U. S. NAVY EXPERIMENTAL DIVING UNIT
U. S. NAVAL WEAPONS PLANT
WASHINGTON 25, D.C.

EVALUATION REPORT 4-60

OXYGEN CELL WARNING DEVICE INTERIM EVALUATION REPORT

PROJECT NS186-202 SUBTASK 2 TEST 17

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8 SEPTEMBER 1959

AD #780-166

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ABSTRACT

An oxygen warning device consisting basically of an oxygen galvanic cell supplied by the National Carbon Company was given practical tests to simulate its application in scuba mixed gas equipment as an indicator of low oxygen percentage. Two improved cell types were also tested. While the hardware of the original device was not considered practical for direct application in the scuba equipment, the cells were found to perform satisfactorily in terms of following the predicted output curve under most simulated conditions. Minor inadequacies which hold promise of correction were found in the cells including zero stability, time of reaction, response to gross wetting, and erratic behavior in presence of carbon dioxide.

SUMMARY

PROBLEM:

Is the oxygen cell warning device developed by the National Carbon Company suitable for use in mixed gas underwater breathing apparatus to indicate low oxygen percentage?

FINDINGS:

The oxygen cell warning device is not suitable in its present form. The following characteristics of the cells are not satisfactory:

(a) Response to carbon dioxide.
(b) Reaction to wetting.
(c) Time response.
(d) Method of sampling.

RECOMMENDATIONS:

It is recommended that development of the oxygen cell be continued.

ADMINISTRATIVE INFORMATION

Ref: (a) BuShips Contract NObs 72374 of 12 January 1958
(b) Telephone conversation of 29 September 1958 with Mr. M. Foran, BuShips (Code 638)
(c) National Carbon Research Laboratories, Cleveland, Ohio Technical Memorandum 361

By reference (a), the Bureau of Ships contracted for the design and development by National Carbon Research Laboratories of the Union Carbide Company of an "oxygen cell" low oxygen warning device for underwater breathing apparatus. The apparatus and descriptive material, reference (c), was delivered to U. S. Navy Experimental Diving Unit on 26 September 1958 and by reference (b), the Bureau of Ships directed evaluation and assigned the project number.

T. W. James, HM1(DV), USN, was assigned as Project Engineer and R. T. Van Orden, LT, MC, USN as Project Officer. Work was commenced about 19 January 1959 and brought to its present state of completion by 15 June 1959. Several delays were imposed while awaiting additional testing materials. Charges incurred in the execution of the project was lodged against allotment 16102/59.

The following breakdown indicates the manhours expended for this project:

DESCRIPTION	MANHOURS
Preliminary setups and calibration	40
Testing and plotting	200
Report preparation	10
Report typing and duplication	10
TOTAL	260

This is the first report under this project number. The number is issued in the Experimental Diving Unit's Evaluation Report series and is distributed only to the Bureau of Ships.

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Figure 8 Output Voltage vs. Time After a 15% Change in Oxygen Percentage (From 29.5% to 15.0%) Oxygen Cell type #2

Figure 9 Output Voltage Curve of National Carbon Oxygen Cell

1. INTRODUCTION

1.1 Background

1.1.1 A danger inherent in any breathing apparatus which recirculates the breathing medium is a lowering of its oxygen percentage. This occurs in semi-closed circuit diving gear as a result of interruption of gas supply or an oxygen consumption greater than that anticipated for a certain dive. In closed circuit gear, simple dilution of breathing bag gas with inert gas released from the body by way of the lungs may bring about a similar lowering of oxygen percentage.

The oxygen-inert gas mixture in the breathing bag of semi-closed circuit mixed gas scuba is determined by: (1) type of work (hence, oxygen consumption); (2) supply mixture; and (3) rate of injection of the mixture into the circuit. A lowering of the oxygen percentage may therefore be indicative of one or more of the following hazards:

(a) Hypoxia or lack of sufficient oxygen to sustain consciousness. A low oxygen percentage, even though safe at depth, becomes increasingly dangerous because of decreasing partial pressure as the diver approaches the surface. It may come about insidiously as in the case of continuing elevated oxygen consumption or rapidly as in the case of interrupted supply flow.

(b) An oxygen percentage high enough to be safe at all depths yet lower than that anticipated for the particular dive may indicate interruption of the flow of supply mixture. Exhaustion of the remaining oxygen in the breathing bag would soon follow, the rapidity depending upon the depth at the time of interruption. In other words, a decreasing oxygen percentage is important as one of the earliest signs of equipment failure even before the fall in the percentage comes near dangerous levels. An extremely rapid indication of O_2 percentage change would be required to fulfill this need for a warning.

(c) An <u>increase</u> in the inert gas percentage over that intended is implied by a decrease in oxygen percentage. Even while breathing a safe level of oxygen the diver may be placing himself in greater need of decompression than anticipated.

1.1.2 From the foregoing, it is apparent that a need exists for a device which would warn the diver of an oxygen percentage lower than that intended for a particular dive. It should be sufficiently portable and economical that it could be incorporated into individual scuba equipment.

1.1.3 The "oxygen cell", manufactured by the National Carbon Company, is essentially a galvanic cell which produces a voltage varying with the oxygen partial pressure to which its carbon cathode is exposed. A voltage varying with the percentage of oxygen instead of the partial pressure is produced by a device utilizing two such cells, one being fed a known constant mixture while the sensing cell in electrical opposition is fed the unknown mixture. Both cells are subjected to the same pressure so that the pressure effect is effectively cancelled out, the differential voltage being proportional to the percentage difference between known and unknown mixtures. The voltage variations produced are thought to be of such magnitude and consistency that a low oxygen warning device could be triggered thereby. The voltage output

of the cell is described by a straight line semilog curve, 29.5 mv increment for each factor of ten (10) in O_2 partial pressure.

1.1.4 The means of giving warning (whether by light signal, sound, meter indication, etc.) as well as the critical level for a warning (particularly in view of the significance of relatively small changes as described in (b) of paragraph 1.1.1 must be left for specific consideration in connection with the equipment to which the device will be applied.

1.2 Objective

1.2.1 An investigation of the characteristics of the oxygen cell for application as a low ox gen warning device, particularly as applied to current semi-closed circuit mixed gas scuba, is the objective of this phase of the evaluation.

1.3 Scope

1.3.1 The scope includes the determination of the amplitude, rate and consistency of change in voltage output of the oxygen cell for various changes in oxygen percentages of gas mixtures under various conditions. The conditions include both helium and nitrogen as background gases; pressures equivalent to surface and various depths; CO_2 contaminated mixtures; and different reference mixtures. Inasmuch as operational use will always include "wet" gases, this evaluation was made using only test mixtures nearly saturated with water vapor.

1.3.2 At the same time, preliminary observations were made of cell life, ruggedness, reaction to condensation, momentary flooding, clogging of reference and/or supply, etc.

2. DESCRIPTION

2.1 Warning Device

2.1.1 The original oxygen warning device supplied by the National Carbon Company consisted of a metal box (see figure 1) containing two type #1 cells. The reference cell is provided with a coupling for connection with reference gas and the unknown cell is set in such a manner that its hollow carbon electrode could be exposed to the interior of the breathing bag. The circuit is provided as figure 2 and in principle consists of a bridge arrangement in each branch of which is placed one oxygen cell. One serves as the indicator, the other as the pressure compensation element. A potentiometer in one branch allows an indicating meter to be set to any desired calibration point.

2.2 Oxygen Cell - Type #1

2.2.1 The sensing element, cell type #1, figure 3, shows the oxygen, carbon /KOH/zinc cell used as oxygen indicator. It consists of a tubular carbon electrode in the center with the activating mechanism attached to it. The carbon is wrapped in a separator which prevents shorting of the zinc powder

anode to the carbon electrode. Before the cell is subjected to pressure tests, this channel has to be opened by means of a needle in order to assure rapid pressure equilibrium inside and outside of the cell. No liquid will flow out through this hole if it is opened after cell activation when most of the electrolyte is already gelled.

2.3 Oxygen Cell - Type #2

2.3.1 Cell type #2 (see figures 4 and 5) consists of two tubular carbon cathodes mounted back to back with a common zinc anode. The external circuit is essentially like that described in paragraph 2.1.1. The electrolyte is 9 normal KOH.

2.4 Oxygen Cell - Type #3

2.4.1 Cell type #3 is externally identical to cell type #2 but has grooved surface in the interior of the tubular cathodes and the cathodes have been produced by an improved process. The electrolyte recommended is 12 normal KO

3. PROCEDURE

3.1 General

3.1.1 The oxygen cells were mounted in such a manner that gases could be delivered by plastic tubes into their tubular carbon cathodes at rates between one and two liters per minute. Gases were supplied from a specially prepared bank of gas cylinders in which were mixtures of varying oxygen content in either helium or nitrogen. Generally, changes in mixtures were made by actually exchanging the plastic supply tubes to the electrodes so there was no appreciable problem of wash out. A galvanometer with divisions equal to 1/4 MV per division was mounted in the circuit in place of the one supplied in the original device. A 125 ohm resistor could be placed in serie with the galvanometer to change the sensitivity to 1/2 MV per division. The general procedure was approximately as follows: Reference gas was delivered to both cells until a stable reading was achieved. The potentiometer was adjusted until this reading was at a convenient point on the meter. A series of mixtures between 15% and 55% oxygen in 5% increments were then delivered to the unknown cell in sequence and repeated several times, the results being recorded. This basic procedure was repeated under various test conditions.

3.2 Effect of Pressure

3.2.1 Pressure response was evaluated by moving the entire assembly into a pressure tank at Experimental Diving Unit.

3.3 Effect of Humidity

3.3.1 The effect of humidity of the gases was tested by supplying cells unde load (flashlight bulb) with dry gas and with gas bubbled through water until the cells began to fail.

3.4 Effect of Wetting

3.4.1 The effect of gross wetting or flooding was tested by simply squirting

water into the electrode during a run and allowing it to dry out.

3.5 Time Response

3.5.1 Time response of the cells was tested by allowing the meter to stabilize with a reference through both cells, switching the unknown cell to another mixture and plotting the meter readings against time.

3.6 Effect of CO_2

3.6.1 The effect of CO_2 in the unknown mixture was tested by directing a reference mixture through the reference cell and directing air through the unknown cell. CO_2 was injected into the air at a realistic rate through an absorbant and the absorbant system was set up to fail gradually as it might actually do in equipment use, allowing the CO_2 level to rise slowly. The output was continuously analyzed by Liston-Becker CO_2 analyzer as it entered the unknown oxygen cell.

4. RESULTS

4.1 Zero Stability

4.1.1 Zero stability was the first problem encountered. The type #1 cells evidenced zero drift in the magnitude of one (1) millivolt in 20 minutes which is equivalent to as much as 5% O_2 change in the upper range (see figure 6) or near 50% O_2. The type #2 and #3 cell evidenced much greater stability, generally drifting less than 1 millivolt in 3 or 4 hours.

4.2 Response to varying percentages of oxygen

4.2.1 The response of the cells was found in the cases of all three types tested to conform to the curve provided by the manufacturer (figure 9). A typical response curve is presented as figure 6 wherein 5% increase in O_2 percentage in the lower range (15%-20%) produces about 3 MV and 5% increase in upper range (50%-55%) produces about 1 MV.

4.2.2 Essentially similar response curves were produced using both helium and nitrogen as background gas.

4.3 Effect of Pressure

4.3.1 When the apparatus was tested under pressure, the same curves were still reliably produced, but there was considerable fluctuation in the indication during the actual application or release of pressure. Variations equivalent to as much as 5% oxygen in <u>either</u> direction were observed. After leveling off, the indication returned to proper reading within 20 to 30 seconds using the type #1 cell. Pressure runs were made at 2 and 4 atmospheres absolute.

4.4 Effect of Humidity

4.4.1 Cells subjected to either dry or wet gas continued to give reliable indications after more than 24 hours continuous load and exposure. Several began to disintegrate shortly after that period but there was no apparent correlation with the gas delivered to them. Only cells of type #1 were so tested.

4.5 Effect of Gross Wetting

4.5.1 Cells of type #2 were subjected to actual wetting as described in paragraph 3.4.1. When both cells were supplied with 26% reference gas, flooding the reference cell caused an increase in O_2 indication of about 3 MV and flooding the unknown cell caused a deviation of about 3MV in the opposite direction. When dry, same cells returned to normal.

4.6 Time Response

4.6.1 Time responses of the type #2 cells were evaluated and are presented as figures 7 and 8 wherein in abrupt changes of 5% O_2 percentage about 80% of the scale change to be expected was achieved in 30 seconds and an essentially level response by 60 seconds. Cells of type #1 were slower but were not timed.

4.7 Effect of CO_2

4.7.1 The effect of CO_2 upon the performance of the cell was to cause large deviations (quantitatively erratic but reaching 3 to 4 MV in the tests) in th indication. It was regularly in the direction of increased O_2 percentage when the CO_2 was introduced into the unknown cell. The magnitude of CO_2% first causing this deviation was consistently in the range of approximately 0.7%. This percentage was obtained in every trial over periods ranging from 5 to 20 minutes. Abrupt changes were not tested since they would so rarely be anticipated in use. The original deviation persisted for 30 minutes and was not tested longer. Restoration of CO_2 free mixture brought the indicatio back to normal within 10 minutes.

4.8 Evolution of Gas

4.8.1 In testing the type #3 cell which (like the type #2) is filled with liquid electrolyte through a side arm on the cell it was noted that there was visible evolution of gas from the surface of the zinc anode. The present side arm construction allowed this gas to push small amounts of electrolyte out before the gas itself escaped.

4.9 Uniformity of Cells

4.9.1 In the use of the type #1 cell best results were obtained by using well matched cells (those which indicated the same voltage on a voltmeter while under load). The uniformity of cells was such that matching was diffic

5. CONCLUSIONS

5.1 General

5.1.1 In general, the oxygen cell as an oxygen monitoring device shows great promise. Most of the characteristics now slightly undesirable are probably correctable. The use presently intended for the O_2 warning device in semi-closed mixed gas scuba equipment makes a modified form of the cell seem desirable. The carbon electrode of the unknown cell in tubular form might

better be utilized if it were open at both ends, and of larger diameter (approximately 1"), so that the entire flow of breathing medium were directed through it. The reference cell as a smaller but similar tube parallel to the unknown cell electrode would appear practical.

5.2 Zero Stability

5.2.1 The zero stability achieved in cells type #2 and #3 is acceptable.

5.3 Output Signal

5.3.1 The voltage output of the cells in response to changing oxygen concentration is of sufficient magnitude to trigger a warning device.

5.4 Effect of Pressure

5.4.1 The consistency of the indication under varying pressures is hampered only by the tendency to be erratic during pressure changes, or descent and ascent. It is thought this may be improved and it may also be possible to ignore the indications of the device while under actual change.

5.5 Effect of Humidity

5.5.1 Effect of humidity of the gas appears to be negligible.

5.6 Effect of Wetting

5.6.1 The vulnerability of the cell to gross wetting of the carbon electrode (6.5) is unacceptable at present in view of the likelihood of its becoming wet with either condensate or sea water while in use. However, the addition of increased amounts of paraffin in the formulation of the carbon electrode has been suggested to make it relatively more non-wettable.

5.7 Time Response

5.7.1 The present time responses (6.6) of the cell and circuit are acceptable for all of the applications described in section 2 except its application as a warning of interrupted supply which requires a very rapid indication. The manufacturer claims that as the magnitude of the resistance in the circuit is decreased, the speed of indication is increased but zero stability is decrease Improvement of zero stability by better quality control in the electrodes would enable improvement of speed of indication by allowing decrease of resistance in the circuit.

5.8 Effect of CO_2

5.8.1 An effect of CO_2 in expected ranges upon the response of the cell was anticipated but it was hoped that the indications change caused by CO_2 in the "unknown" gas would be in the same direction as lowering oxygen concentration. In that case, the device might have served at once as both low oxygen warning and high CO_2 warning. The opposite effect, however, was found with gradual CO_2 build up similar to that expected operationally. This effect is unacceptable since the presence of CO_2 would tend to mask the effects of lowering oxygen percentage. Changes in the cell to eliminate CO_2 effect are thought to be possible.

6. RECOMMENDATIONS

6.1 Further Development

6.1.1 It is recommended that the development of the oxygen cell for use in a warning device for underwater breathing apparatus be continued. The following characteristics of the present cells should be improved:

(a) Effect of carbon dioxide - the cell should be made less sensitive to the presence of carbon dioxide in the gas sample.

(b) Effect of wetting - the effect of temporary contact of the cathode with water should be minimized.

(c) Time response - the time response of the cell should be improved.

(d) Sampling - the method of sampling should be improved.

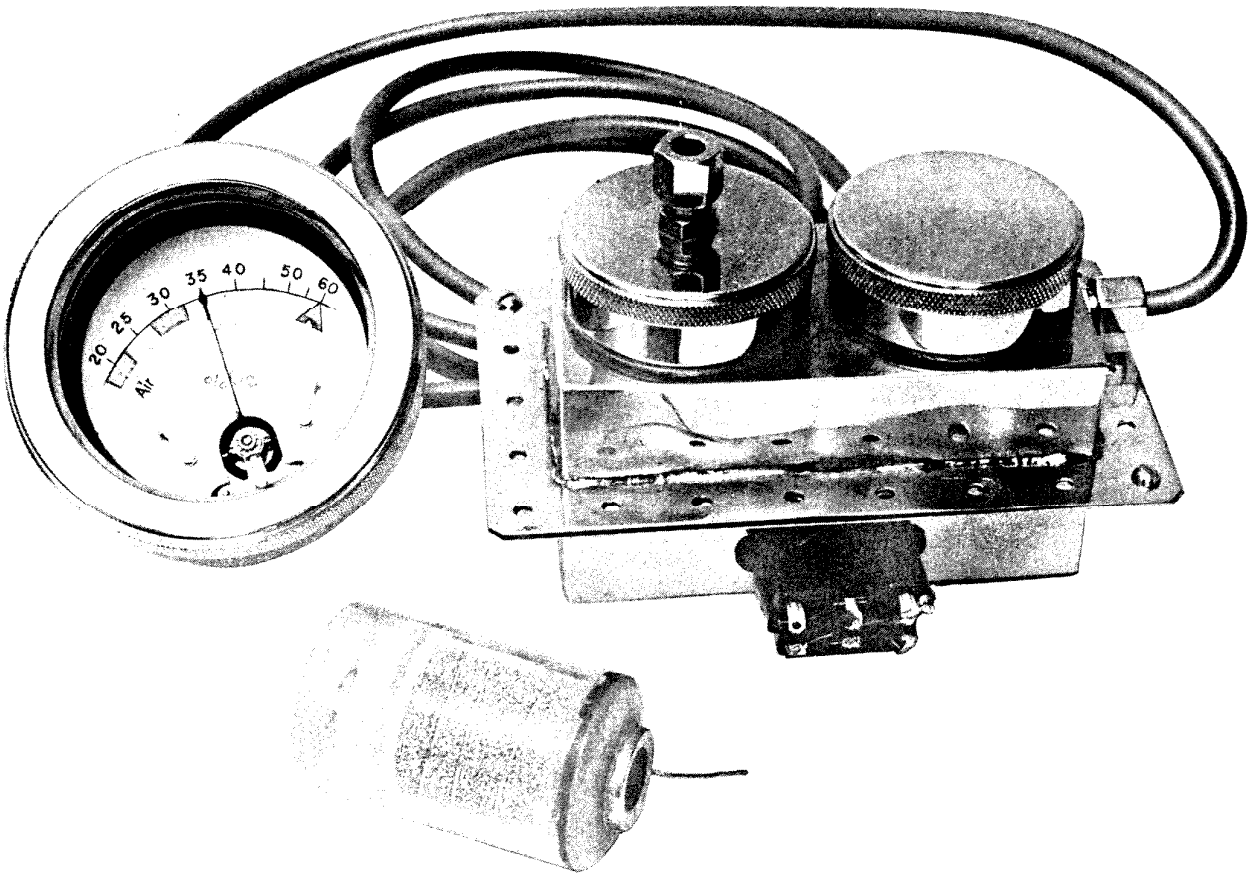


FIGURE I. OXYGEN CELL WARNING DEVICE (WITH TYPE # I CELL)

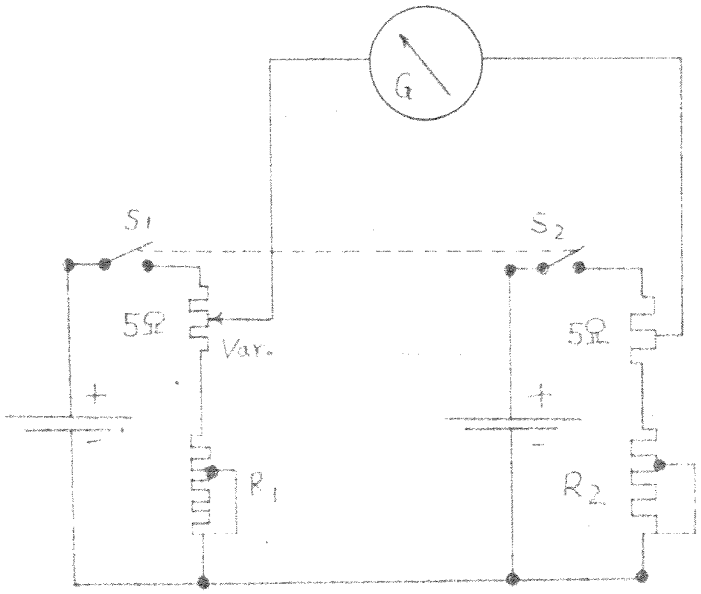


FIGURE 2.
CIRCUIT DIAGRAM OF OXYGEN CELL WARNING DEVICE

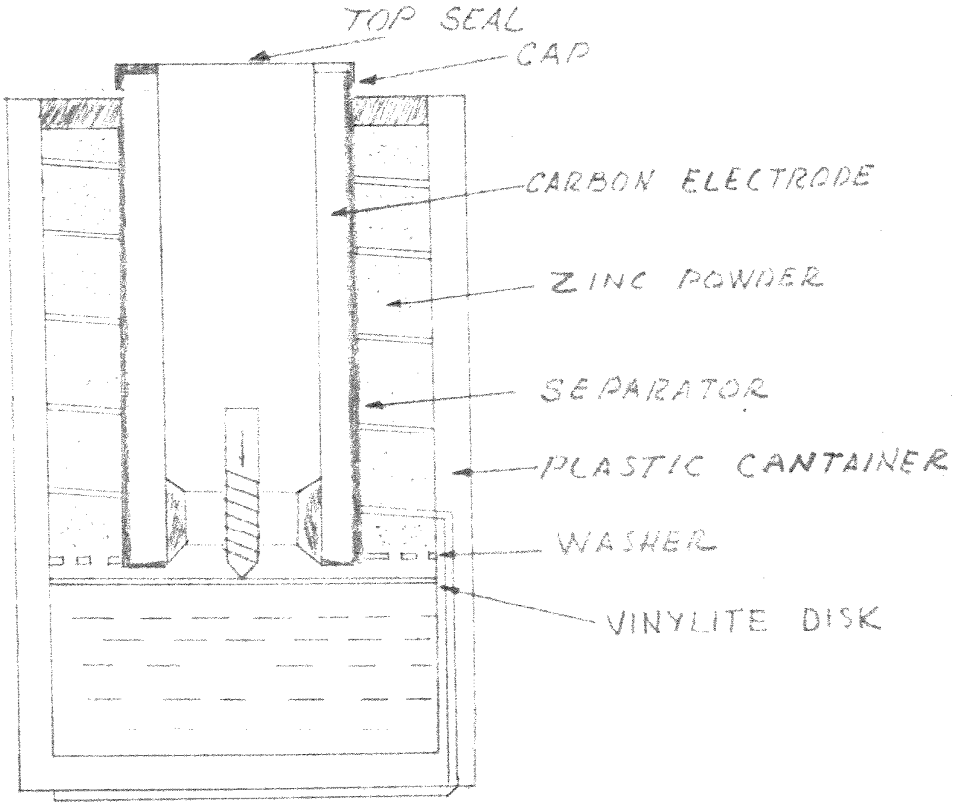


FIGURE 3.
DIAGRAM OF TYPE #1 OXYGEN CELL

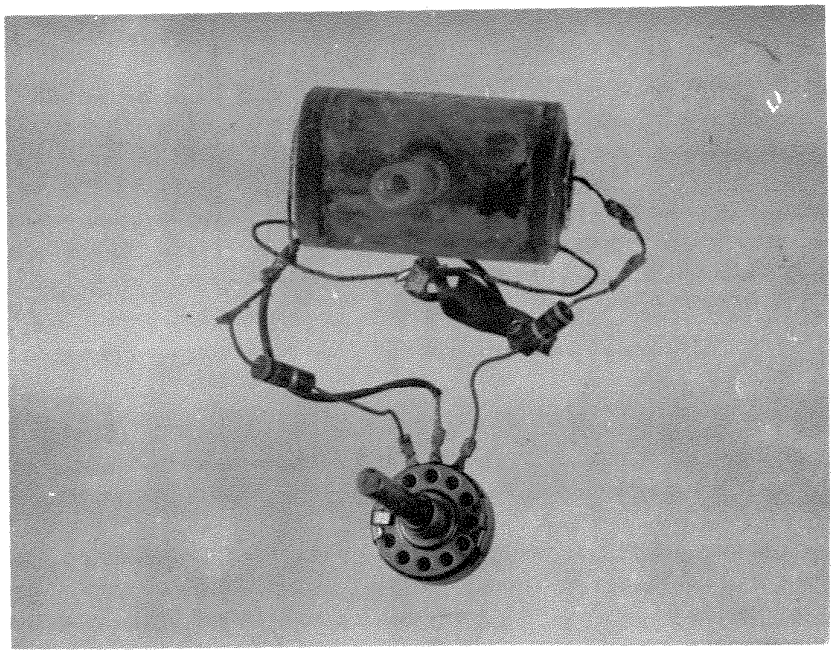
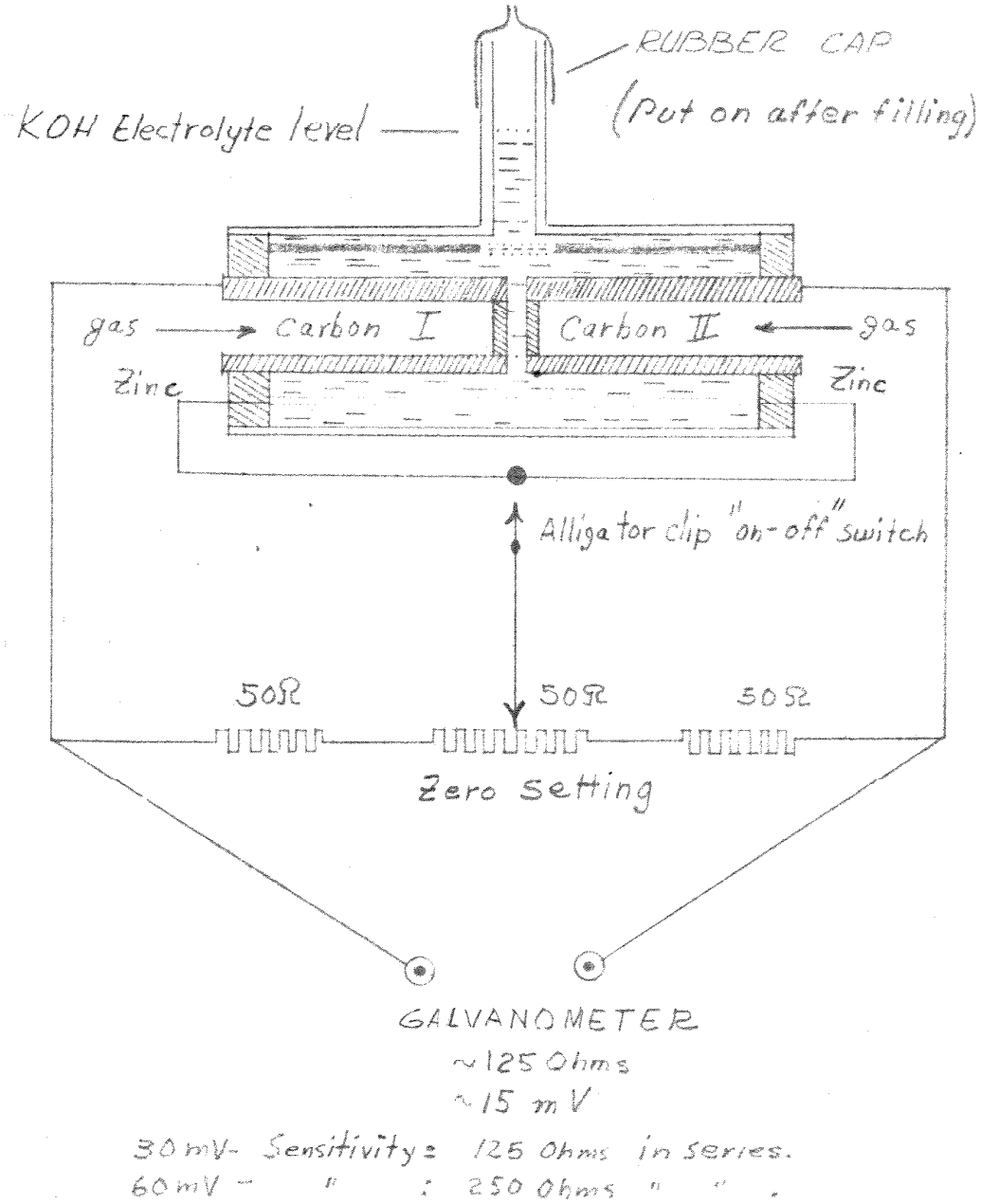


FIGURE 4. OXYGEN CELL TYPE #2 WITH POTENTIOMETER AND RESISTORS ATTACHED.



30 mV- Sensitivity: 125 Ohms in series.
60 mV - " : 250 Ohms " " .

FIGURE 5.
DIAGRAM OF TYPE #2 OXYGEN CELL AND ELECTRICAL CIRCUIT

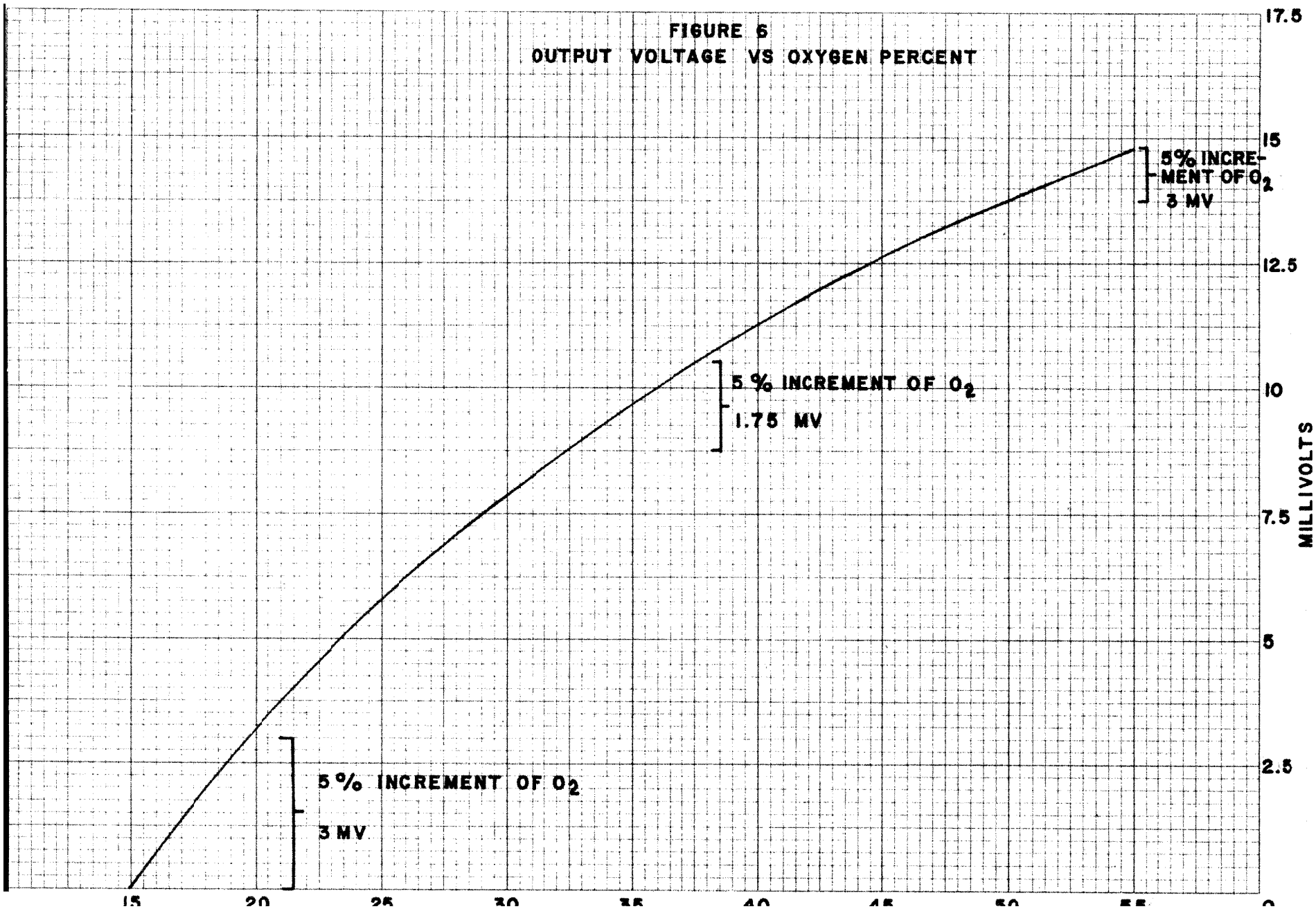


FIGURE 6
OUTPUT VOLTAGE VS OXYGEN PERCENT
5% INCREMENT OF O_2
3 MV
5 % INCREMENT OF O_2
1.75 MV
5 % INCREMENT OF O_2
3 MV
17.5
15
12.5
10
7.5
5
2.5
0
MILLIVOLTS
15
20
25
30
35
40
45
50
55

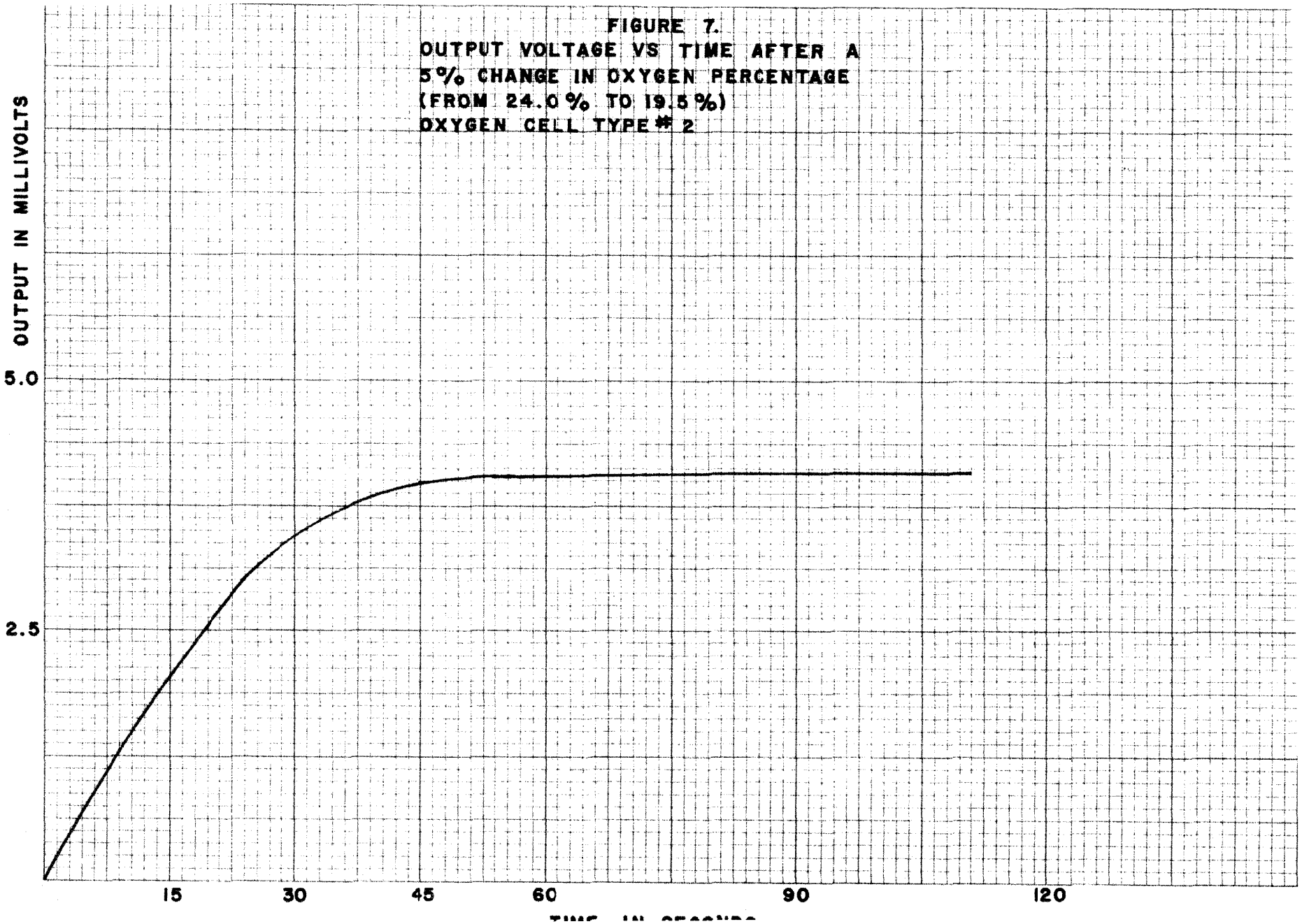


FIGURE 7.
OUTPUT VOLTAGE VS TIME AFTER A 5% CHANGE IN OXYGEN PERCENTAGE (FROM 24.0% TO 19.5%)
OXYGEN CELL TYPE # 2

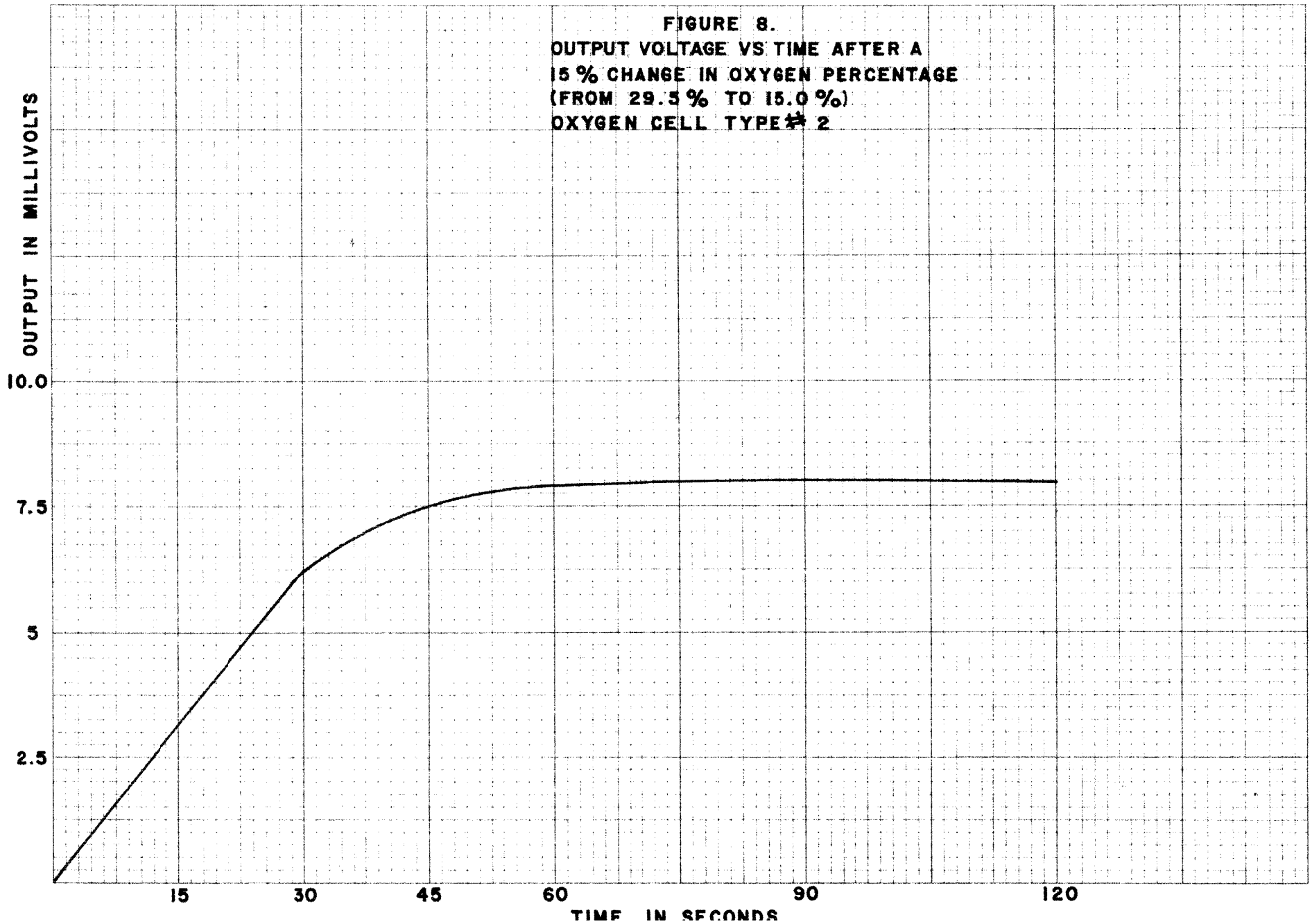
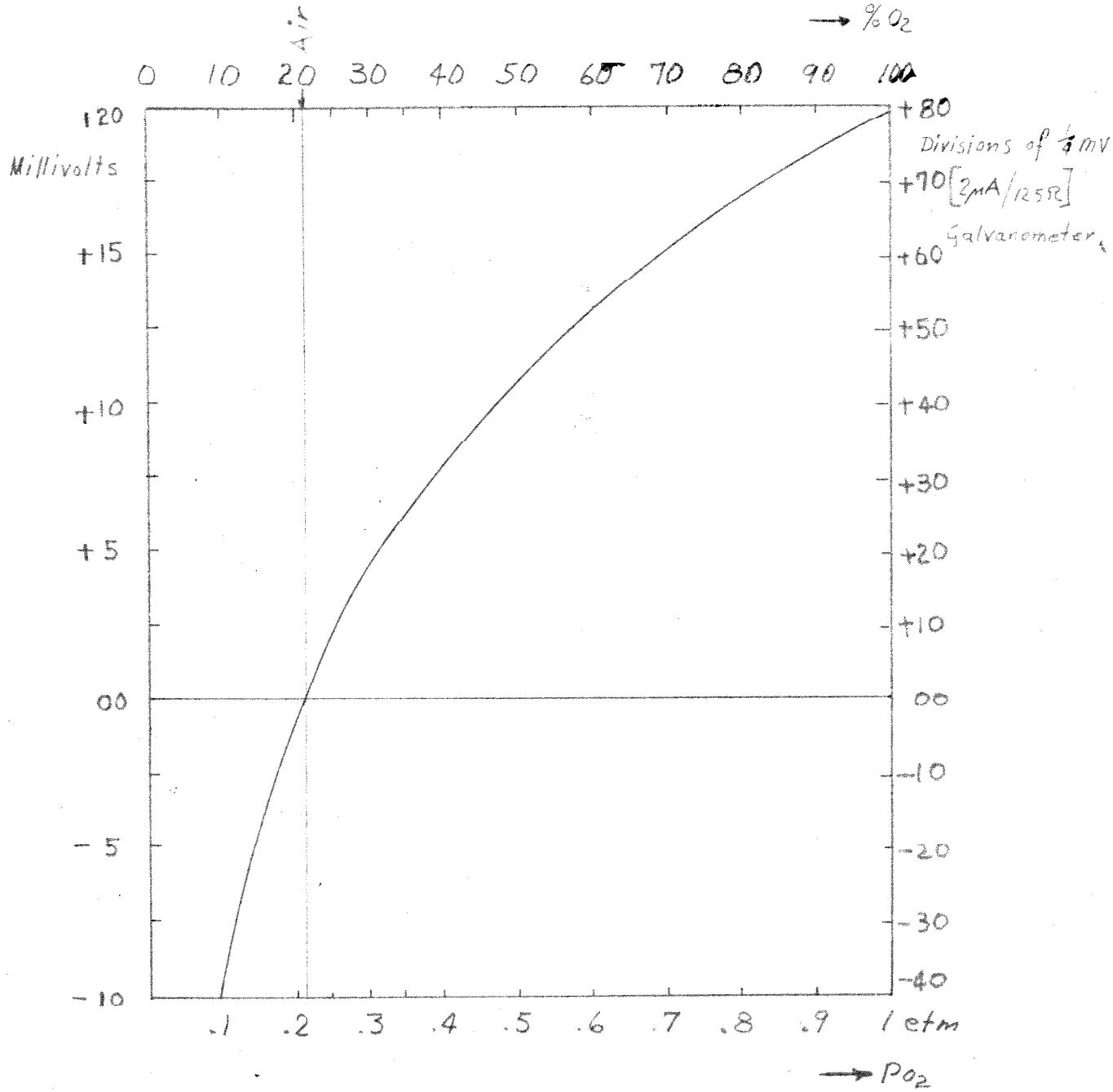


FIGURE 8.
OUTPUT VOLTAGE VS TIME AFTER A
15 % CHANGE IN OXYGEN PERCENTAGE
(FROM 29.5 % TO 15.0 %)
OXYGEN CELL TYPE # 2



$$\Delta V = 0.029 \log \frac{p_2}{p_1}$$

FIGURE 9. OUTPUT VOLTAGE CURVE OF NATIONAL CARBON OXYGEN CELL

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U. S. Navy Experimental Diving Unit Washington Navy Yard Washington, D.C. 20374	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

Oxygen Cell Warning Device Inerim Evaluation Report

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

R. T. Van Orden, LT, MC, USN; T. W. James, HM1(DV), USN

6. REPORT DATE 8 September 1959	7a. TOTAL NO. OF PAGES 15	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO. b. PROJECT NO. NS186-202 Subtask 2 Test 17 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) E. R. No. 4-60 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Experimental Diving Unit Washington Navy Yard Washington, D.C. 20374

13. ABSTRACT

An oxygen warning device consisting basically of an oxygen galvanic cell supplied by the National Carbon Company was given practical tests to simulate its application in scuba mixed gas equipment as an indicator of low oxygen percentage. Two improved cell types were also tested. While the hardware of the original device was not considered practical for direct application in the scuba equipment, the cells were found to perform satisfactorily in terms of following the predicted output curve under most simulated conditions. Minor inadequacies which hold promise of correction were found in the cells including zero stability, time of reaction, response to gross wetting, and erratic behavior in presence of carbon dioxide.

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S/N 0101-807-6801

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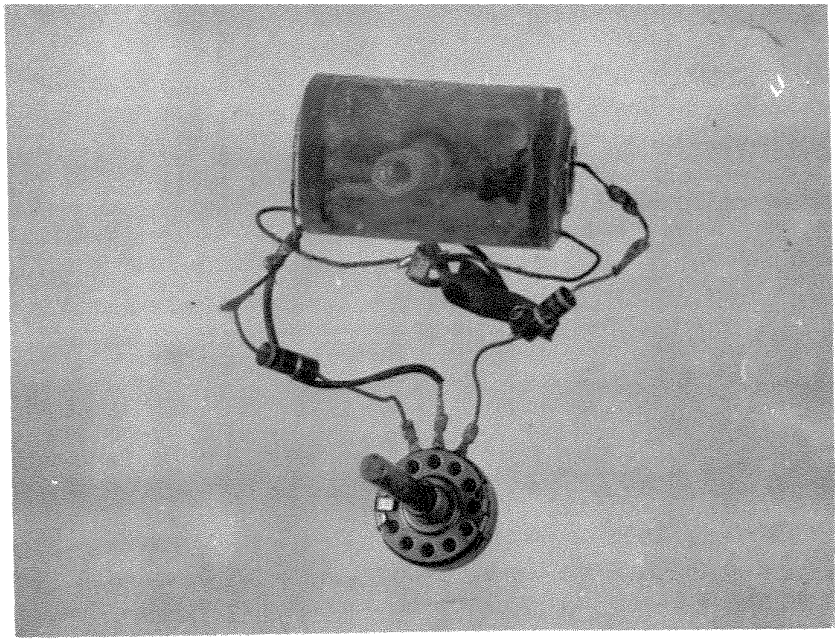
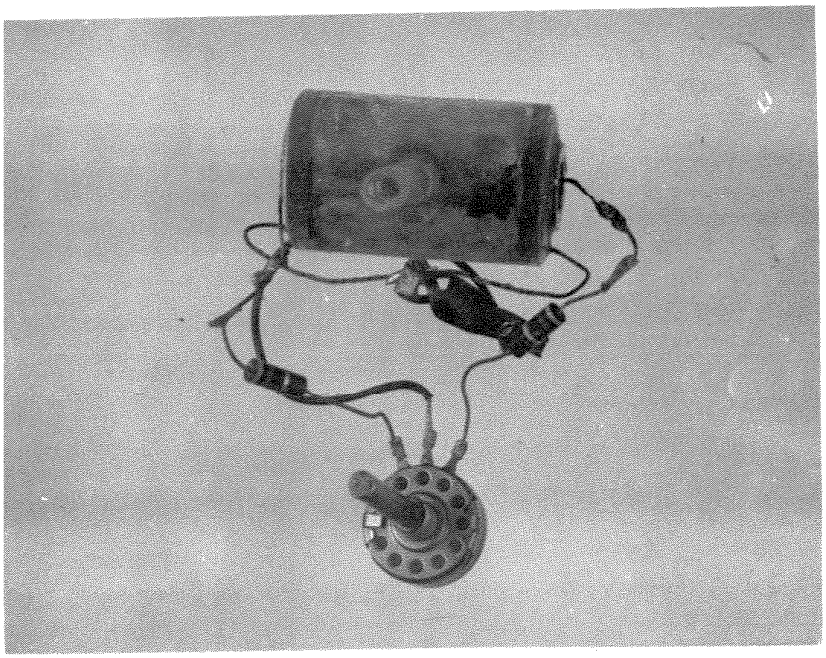


FIGURE 4. OXYGEN CELL TYPE #2 WITH POTENTIOMETER AND RESISTORS ATTACHED.



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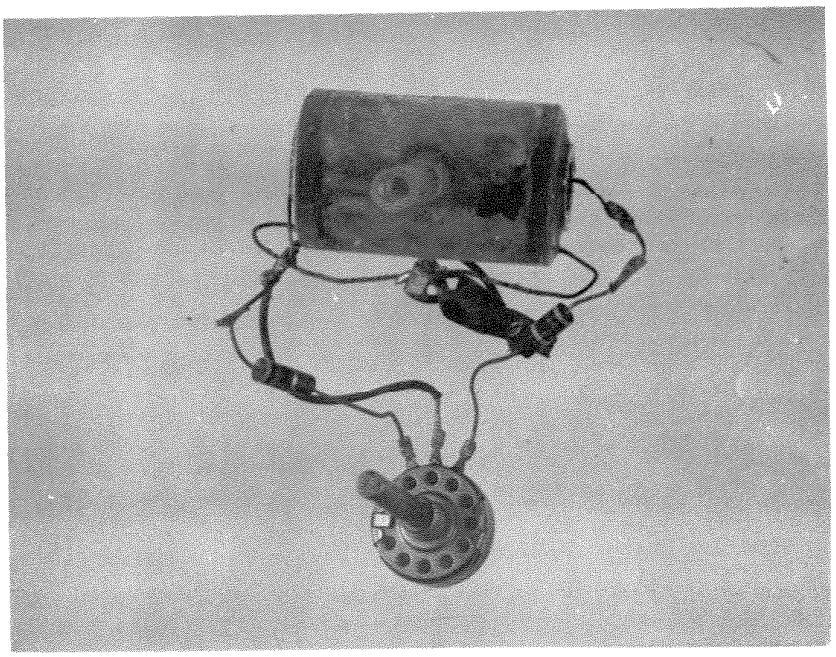

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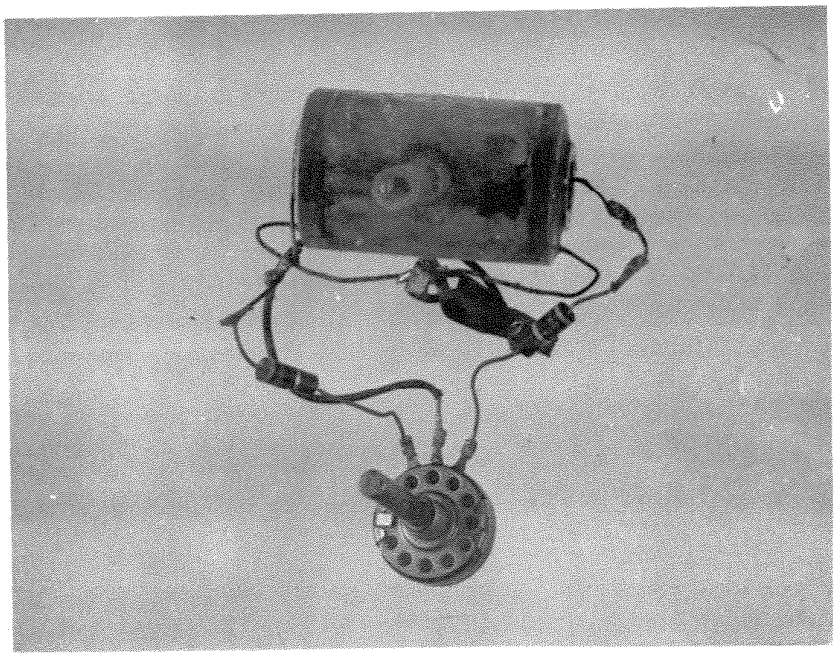

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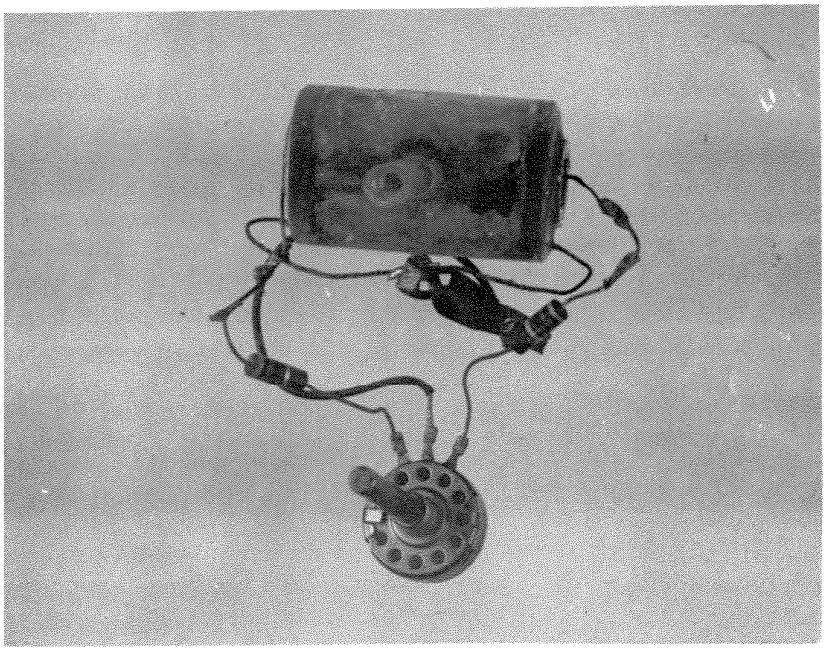

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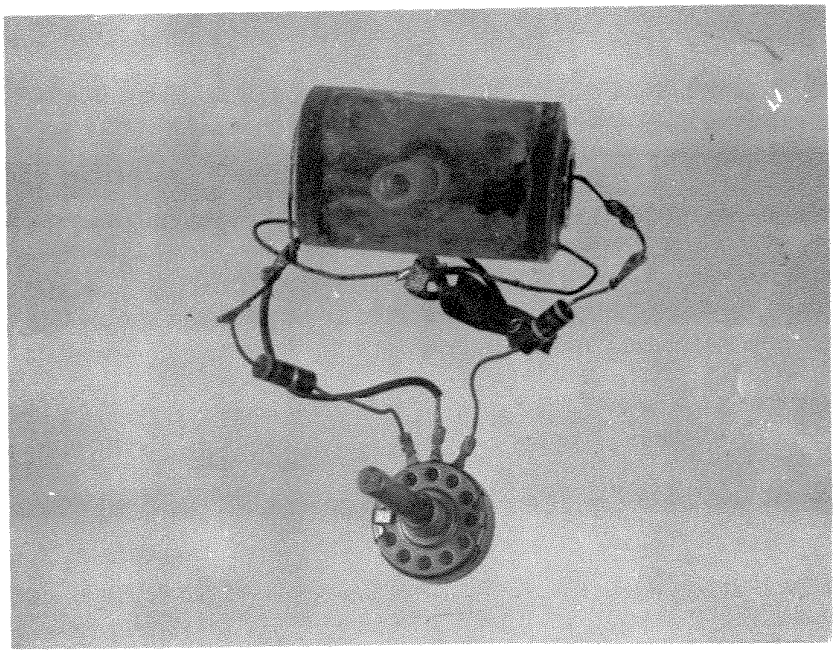

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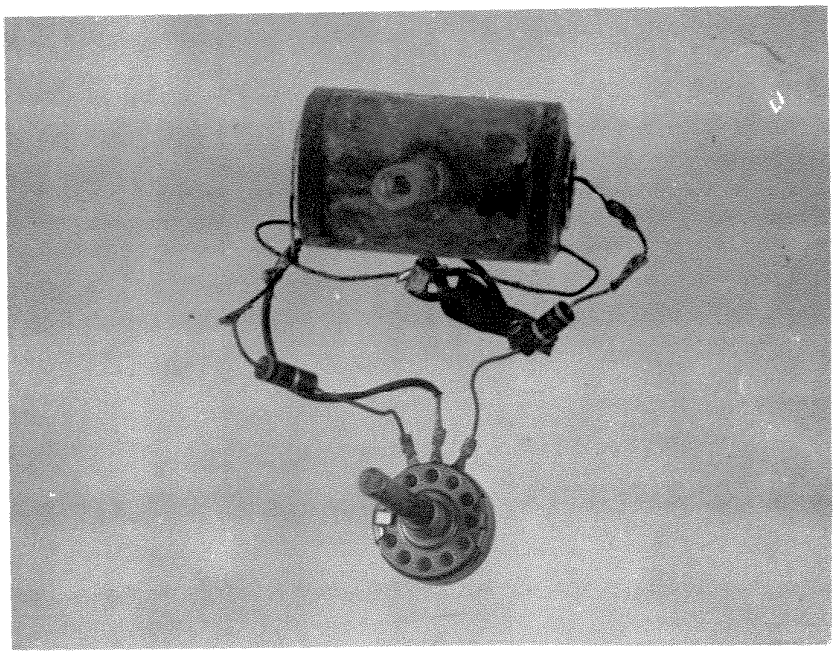

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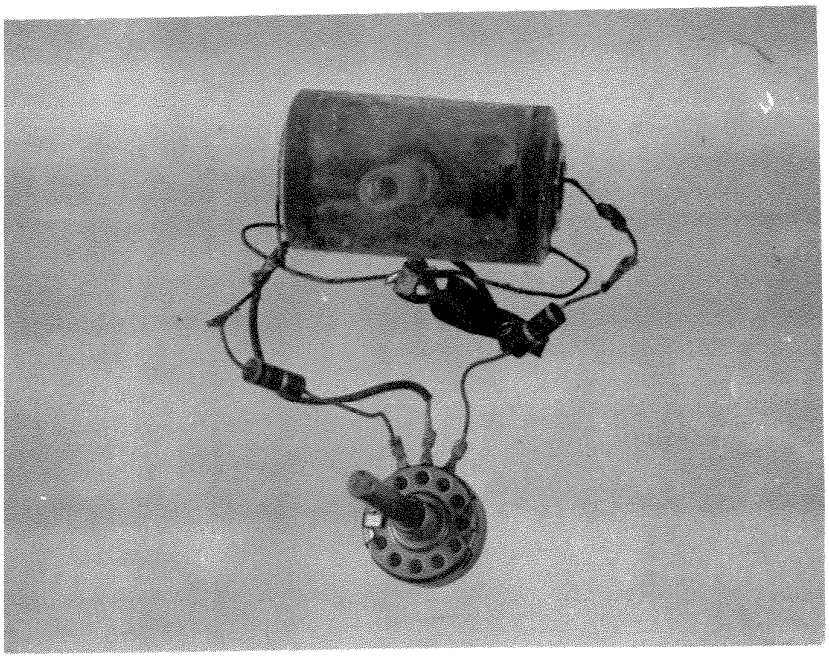

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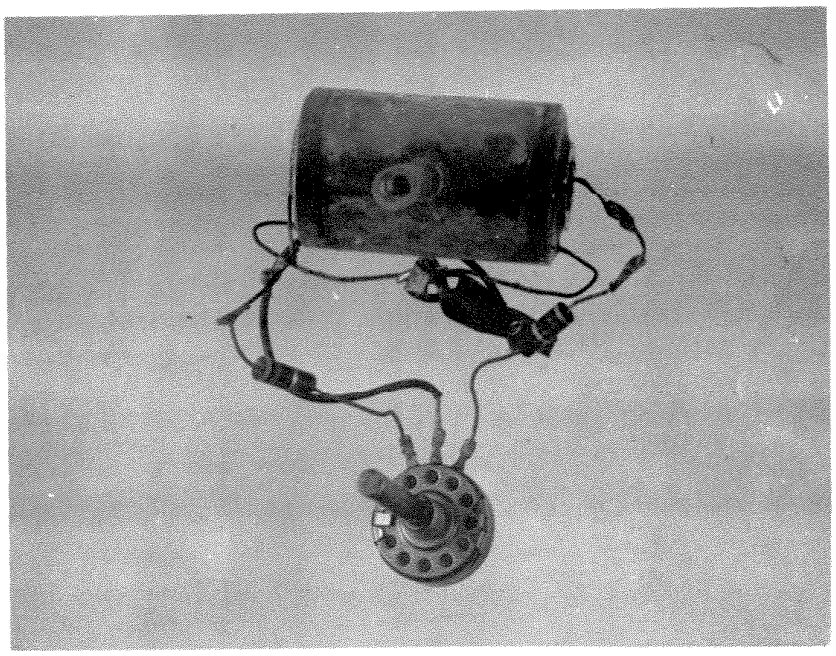

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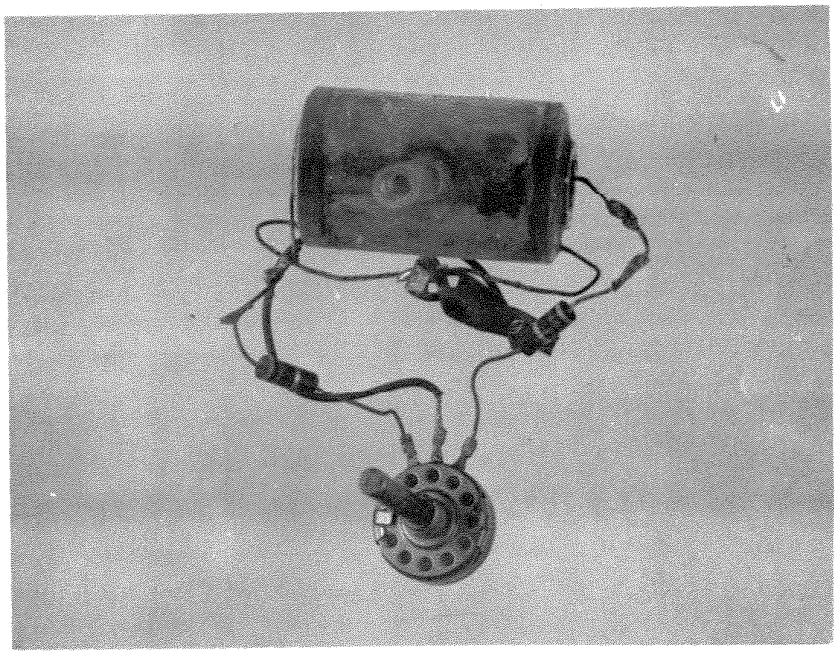

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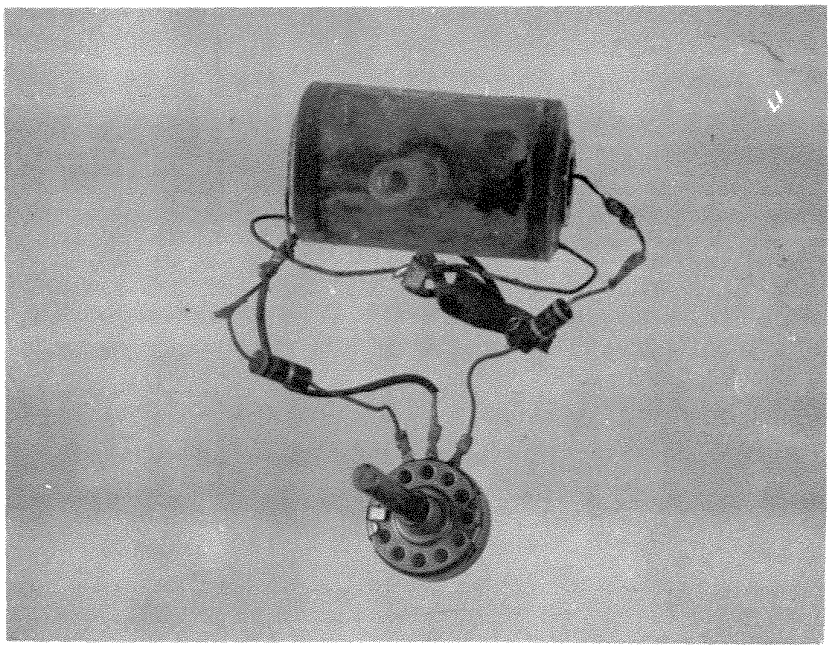

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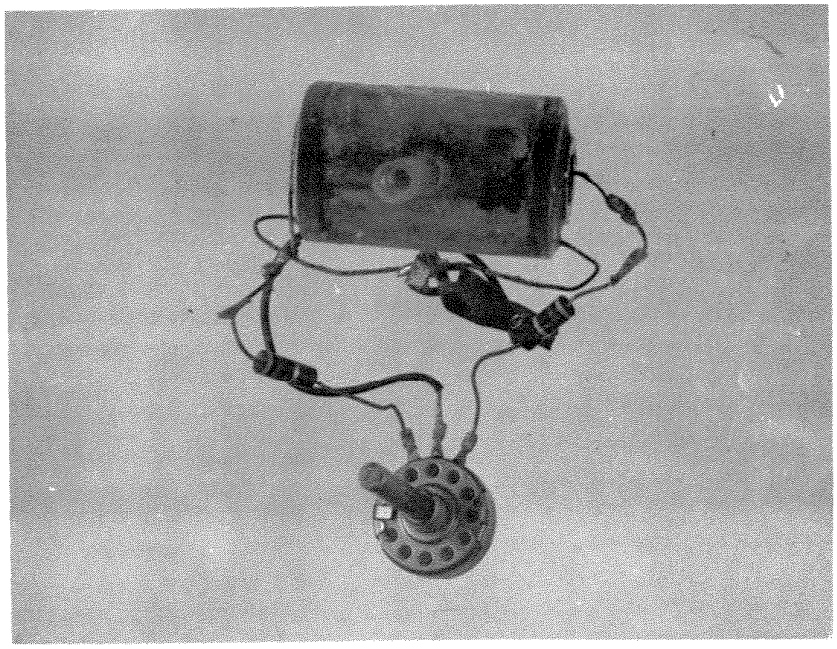

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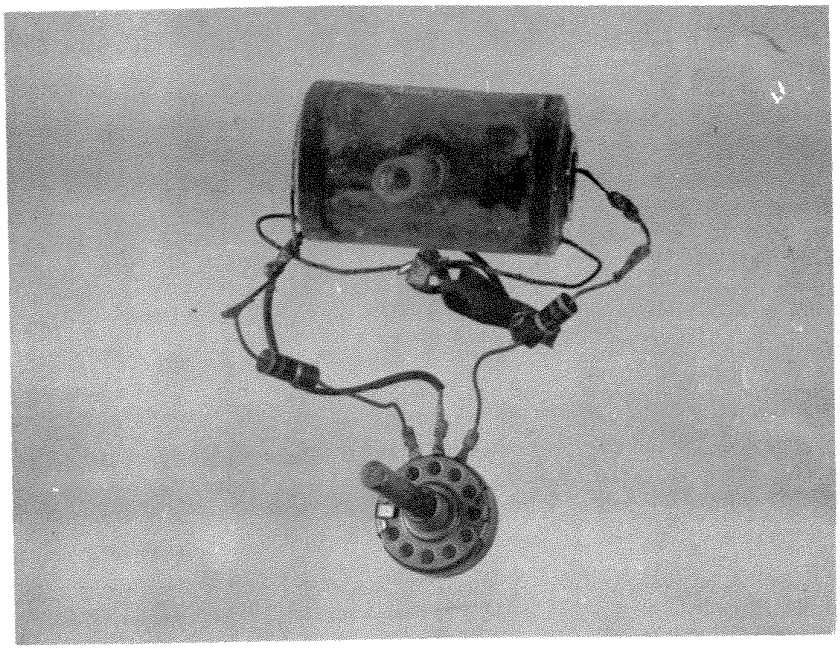

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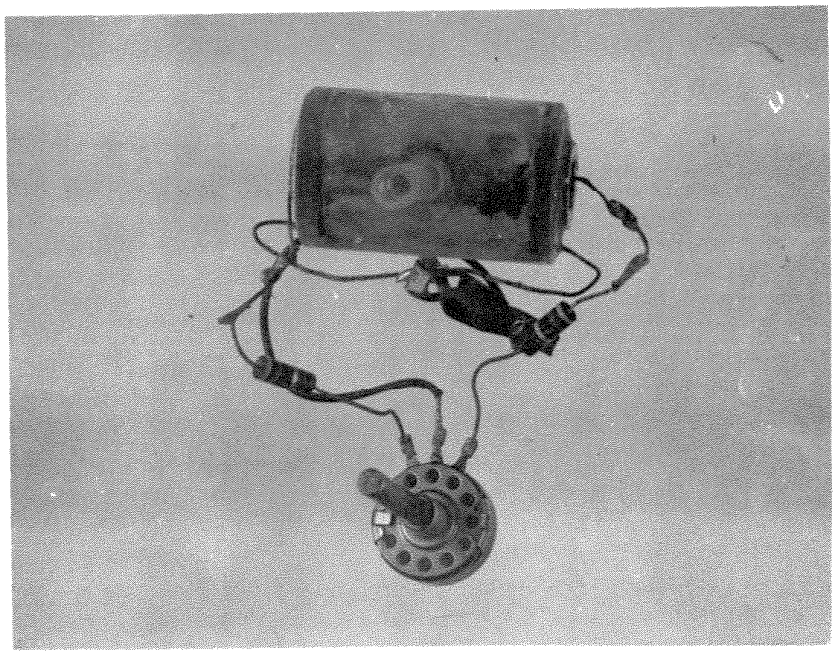

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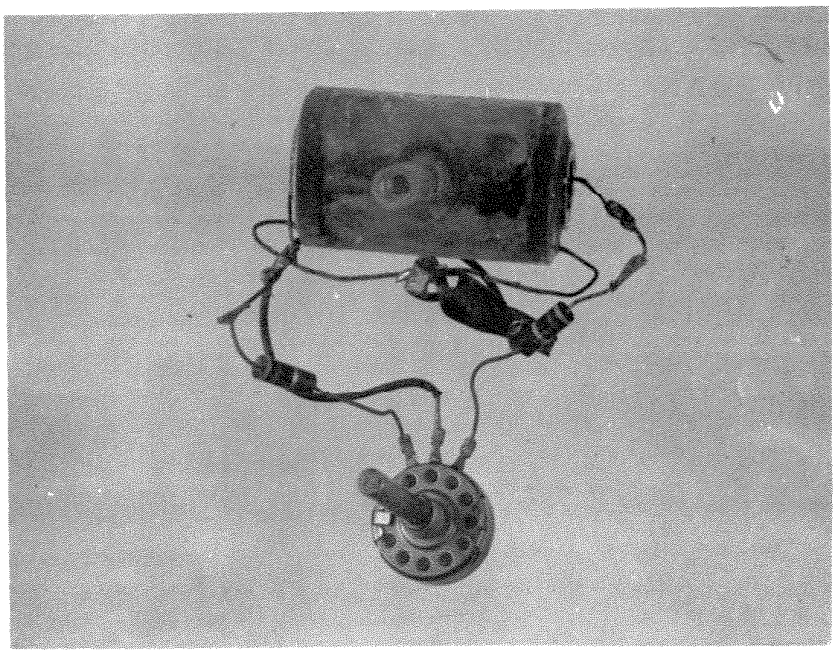

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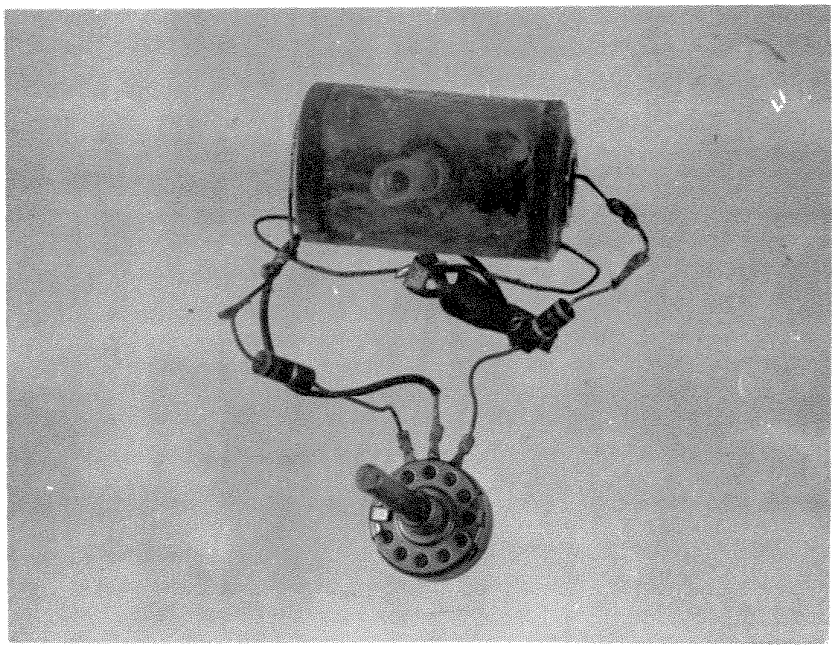

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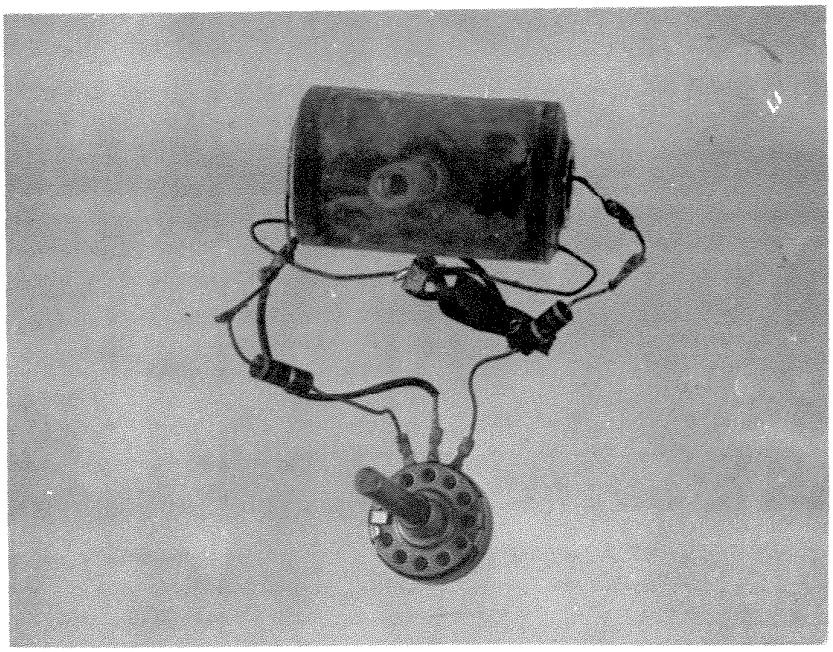

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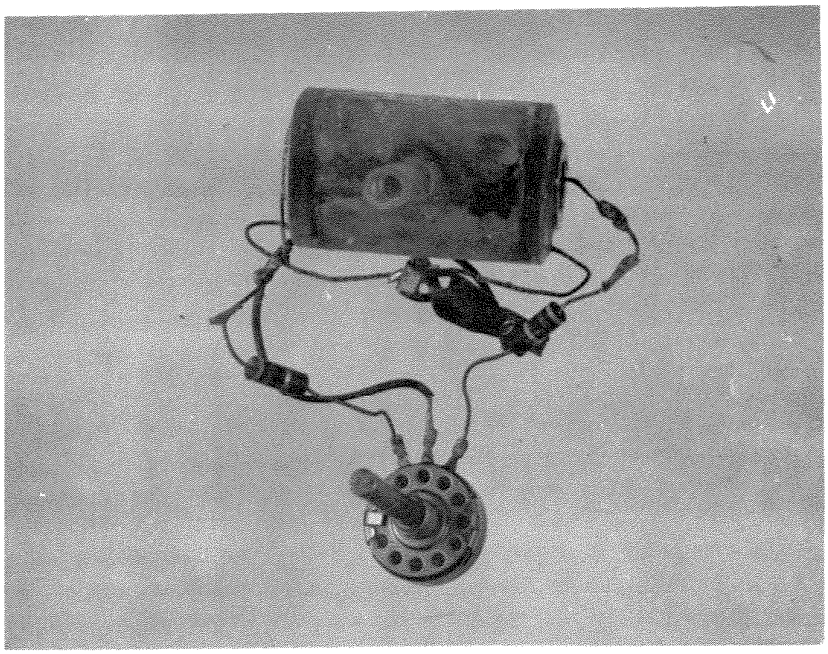

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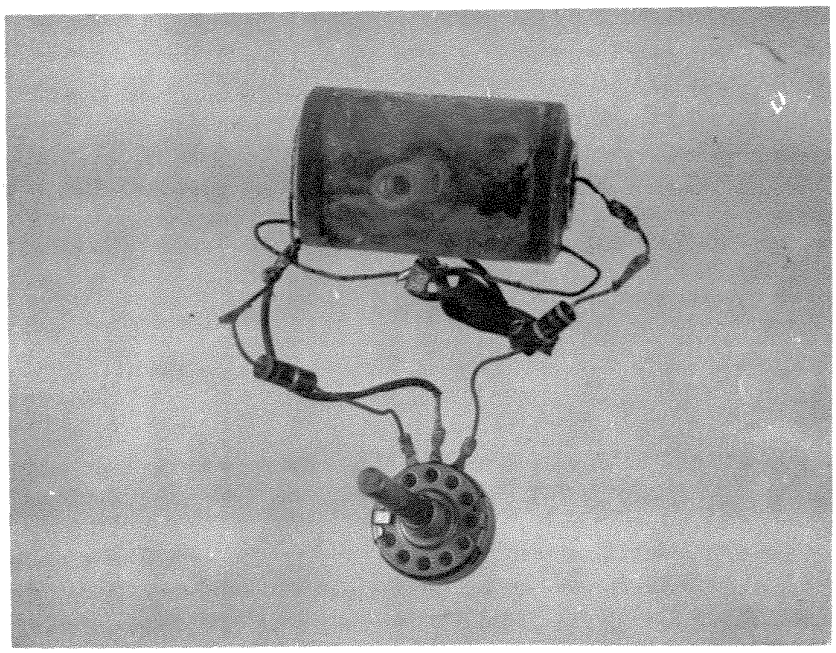

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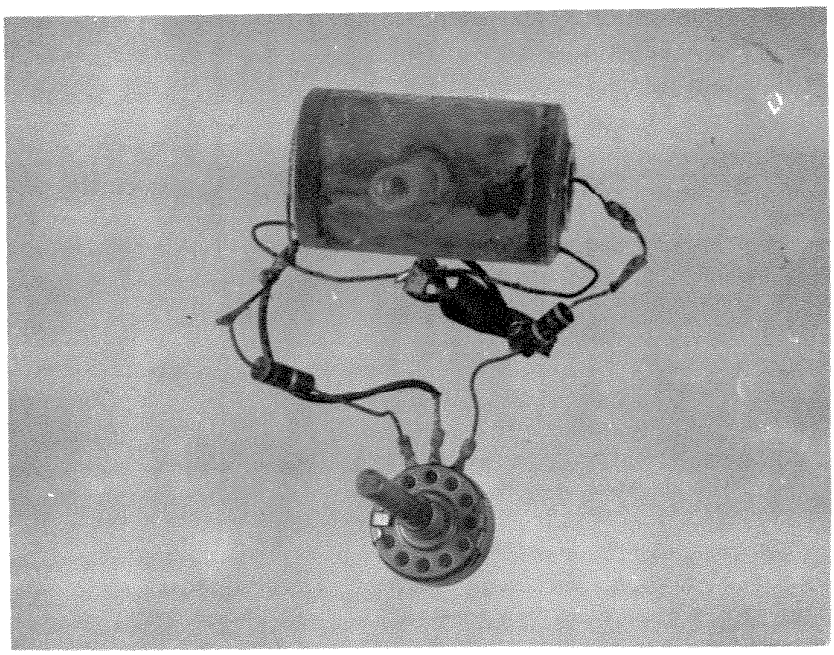

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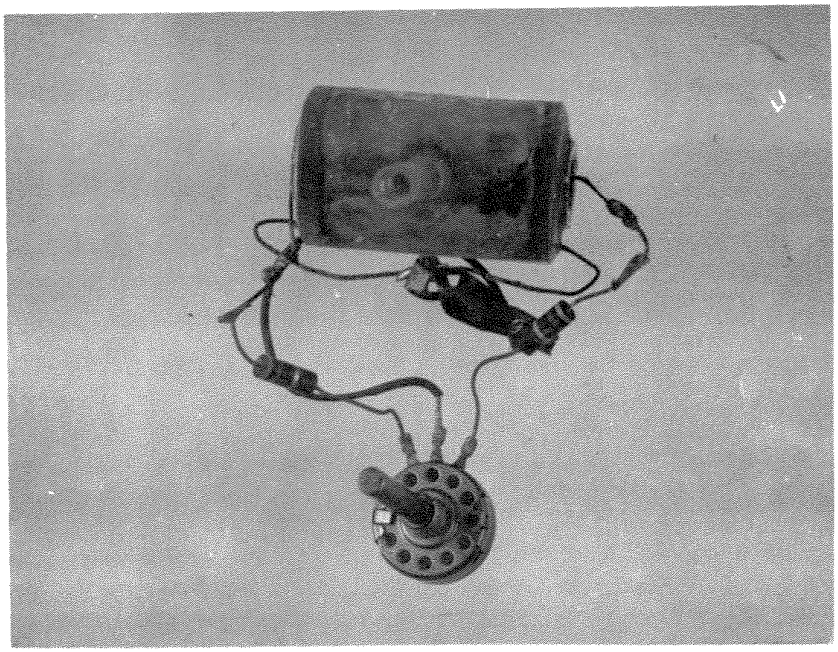

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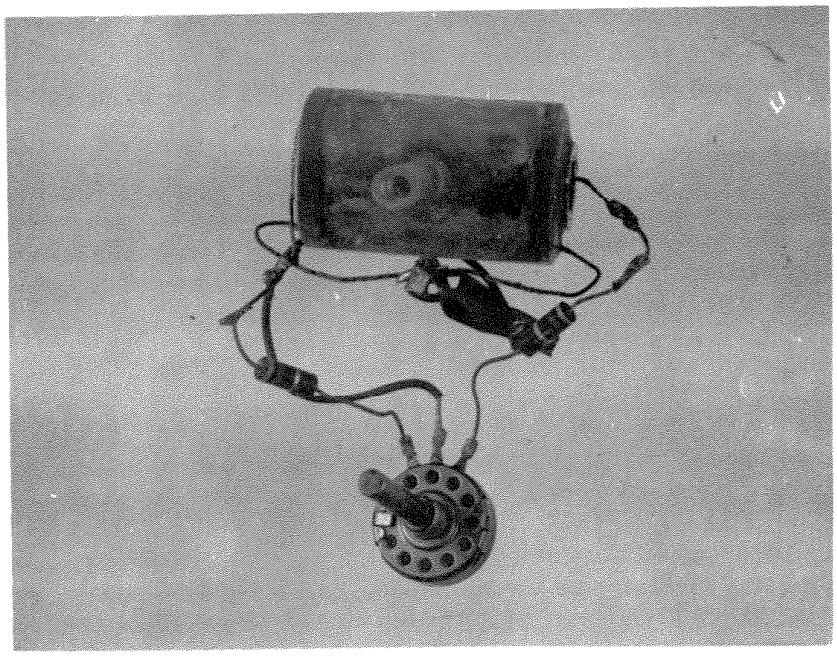

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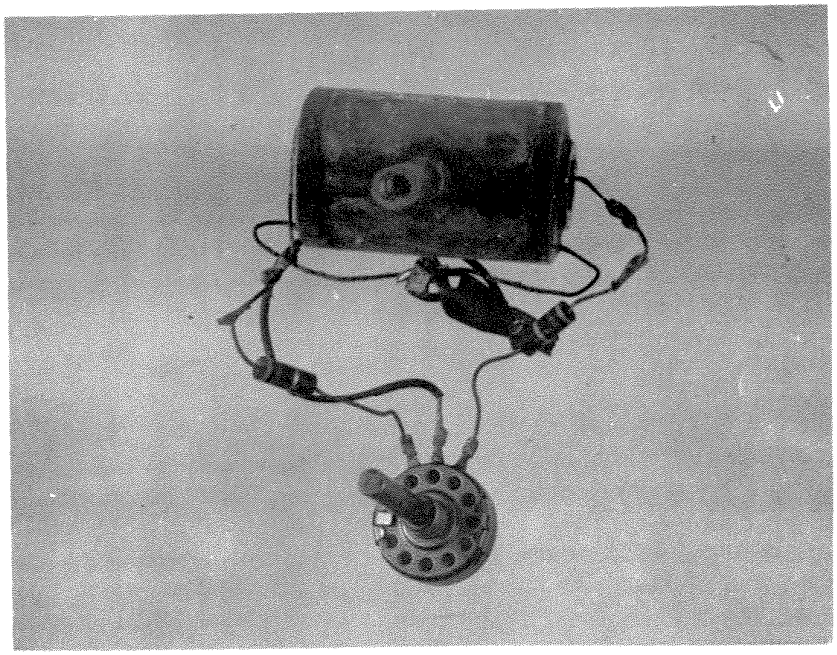

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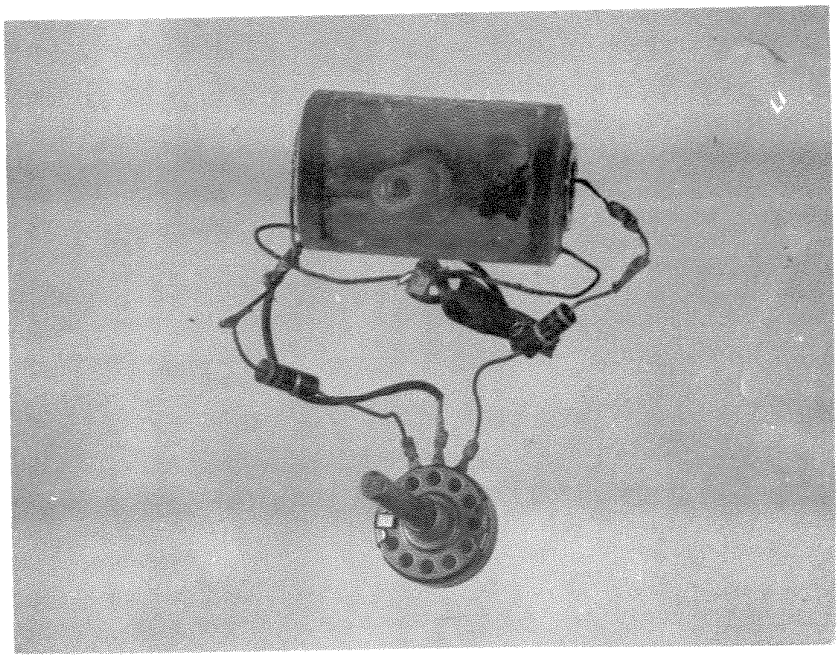

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