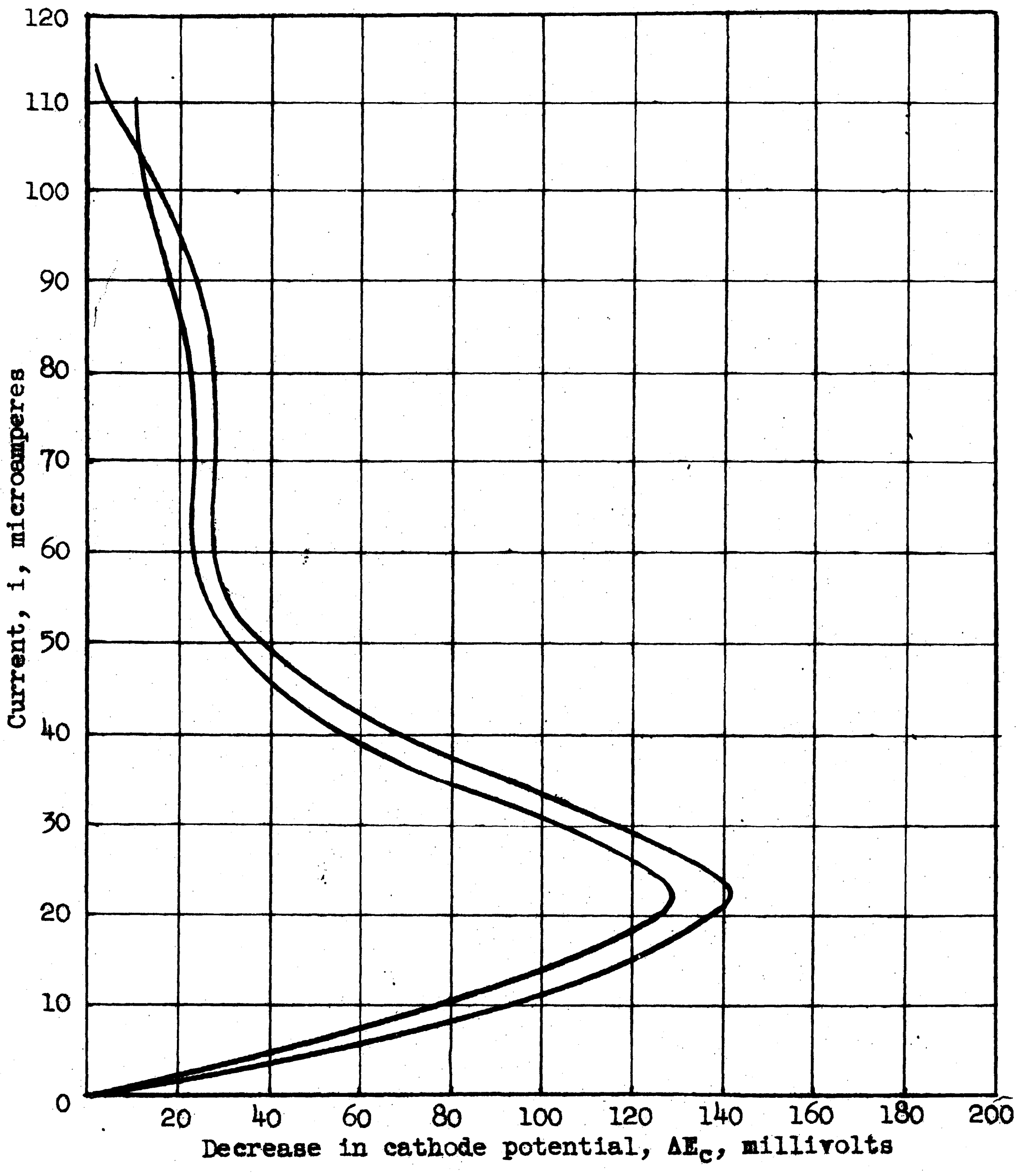

Fig. 2. Effect of Magnetostriction on Cathode Potential.
Silver cathode stabilized against Ag-Ag_2SO_4 before run; 9.5 kc.

As an illustration of this effect, Fig, 3b is presented, showing the values of ΔE_c obtained both on increasing and on decreasing the charging current. Fig. 3a also shows the current-potential curves without magnetostriction obtained in the same experiment. It is evident that the effect of ultrasonics is not merely to eliminate the hysteresis effect in the descending branch. It should be noted that the data presented in all three figures apply to potentials below the decomposition point, where the effects are more pronounced. At the highest values shown the current density is only about 0.1 milliampere per square centimeter. In experiments above the decomposition potential, the values of ΔE_c are limited to the range of 20 to 30 millivolts.

In the work so far described, potential readings were made with a potentiometer. However, as has frequently been noted in earlier experiments involving rapid change of potential, the potentiometer method of measurement is unsatisfactory for any but preliminary indications. In order, therefore, to obtain a continuous record of the changes occurring, it was necessary to make arrangements to transfer the potentials to an oscilloscope and photograph the resulting traces. The necessary equipment included: a suitable d-c amplifier, an oscilloscope (a second oscilloscope purchased for the project was already in use with the magnetostriction oscillator), and a camera. Fortunately, all these items were available from other projects, although considerable modification of the amplifier was required in order to adapt it to use with the other equipment.

A block diagram of the present assembly is shown in Fig. 4. The functions of the various items will be clear from the explanatory key to the figure and from the following outline of a typical procedure:

GENERAL DIRECTIONS FOR TYPICAL RUN

While a great many different types of experiments have been carried out, depending on the experimental conditions under investigation, the sequence of operations given below is for a typical run in which the effect of magnetostriction on cathode potential is the objective.

1. Preliminary Period.

(a) Pass hydrogen through purification train (XIII) into assembled cell for sufficient time to attain saturation.

(b) Pass small current through electrolytic cell (XVII) for

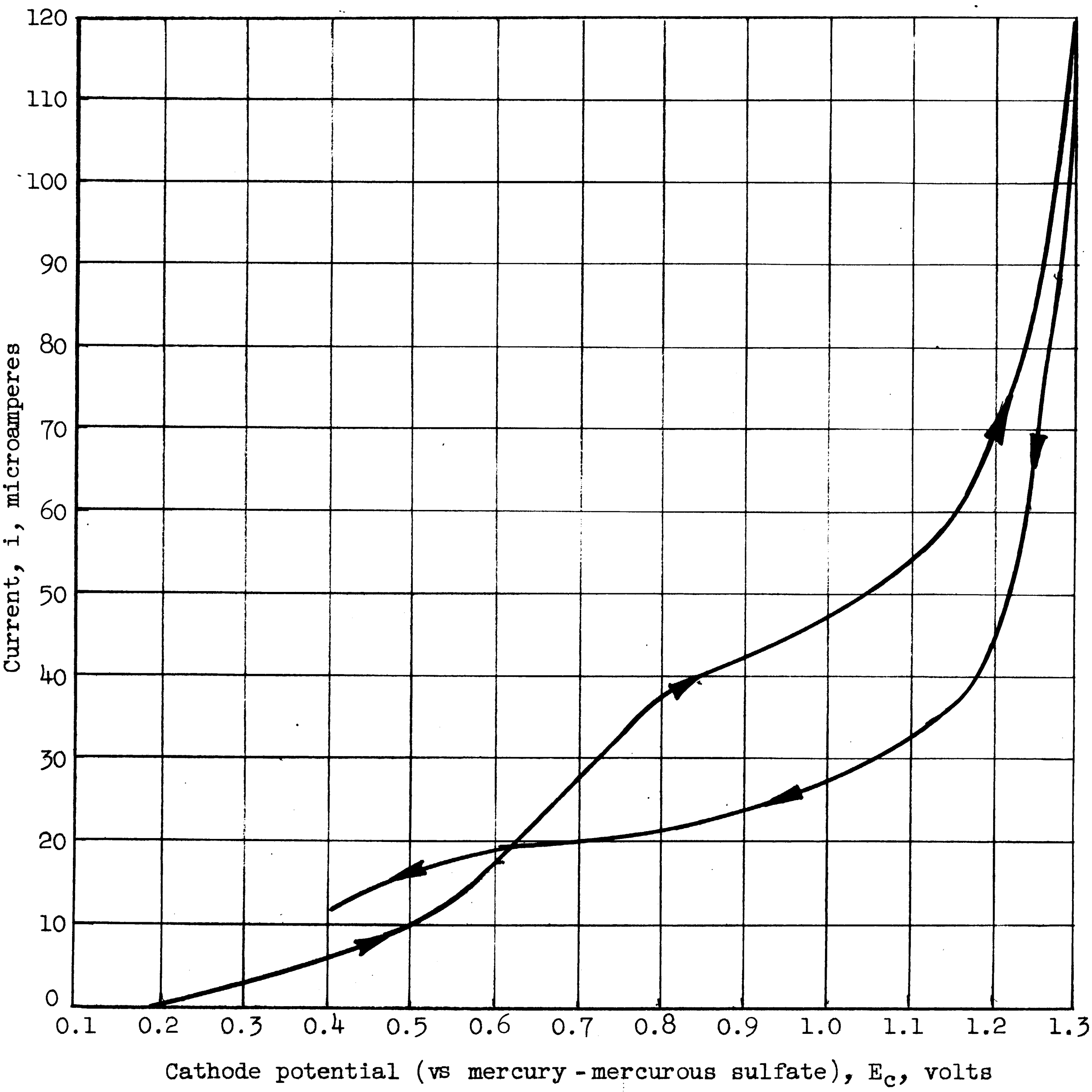

Fig. 3a. Effect of Magnetostriction on Cathode Potential.
Increasing and decreasing charge currents; 9.5 kc.

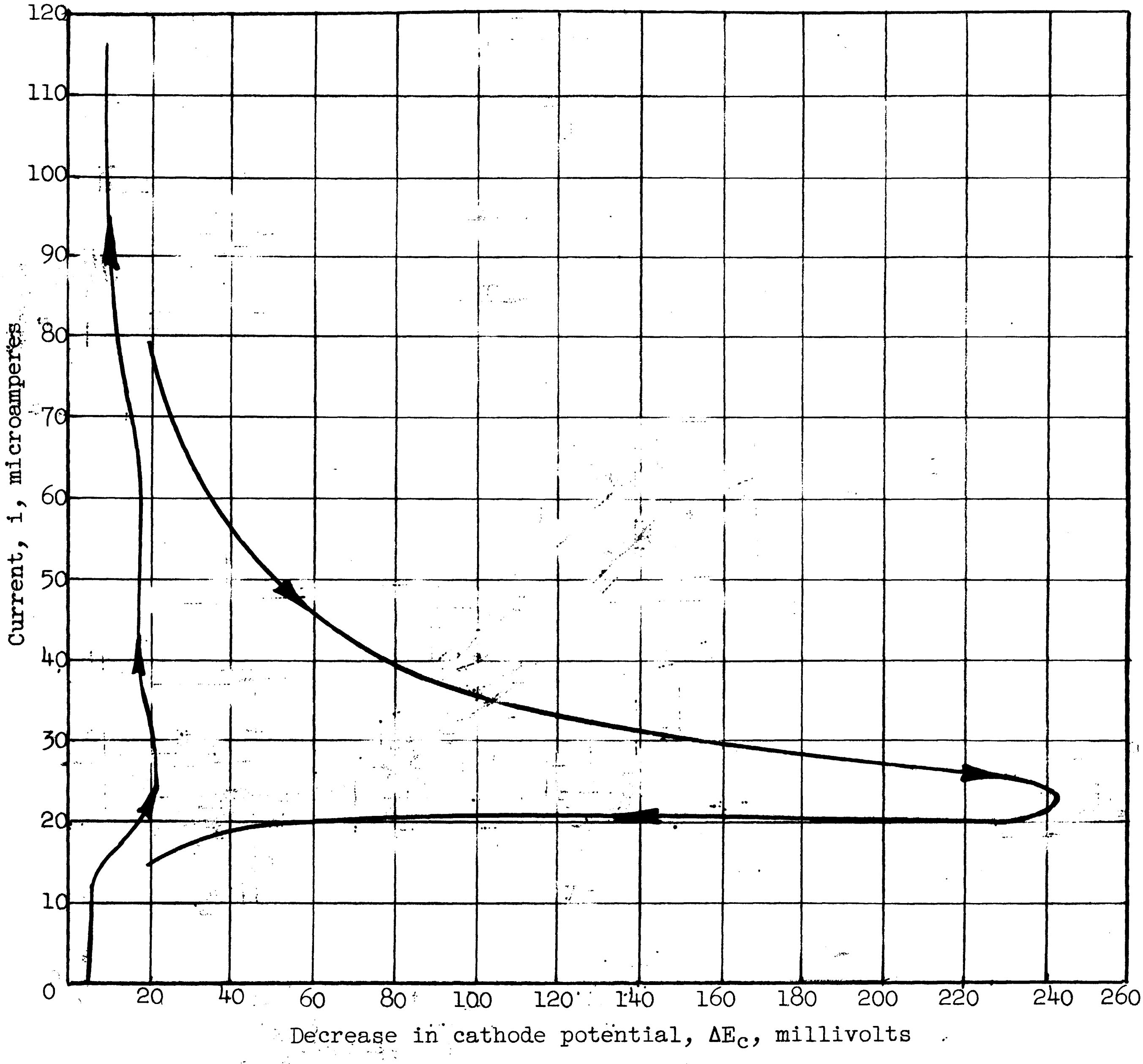

Fig. 3b. Effect of Magnetostriction on Cathode Potential.
Increasing and decreasing charge currents; 9.5 kc.

selected period to produce relatively stable starting potential.

2. Warm-up Period.

Turn on (a) magnetostriction filament current (XVIII), (b) d-c amplifier filament current (V), (c) oscilloscope 250H (IV), (d) d-c voltage source for slow horizontal sweep (VII), and, if used, (e) amplitude- and frequency-measuring systems (II and XV).

3. Check Period.

(a) Measure starting current and potential by potential-measuring system (XIV). (Up to the present, the potential-measuring system has not included the vacuum-tube feature shown in the diagram.)

(b) Apply plate and bias voltage on input-grounded d-c amplifier (V).

(c) Adjust to zero output as indicated on zero-balance meter (IV).

(d) Set controls on scopes, oscillator, magnetostriction unit, camera and amplitude-measuring unit at positions selected for run.

(e) Recheck adjustment of grounded amplifier.

4. Run Period.

(a) Apply potential to be measured to amplifier (IV) through switch box, leaving cathode grid grounded.

(b) Establish desired initial position of spot on scope 250H (IV).

(c) Adjust sweep rate to desired value.

(d) Observe the movement of the spot on the scope until it is noted that the potential is relatively steady.

(e) Measure the potential with the potentiometer.

(f) Open the camera shutter and photograph a trace without

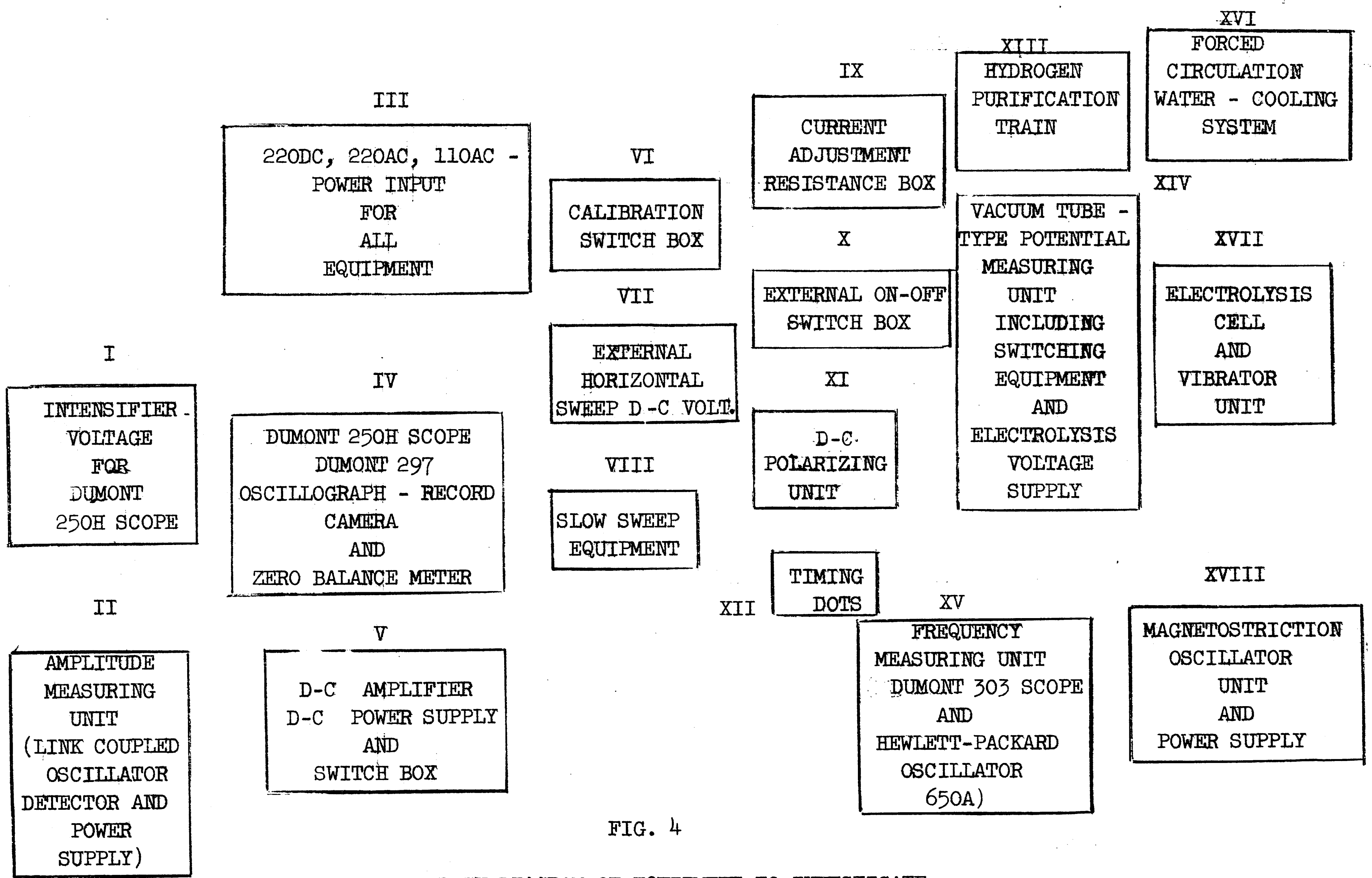

FIG. 4

BLOCK DIAGRAM OF EQUIPMENT TO INVESTIGATE

THE EFFECT OF VIBRATION UPON AN ELECTRODE POTENTIAL

KEY TO BLOCK DIAGRAM

I. DuMont 250H intensifier for fast sweep rates.

II. Measurement of the amplitude of vibration as picked up by capacitor-pick-up-plate and shown photographically on DuMont 250H scope.

III. Required input power supply for all units.

IV. Flat-face scope by which the amplitude effect of magnetostriction is photographed.

V. Switch box, through which calibration voltage and potential changes are passed to d-c amplifier, the out-put of which is connected to vertical deflection plates of DuMont 250H.

VI. Calibration switch box used in conjunction with switch box in (V) for application of potentials to d-c amplifier.

VII. D-c sweep voltage applied to x-axis of DuMont 250H.

VIII. Sweep motor and gear boxes used with DuMont 250H scope for very slow sweeps.

IX. Variable resistors to adjust current.

X. Main control switch box for electrolysis current, magnetostriction oscillator, etc.

XI. D-c polarizing unit to set up constant magnetic field around vibrator.

XII. Timing dots placed on DuMont 250H scope by means of intensity modulation key.

XIII. Purification train for hydrogen (or other gases).

XIV. Vacuum tube potential measuring system in isolated box for measuring cell potentials and for calibration marks. Electrolysis voltage supply source.

XV. Measurement of the frequency of forced vibration by use of Lissajou's patterns.

XVI. Cooling water which is forced as a spray into the hollow vibrating tube.

XVII. Electrolysis cell system containing electrodes, reference electrodes and cell. Vibrator, magnetostriction oscillator coil and capacitor pick-up holder are also in the steel box.

XVIII. Magnetostriction oscillator system.

magnetostriction.

(g) Return spot to original position.

(h) Turn on d-c polarizer.

(i) Start sweep motor.

(j) Open camera shutter to start trace.

(k) Turn on magnetostriction for desired interval.

(l) Close shutter.

(m) Turn off sweep motor at end of trace.

The operations outlined above are repeated for each electrolyzing current desired in the series.

Timing dots (XII) may be placed in the film at any time, as well as voltage calibration marks by means of the calibration switch box (VI) and potential unit (XIV) through the switch box and amplifier (V).

CONCLUSION

In general the pictures obtained with this equipment have confirmed the effects previously noted with the potentiometer. However, the much greater detail now obtainable has indicated hitherto unsuspected variations with the system under study, both with and without ultrasonic vibrations. The disturbing factors are under investigation.