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Report on

Gassing Characteristics of Flat Plate
Lead-acid Storage Cells During Discharge

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NAVY DEPARTMENT
BUREAU OF ENGINEERING

Report on

Gassing Characteristics of Flat Plate
Lead-Acid Storage Cells During Discharge

by

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

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ABSTRACT

Gassing studies have been conducted on two cells taken from the battery of the S-1. The purpose of the studies was to obtain information that would explain recent fires and other conditions associated with high hydrogen percentages on certain of the submarines equipped with flat plate batteries.

It has been found that these cells gas abnormally after charge. The extent of the gassing is a maximum when the cells are allowed to remain on open circuit and it diminishes with the magnitude of the discharge current. The gassing increases very rapidly with increase of temperature and with increase of acid gravity. Complete data is submitted to substantiate these conclusions.

Batteries composed of cells of this type and in the condition of those used in the tests are totally unfit for use on submarines. Increase of temperature with acid of 1210 gravity would result in dangerously high concentration during dives with low rates of discharge. With acid of 1280 gravity use of the battery under war-time conditions would be impossible.

A theoretical discussion is given of the possible ionic reactions at the plates in an attempt to explain the results found. This involves a discussion of the possible role of antimony and the effects of temperature and gravity change and the effect of the magnitude of the discharge current.

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INTRODUCTION

(a) Authorization.

1. This problem was authorized by Bureau of Engineering letter SS/S62(3-31-Y1) over SS 105/S62(3-31-Y1) of 7 April 1937, and Bureau of Engineering letter SS/S62(3-31-Y1) over SS 105/S62 of 8 July, 1937.

(b) Statement of Problem.

2. Restricted literature (1) in the files of the Bureau of Engineering shows that during 1936 and 1937 on at least sixteen occasions conclusive evidence has been found of excessive hydrogen concentrations on certain submarines during diving maneuvers. The boats concerned were of the S class and were equipped with batteries composed of lead cells of the pasted-plate type. All batteries concerned were old from the standpoint of service. Several fires resulted, some small, others of major magnitude. The worst was on the S-1. A more detailed discussion of the evidence and the facts as found on these occasions will be given later in the report in the light of the results of the experiments which are the subject of the investigation herein being reported on.

3. The high concentrations in a general way were found during dives in which the current being drawn from the battery was small and in which the cells showed a comparatively high temperature. The seriousness of the fires was such that a general investigation of the situation was deemed advisable and a study was authorized on the battery of the S-1, which was ready to be decommissioned. Part of the tests in connection with this study were to be made on shipboard at the Philadelphia Navy Yard. The results of these tests are given in a report (2) from the Director of the Naval Research Laboratory to the Bureau of Engineering. From the standpoint of the work which is the subject of the present report the important facts found are that stratification of gases does not take place on shipboard during dives and that the battery of the S-1 did not gas excessively when a current of 300 amperes is withdrawn and when the cell temperature is approximately 90° F.

4. In addition to the shipboard tests on the S-1, tests were requested on two cells to be removed from the main battery when the boat was decommissioned. These two cells were to include one of the best and one of the worst cells as indicated by the battery log. The tests on these cells were to include necessary studies to bring out the effect of cell temperature and acid gravity on the gassing characteristics during discharge and during the idle periods following charge. The comparative performance of the two cells from the gassing standpoint was to be determined. From the results it was hoped that the characteristics found on the occasions reported in (1) and (2) could be explained and conclusions drawn as to the serviceability of the flat plate batteries now in use on certain of the submarines. It was also hoped that conclusions could be drawn as to why flat plate cells show different gassing characteristics from cells of the iron-clad type.

5. Briefly, the objects of the experiments which are the subject of this report are as follows:

(a) To determine the effect of cell temperature on the hydrogen evolved from the two cells taken from the S-1. This effect is to

be studied both with the cell during discharge and during the idle period after the securing of a charge.

(b) To determine the effect of acid gravity on the hydrogen evolution both during discharge and during the idle period following a charge.

(c) To compare the gassing characteristics of the two cells under test.

(d) To correlate the results found with the facts and evidence associated with the occasions upon which high hydrogen concentrations were found on certain of the S-boats.

(e) To determine the efficiency and performance to be expected of flat plate batteries now in service on certain of the submarines.

(c) Explanation of Report.

6. In submitting this report the author wishes to point out certain aspects in connection with the way in which the subject matter has been presented and discussed. Only that part of the data pertinent to the particular problem has been included. Much more data were collected. As far as possible data were condensed in the interest of brevity. Under the sections Results and Conclusions the author has attempted to be as brief as possible, a general discussion of the work being given under Discussion of Results. This latter section also includes an attempt to correlate the phenomena found on the boats during the various dives on which high hydrogen concentrations were found and the results obtained from the experiments on the S-1 with the results of the tests conducted by the author. Also included in this section is an attempt to develop an explanation of the phenomena found in the light of the possible ionic and electrode processes involved. From the standpoint of the practical results of the experiments, Section IV, Discussion of Results, is the most important section of the report.

(d) Theoretical Considerations.

7. Explanation of Calculations. In connection with the tests the following magnitudes were recorded: current, voltage, rate of ventilation, cell temperature, gravity, and percent of hydrogen. The gassing current was obtained from the formula given below. This formula is derived from Faraday's Law which states that 96,500 coulombs (ampere-seconds) will release at an electrode one equivalent, or 1.008 grams of hydrogen, which at 0° C and 1 atmosphere pressure will occupy a volume of 11,200 cubic centimeters (cc).

$$\text{gassing current} = \frac{\text{rate of ventilation} \times \frac{\%H_2}{100} \times \frac{273}{T + 273} \times 1,608}{\frac{11,200}{28,316}}$$

In this formula the cubic feet of ventilating air is the rate of ventilation per minute and therefore the 96,500 ampere-seconds must be changed to ampere-minutes, hence the term: 1,608. The factor, 28,316, is used to convert cc

to cu.ft. T is the temperature of the ventilating air in degrees Centigrade. The temperature correction in the above formula is necessary to convert the volume of hydrogen to 0° C. No attempt is made to correct for changes in the barometric pressure as this effect would be too slight to have any effect on the results.

8. Now by plotting the gassing amperes against the time and graphically integrating the areas under the curves the total ampere-hours of gassing can be determined for various periods of time. In this procedure some uncertainty is introduced in the first few minutes following the securing of the charge for during this time the gassing amperes are changing very rapidly. However, this uncertainty is not large enough to affect materially the calculated magnitudes.

9. Again employing Faraday's Law it can be shown that 10 ampere-hours of gassing will produce 0.162 cu.ft. of hydrogen gas at 80° F and under a pressure of 1 atmosphere. Therefore, by multiplying the ampere-hours of gassing per cell by 0.0162, the number of cubic feet of hydrogen evolved can be computed for a desired period of time. Furthermore by multiplying this magnitude by 120 (the number of cells in the battery of the S-1) and dividing by 21,805 cu.ft. (the total capacity of the S-1) the percentage of hydrogen at the end of a given period of time to be expected in a boat of the volume of the S-1 during a dive can be calculated.

EXPERIMENTAL PROCEDURE

Methods

(a) Preparation of Materials, etc.

10. Apparatus. The cells selected for study were Nos. 83 and 68, the latter being one of the best cells of the battery and the former one of the worst as shown by the battery log. These cells are of the UL-53 Exide type with a capacity of 10,000 ampere-hours. The service ratings are as follows:

6 hr. discharge rate	1210 gravity	1660 amperes
6 " " "	1280 " "	2230 "
3 " " "	1210 " "	2850 "
3 " " "	1280 " "	3830 "

These cells require 29-1/2 gallons of electrolyte with wet separators. The charging rates are: 2000-2600, 1600, 1200, 800, 600, and 500 amperes. Cuts in the charging current are made with the temperature-gravity curve.

11. The cells were charged in the usual way with a motor-generator set. Discharges were effected by means of a bank of wire resistors. The six hour discharge rate was selected as that which would give results of the maximum value. At this rate the capacity of Cell 68 proved to be approximately 85%.

12. Hydrogen evolution was obtained by measuring the hydrogen percentage in the ventilating air by means of a Naval Research Laboratory Mark I Hydrogen Detector. The rate of flow of the ventilating air was measured by means of a differential pressure membrane indicator operating on the two sides of an orifice plate in the ventilating duct.

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13. Gravities were measured by means of a hydrometer, the samples of the electrolyte being drawn from the top of the cell. Cell temperatures were measured on these same samples with a mercury thermometer.

14. The cell temperatures were controlled by immersing the cells when necessary in a large tank of water, the temperature of which was controlled by electric heaters.

15. Voltage and amperage were measured on precision instruments.

16. All measuring instruments were properly calibrated.

(b) Description of Experiments.

17. In order to carry out a test the cell was charged fully, the final hydrogen percentage being allowed to increase to a value of somewhat over one percent. The capacity of the motor-generator set did not permit the use of a charging current over 1600 amperes so that it was impossible to carry out a test with the current during the initial stages of the charge at the maximum rating. However, the effect of this was only to lengthen the time for charge and in no way affected the final results.

18. After the cell was charged the hydrogen percentage and rate of ventilation were recorded over the desired period of time. For certain of the tests the cells were allowed to remain on open circuit. In other cases discharges were allowed to follow this period of open circuit.

19. The desired cell temperatures were obtained by proper regulation of the temperature of the water in the surrounding bath. Of course, this regulation could only be approximate due to the size and bulk of the cells. It must also be remembered that the cell temperatures recorded were measured in the electrolyte above the elements and no doubt variations from the values given of from five to ten degrees may at times have existed in other parts of the cell. In order to bring a cell temperature up to one of the higher values the normal heating effect of the charge was used along with the heat taken up from the bath. In the case of the higher temperatures with acid of 1280 gravity it was found necessary to charge the cell at a lower temperature and then raise the cell temperature to the desired value. It was found impossible to effect a charge with 1280 acid at a temperature of 130° F.

RESULTS

Data Obtained

20. In all sixteen tests were completed. A summary of these follows:

<u>Test No.</u>	<u>Cell No.</u>	<u>Gravity</u>	<u>Cell Temp.</u>	<u>Time</u>	<u>Characteristics</u>
1.	83	1180	100°	2.5 hrs.	open circuit
2.	83	1180	100°	-	discharge
3.	83	1207	100°	3 hrs.	open circuit
4.	68	1207	98°	-	effect of mag-
					nitude of discharge current on gassing
5.	68	1207	95°	13 hrs.	open circuit
6.	68	1207	95°	-	discharge
7.	68	1207	124°	5 hrs.	open circuit

<u>Test No. (Cont.)</u>	<u>Cell No.</u>	<u>Gravity</u>	<u>Cell Temp.</u>	<u>Time</u>	<u>Characteristics</u>
8.	68	1206	130°	2.5 hrs.	open circuit
9.	68	1206	130°	-	discharge
10.	68	1245	100°	5.5 hrs.	open circuit
11.	68	1280	90°	15 hrs.	" "
12.	68	1280	90°	-	discharge
13.	68	1280	100°	10.5 hrs.	open circuit
14.	68	1280	100°	-	discharge
15.	68	1280	130°	7 hrs.	open circuit
16.	68	1280	130°	-	discharge

21. The gravity and temperature values given above are only approximate. It will be noted that Tests 1, 2, and 3 can be used for purposes of comparison with the other tests to determine the comparative performance of the two cells. Test 4 and Plate 1 show the effect of change of discharge current on the amount of hydrogen evolved. Tests 5-9 inclusive are with acid of 1210 gravity and therefore may be compared with Tests 9-16 in order to study the effect of change of acid gravity. Tests 5, 7, 8, 10, 11, 13, and 15 show the effect of temperature on the gassing of a cell on open circuit. Plates 7 and 8 show graphically the magnitude of the gassing current as affected by gravity and temperature at the end of the first hour and the end of the third hour after the securing of a charge. The gassing data for a cell on open circuit is summarized in Table 1. This table also gives the total hydrogen percentage that may be expected in a boat of the capacity of the S-1 with a battery of 120 cells of the condition of the cells under test at the end of various periods of time during a dive in which small discharge currents are employed.

22. An inspection of the data and plates shows at once that the cells under investigation are abnormal in that the hydrogen percentage, which is not abnormally high during charge, does not fall off at once after the securing of the charge as is the case with a normal cell. Instead the hydrogen evolution continues for long periods of time; the magnitude and length of the periods depending upon the acid gravity and the cell temperature. Under similar conditions of temperature and gravity Cell 83 gases much more than Cell 68. The former was one of the poorer cells as recorded in the battery log. The latter was one of the better cells. It may be concluded therefore, that, as a very general approximation, the average performance of the cells of the battery of the S-1 would be about an average of the two cells under test.

23. The data shows that fully-charged cells from which no discharge current is being taken gas more than cells under discharge. In other words discharge does not result in gassing. Rather it diminishes it. This is brought out in Tests 2, 4, 6, 9, 12, 14, and 16. See Plates 1, 2, and 3. After a discharge is secured the hydrogen evolution may again increase. This increase, if it does occur, depends upon the cell temperature and the acid gravity. See Tests 4 and 16.

24. The extent of the gassing is a function of the temperature of the cell, the higher the temperature the greater the gassing, other factors being equal. This is best brought out in the tests made with a cell on open circuit and is illustrated with Plates 4, 5, 7, and 8. The summary in Table 1 further illustrates this. As is seen on Plate 5, an increase in temperature from 97° to 124° with acid of 1210 gravity produces an increase in the gassing of about 150%. The corresponding increase with the same temperature interval but with acid of 1280 gravity is about 80%. This is

illustrated on Plates 7 and 8.

25. The extent of the gassing is a function of the gravity of the acid, the greater the gravity of the acid the greater the gassing, other factors being equal. While this is illustrated in all the tests it is best brought out in Tests 5, 10, and 13. With a cell temperature of approximately 100° F an increase in gravity from 1210 to 1246 produces an increase of about 100% in the gassing. At the same temperature an increase of gravity from 1210 to 1280 produces an increase in the gassing of about 200%. It is pointed out that these increases are only approximate and vary with the time which has elapsed from the point of the securing of the charge. The decrease in gassing which accompanies a discharge is due only to a slight extent to the change in gravity, the largest part especially in the first half of the discharge being due to factors discussed in the next section. At approximately 100° gassing stops at an acid gravity of about 1130.

DISCUSSION OF RESULTS

26. Correlation of Results with Conditions Found on Shipboard. A number of factors make it difficult to correlate exactly the results found with the conditions reported on shipboard during the periods when high hydrogen concentrations were found. The condition of the batteries will vary from boat to boat. The condition of the individual cells in a battery will vary as was found with Cells 83 and 68. Moreover, in the same battery with the same cells the conditions may vary from time to time. The acid gravity in the batteries in service will probably average more nearly 1180-1190 rather than 1210 as used in the cells in the tests conducted. This would tend to produce slightly less gassing than that estimated from the data of the tests. In most cases during the periods of high hydrogen concentration on shipboard small currents were being taken from the batteries. This would tend to reduce the magnitude of the gassing. However, a general agreement is found. High hydrogen concentrations were found only on long dives and during these long dives only small discharge currents are employed. This agrees with the conclusion from the tests that the discharge current, if large, would reduce materially the amount of gassing. It was at first thought that the gassing was produced principally by the discharge current. This conclusion has been proven incorrect. High hydrogen concentrations on shipboard are reported only in those cases where the battery temperatures were high, 120° or higher. This agrees with the results of the tests. It would be impossible to correlate the results with the reports from boats other than the S-1 except in a general way as stated above. However, in the case of this boat a rather close correlation is found.

27. An examination of Table 1 shows that Cell 83 under similar conditions gasses at approximately twice the rate of Cell 68. It is, therefore, reasonable to conclude that the gassing of the battery as a whole will be at a rate midway between that predicted from each of these cells. In the following calculations, therefore, the value as calculated from Cell 68 is multiplied by 50%. It must also be kept in mind that small currents were being drawn from the battery and the average battery gravity was somewhat less than the 1210 gravity used in the cell when the data was obtained. These factors would make the calculated hydrogen percentage perhaps slightly higher than that which would be expected. In the case of the major fire on the S-1 the first flash of flame was noted 7 hours after the boat was secured for diving and approximately 11 hours after the discharge was secured. The battery temperature averaged 125°. According to Table 1 the percentage at the end of 7 hours should be about 4.5% after allowing for the hydrogen that was ventilated

outboard before the boat was secured for diving. Since the burning percentage of hydrogen is about 4% this agrees with the facts as found. Undoubtedly the first fire did not burn all the hydrogen from the boat. Rather it is to be expected that only a small portion was destroyed. Now the major fire occurred about 1-1/2 hours after the first fire. During this period an additional .4% should accumulate and another and more general fire expected. The hydrogen percentages reported do not agree with the facts as found nor with the results of the test. The hydrogen percentage shown by a detector during a dive should show the percentage present in the boat, assuming no stratification, plus a factor for the rate of evolution at the particular time the reading is made. But according to the Machinery Derangement Report (1) the cells were gassing at a rate of only .10% shortly after the charge was secured. Since the air flow velocity is not known, it is of course impossible to calculate exactly the gassing current. But certainly the value seems too low to accord with the hydrogen accumulation later found. After the first fire the detectors were started and showed only .10%. At the time of the major fire the detectors appeared to jump instantly to 3-4%. These values are hard to understand. Perhaps the catalyst was in poor condition but became suddenly active after the second explosion, due perhaps to the rush of hot gas through the detector.

28. In the same report it is stated that a normal charge was put in the battery following the above and that the hydrogen percentage did not exceed 1.8% during any stage of the charge and dropped to 1% shortly after the charge was secured. These values appear reasonable in the light of the tests conducted. The boat dived 40 minutes after the charge was secured. A hydrogen percentage of 1% was found in two hours and ten minutes after the dive was started. Forty minutes elapsed after the securing of the charge and the rigging of the boat for diving. According to Table 1 this is the amount that would be expected. During this dive the boat operated with one motor parallel.

29. In the case of the shipboard tests conducted by the Laboratory on the S-1 (2) on 27 July 1937 the temperature of the pilot cell was 92° and the gravity 1180. At the end of 4 hours after the battery compartment was sealed for diving a hydrogen percentage of 2% was obtained. Ventilation was inboard into the aft battery room only. The room was secured about four hours after the charge was stopped. According to Table 1 under these conditions the rate of gassing during the 4-8 hour period after the securing of the charge should produce a percentage of 1.95. In this calculation it must be remembered that only 60 cells were ventilating into the battery compartment. Of course, had this same volume of hydrogen been ventilated into the boat as a whole, approximately one fifth of this percentage would have accumulated. The agreement is not so good if the gravity of the pilot cell is indicative of the gravity of the battery as a whole.

30. Efficiency of Batteries of the Type and Condition of that of the S-1. The tests show that 80-85% of the rating capacity of the batteries may be expected. Of course, this varies with the discharge rate and certain other factors. The present discussion will be limited to gassing considerations. Table 1 summarized what may be expected from a battery composed of cells similar in condition to No. 68 in a boat of capacity of the S-1. Of course, it must always be kept in mind that the data are for an idle cell. For a gravity of 1210 and a cell temperature of less than 100° excessive concentrations are not found even after a period of ten hours. For the same gravity but with a temperature of 120° burning concentrations would be found

by the end of 6-7 hours. With gravity of 1246 and a temperature of 100° burning concentrations will be found at the end of about six hours. But with the acid gravity at 1280 the concentration will reach the burning percentage at 90° at the end of 6-7 hours. At 100° only 4 hours is necessary and at 130° only 3 hours. Now if to the above considerations you also account for certain bad cells by increasing the concentrations by 50% it can be seen that the use of the battery is very restricted indeed. It may therefore be concluded that the batteries in such a condition are of extremely doubtful value with acid of 1210 gravity. They could not be employed at all with acid of 1280 gravity except at very low temperatures. Of course, each battery is an individual problem in itself as their condition will vary from boat to boat. Of course, the batteries could be used if a means is supplied for burning the hydrogen on shipboard as fast as it is formed. Such devices have been proposed in the past.

31. Considerations Concerning Loss of Gravity. A gassing current of 25 amperes, no matter what the cause or type of action producing it, will cause a loss of 600 ampere-hours per day. Now in the case of the cells under test a discharge giving approximately 8500 ampere-hours will cause a drop in gravity of roughly 0.1000. Therefore, a gassing current of 25 amperes should cause a drop in gravity of roughly .0007 per day. This figure can be roughly checked by means of calculations involving the grams of sulphuric acid destroyed and the volume of electrolyte in the cell. At any rate, even with high gassing currents, little change in gravity would be expected except over rather long periods of time. As an example, take Test 13. At the end of 10 hours 818 ampere-hours of gassing has taken place. This is equivalent to a gravity drop of about .0010. The actual drop found by the hydrometer reading is only .0002. However, this is not surprising as the gravity change takes place on the surface or in the active material of the negative plate and no means is at hand to mix the electrolyte sufficiently to produce an even distribution of gravity. The situation is similar to the one existing during a charge. Only when the gassing is sufficient to thoroughly mix the electrolyte do we find the top gravity value representative of the electrolyte as a whole. In the report on the experiments on the S-1 (2) the use of gravity change as a means of periodically checking the battery as to its safety from a gassing standpoint was discussed. Several difficulties were pointed out which would exclude its use. The results of the tests conducted in connection with this report further substantiate this conclusion.

32. Considerations Concerning the Cause of Excess Gassing. Experience has shown that gassing of the type and extent encountered in these studies is characteristic of cells with pasted positive plates. Cells of the iron-clad type do gas excessively when old but to only a fraction of the extent found with the flat plate cells. The trouble therefore is inherent in the type of grid structure and since the main difference is in the type of positive plate it is reasonable to conclude that the difficulty is due to action arising from this source.

33. Now with pasted-plate positives increasing corrosion of the grid takes place as the cell is repeatedly cycled. Since the grid is composed of a lead-antimony alloy this corrosion in part at least is due to the antimony metal forming antimony ions through the action of the charging current or perhaps to a slight extent through direct action of the sulphuric acid. This latter is probably unimportant. Whatever the cause and mechanism antimony ions are produced in the electrolyte and are in turn electrolytically

precipitated or plated out on the negative plate. Thus is produced on the negative plate antimony-lead couples connected by the lead of the grid. This combination in the presence of the electrolyte constitutes a voltaic cell with a definite voltage the magnitude of which depends upon the temperature, concentration of the electrolyte, and physical state of the antimony.

34. This local cell is capable of producing an electric current. The passage of the current is effected by a discharge of hydrogen ions on the antimony and a discharge of sulphate ions on the lead. Thus the positive electricity flows from the lead to the antimony with the grid as the conductor between the two poles. The result of the secondary electrode reactions is the production of hydrogen gas on the antimony and lead sulphate on the lead. Thus the negative plate undergoes self-discharge and the cell gasses.

35. The evolution of hydrogen from the antimony is made possible through the fact that the overvoltage of antimony towards hydrogen discharge is much less than the corresponding overvoltage of lead, which has one of the highest overvoltages of any metal.

36. The voltage of such a cell is a function of the concentration of the ions in the solution. Hence the higher the gravity the greater the potential and the greater the magnitude of the self-discharging current. Therefore, the higher the gravity the greater should be the rate of gassing.

37. The higher the temperature the greater the mobility of the ions and therefore the greater the magnitude of the gassing. In other words the higher the temperature the lower will be the resistance of the electrolyte. For this reason a rise in temperature should produce an increase in the rate of gassing.

38. The overvoltage of a metal decreases with temperature rise. Therefore, higher temperatures should make easier the discharge of hydrogen from the antimony. This presents another reason why gassing should increase with rise in cell temperature. The overvoltage is also a function of the physical state of the metal. One would expect pure antimony to have a lower overvoltage than antimony which has alloyed with the lead of the grid. As a matter of fact we know that the antimony in the original grid alloy does not produce local action. Now when the antimony is first precipitated on the negative grid it is in the pure state. No doubt with the passage of time an alloying process takes place. Therefore, we would expect newly-precipitated antimony to have a much greater effect on gassing than the same antimony after it has remained for some time in contact with the lead. Another explanation as to why antimony when first formed is more reactive than the same antimony after a period of time is based on a theory that a change in the physical state, perhaps in the crystalline structure, takes place. This explanation seems inadequate to the author. A discussion of the effect of antimony on the negative plate is given by Vinal (3) in his book on storage batteries.

39. The above explanation of the cause of gassing from the negative plate seems to fit in well with the facts as found. Of course, in the iron-clad type of plate one does not have an alloy grid at the positive plate exposed to the electrolyte. Hence it is far more difficult for antimony ions to find their way into solution later to be electrolytically-precipitated on the negative plate.

40. The question may be raised as to why discharge lowers the rate of gassing. In discharge hydrogen ions pass to the positive plate. Due to their small size these ions move very rapidly through the electrolyte and as a result their concentration will be greatly decreased around the negative plate and correspondingly increased around the positive plate. This type of polarization is known as concentration polarization. The greatly-reduced hydrogen ion concentration around the negative plate results in a decrease in the gassing since the magnitude of the gassing is a function of the acid concentration. Now when the discharge is stopped there is at once an equalization of gravity. Gassing will then increase provided the discharge has not reduced the total acid gravity to too low a value. The magnitude of this value depends on the temperature.

41. It must be kept in mind that while antimony is assumed, and probably rightly, to be the cause of battery trouble in connection with gassing in old cells the experimental evidence to support this idea is not particularly extensive. The theory is built upon evidence to a great extent of the circumstantial kind. However, most of the attempts to solve the gassing problem have been built upon this assumption. Among these attempts are efforts to develop new antimony-free alloys for use in grid construction and efforts to develop practical methods of shielding the grid metal by coverings of rubber or other material.

CONCLUSIONS

42. Flat plate cells of the age, type, and condition of those used in the tests gas abnormally after charge.

43. For a given set of conditions the magnitude of this gassing is greatest on open circuit and diminishes as the charging current is increased.

44. The higher the cell temperature the greater the gassing, other conditions being equal. A temperature increase of approximately 25° increases the gassing approximately 150% in the case of Cell 68 with acid of 1210 gravity.

45. The greater the acid gravity the greater the gassing, temperature and other conditions being equal. At approximately 100° with Cell 68 an increase of gravity from 1207 to 1246 increases the gassing approximately 100%. An increase from 1210 to 1280 increases the gassing about 200%. Gassing ceases at a gravity of approximately 1130 at temperatures of approximately 100° .

46. Batteries composed of cells of the condition of those in use on the S-1 are unsuited for submarine operation. Even with acid of 1210 gravity a temperature of 125° will produce hydrogen in such quantities that burning mixtures may be expected in the S-1 on a dive using small discharge currents by the end of five hours. With low battery temperatures and gravities around 1210 large concentrations are not to be expected. With acid of 1280 gravity burning concentrations may be expected on a dive by the end of five hours if the battery temperature is about 100° with low discharge currents.

RECOMMENDATIONS

47. While many tests could be conducted with different conditions of temperature, gravity, and rates of discharge, the author is doubtful if the work necessary would be justified. It is thought that the experiments conducted to date are sufficient from a military standpoint to explain the phenomena noted and in general to clear up the performance to be expected from old flat plate batteries of the type now in use on several of the S-boats.

48. The author does recommend a general series of studies on the antimony problem and certain specific studies on the cells from the S-1 which were used in the tests reported on at this time.

49. As has been pointed out the role of antimony as it affects the gassing characteristics of lead storage cells has been the subject of little experimental work and the conclusions as to its part are based on evidence that can be considered only as circumstantial. It, therefore, seems well worthwhile as a guide to future storage battery development and use to make a thorough study of this problem. Such a study would include the thermodynamics and mechanism of antimony loss from the positive plate. Perhaps a chemical substance could be found which when added to the electrolyte would precipitate the antimony before it could be electrolytically precipitated on the negative plate. Perhaps means could be developed to prevent its electrolytic corrosion into the electrolyte. The voltage relationships of antimony and lead should be studied under various conditions in order to properly clear up the local action involved. It might prove to be that antimony is not after all the primary factor in self-discharge of old cells. The author, however, personally believes this to be the case. Vinal (3) has demonstrated experimentally that antimony does produce local action on the negative grid.

50. The cells used in the tests which are the subject of this report furnish a most excellent opportunity to study the possible role of antimony in connection with the gassing problem. It is, therefore, strongly recommended that these cells be carefully dismantled and the electrolyte, sediment, active material, and various parts of the grid surface be tested for antimony. This would show where antimony is most likely to be found in the cell and if antimony is the cause of the gassing it will show where most of the gassing is taking place. The condition of the grids and active material should be carefully examined for sulphation. Maximum sulphation should be found where maximum local action has taken place.

51. It has also been suggested that certain tests be made with certain of the plates after the surface layer has been removed in order to see if gas evolution still exists. This is heartily endorsed as another means of studying the effect of antimony. Quantitative and qualitative tests for antimony in various parts of the cell and gassing studies on the grids would undoubtedly go far to help clear up the question as to the part of antimony in the life of lead-acid storage cells.

BIBLIOGRAPHY

1. BuEng. Restricted letter, SS/S62 (3-31-Y1) SS105/S62(3-31-Y1) of 7 April 1937, with enclosures, to Naval Research Laboratory.
2. Submarine Main Storage Batteries; Hydrogen Exploratory Tests on USS-1 - Naval Research Laboratory Restricted letter SS/19 dated 17 August 1937.
3. Vinal, "Storage Batteries."

TABLE 1

Total Ampere-hours of Gassing for Various Periods of Time and Corresponding Hydrogen Percentages to be Expected in S-1

Test Number	1	3	5	7	8
Gravity	1180	1207	1208	1207	1207
Temperature	99°	105-102°	97-84°	124-125°	130-128°
Cell No.	83	83	68	68	68

	*	1.	2. : 1.	2. :1.	2. :1.	2. :1.	2.
Time. (hrs.)							
1		35	.31: 86	.77 :39	.35 :90	.80:90	.80
2		60	.53: 160	1.42 :74	.66 :172	1.51:163	1.45
3		-	- : 240	2.14 :104	.93 :243	2.37:223	1.98
4		-	- : -	- :130	1.16 :315	2.80: -	-
5		-	- : -	- :155	1.38 :373	3.33: -	-
8		-	- : -	- :221	1.97 : -	- : -	-
10		-	- : -	- :265	2.36 : -	- : -	-

Test Number	10	11	13	15
Gravity	1248	1280	1274	1275
Temperature	102-96°	89-78°	105-98°	125-128°
Cell No.	68	68	68	68

	1.	2. : 1.	2. :1.	2. :1.	2.
Time (hrs.)					
1	83	.74 : 74	.66 : 135	1.20 : 174	1.55
2	153	1.36 : 139	1.24 : 248	2.20 : 340	3.03
3	215	1.91 : 200	1.79 : 348	3.09 : 500	4.45
4	302	2.69 : 255	2.27 : 438	3.90 : 655	5.83
5	353	3.14 : 308	2.74 : 523	4.65 : 800	6.12
8	-	- : 457	4.06 : 678	6.03 : -	-
10	-	- : 541	4.81 : 818	7.28 : -	-

* 1. Ampere-hours of gassing per cell for period shown.

* 2. Hydrogen percentage to be expected in submarine of capacity of S-1.

Note: Above percentages have been calculated for a battery composed of cells of the conditions of Cells 83 and 68. Data for Cell 68 should be multiplied by 1.25-1.50 in order to account for effect of bad cells.

TABULATED DATA

Test 1. Hydrogen evolution on open circuit.
Temperature approx. 100° F

Cell No. 83
Gravity: 1180

Time	Amperes	Voltage	Air Flow cu.ft./min.	%H ₂	Gassing Current	Cell Temp.	Gravity
1800	500-0	2.31	2.625	1.22	114	99°	1180
1815	0	2.15	1.90	.60	40	"	"
1830	0	2.13	"	.50	34	"	"
1900	0	2.10	"	.40	26	"	"
1930	0	2.09	"	.38	25	"	"
2000	0	2.08	"	.36	24	"	"
2030	0	1.89	"	.23	15	"	"

Test 2. Hydrogen evolution on discharge.
Temperature approx. 98° F

Cell No. 83
Gravity: 1180

2030	0-1920	1.89-1.87	1.90	.15	10	97°	1180
2100	1920	1.87	"	.15	10	97	1174
2130	"	1.84	"	.10	7	97	1164
2200	"	1.82	"	.05	3	98	1150
2230	"	1.80	"	.02	1	98	1141
2300	"	1.78	"	.01	0	98	1133
2330	"	1.73	"	0	0	98	1103
0015	1920-0	1.61-1.84	"	0	0	98	1097

Test 3. Hydrogen evolution on open circuit.
Temperature approx. 100° F

Cell No. 83
Gravity: 1207

1145	500-0	2.28-2.20	2.625	2.22-1.60	147	105°	1207
1200	0	2.14	"	1.00	92	"	"
1230	0	2.12	"	.90	82	"	"
1330	0	2.09	"	.80	73	"	"
1430	0	2.07	"	.75	69	"	1206
1500	0	2.07	"	.78	72	102	1206
0900 (3 days later)	0	2.02	"	.20	13	82	1191

Test 4. Hydrogen evolution as affected by various magnitudes of discharge current.

Temperature approx. 97° F

Cell No. 68
Gravity: 1207

1330	500-0	2.32-2.26	2.625	1.50-.50	138-46	97°	1207
1345	0	2.16	"	.45	42	-	-
1400	0	2.14	"	.45	42	-	-
1430	0-1000	2.00	"	.43	40	97	1207
1440	1000	1.95	"	.32	30	-	-
1450	1000	1.95	"	.35	33	-	-
1500	1000-0	1.95	"	.32	30	96	1206

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Test 4. (Continued)

Time	Amperes	Voltage	Air Flow cu.ft./min.	%H ₂	Gassing Current	Cell Temp.	Gravity
1510	0	2.03	2.625	.40	37	-	-
1520	0	2.04	"	.38	36	-	-
1525	0	2.04	"	.40	37	-	-
1530	0-2000	1.88	"	.27	24	-	-
1540	2000	1.88	"	.25	23	-	-
1545	2000-0	1.88	"	.26	23	-	-
1547	0	1.88	"	.35	33	96°	1200
1555	0	2.02	"	.37	35	-	-
1600	0	2.02	"	.37	35	-	-

Test 5. Hydrogen evolution on open circuit.
Temperature approx. 90° FCell No. 68
Gravity: 1207

1900	500-0	2.32-2.20	2.625	1.35-.95	126-89	97	1207
1910	0	2.18	"	.45	42	-	-
1930	0	2.14	"	.40	37	-	-
2030	0	2.11	"	.40	37	96	1208
2200	0	2.08	"	.30	28	94	1208
0000	0	2.07	"	.27	26	93	1208
0400	0	2.05	"	.25	24	90	1208
0700	0	2.04	"	.22	22	88	1207
1000	0	2.04	1.90	.30	22	87	1206
1200	0	2.04	"	.30	22	87	1206
1600	0	2.03	"	.25	17	-	-
0830	0	2.04	"	.16	12	84	1203

Test 6. Hydrogen evolution on discharge.
Temperature approx. 90° FCell No. 68
Gravity: 1203

0830	0-1660	2.04	1.75	.16	11	84	1203
0830	1660	1.90	"	.10	6	-	-
0930	1660	1.88	"	.14	9	86	1197
1030	1660	1.84	"	.07	5	87	1182
1100	1660	1.83	"	.05	3	89	1165
1200	1660	1.78	"	.03	2	90	1146
1330	1660-0	1.60-1.81	"	.01	1	91	1107
1400	0	1.87	"	.00	0	-	-

Test 7. Hydrogen evolution on open circuit.
Temperature approx. 125° FCell No. 68
Gravity: 1207

1545	500-0	2.24-2.14	2.625	2.2-1.15	182-95	124	1207
1550	0	2.14	"	1.15	95	-	-
1600	0	2.12	"	1.12	93	-	-
1700	0	2.08	"	1.00	83	-	-
1800	0	2.05	"	.93	77	-	-
2000	0	-	"	.85	70	-	-
2100	0	-	"	.82	68	125	1206

Test 8. Hydrogen evolution on open circuit.
 Temperature approx. 130° F

Cell No. 68
 Gravity: 1207

Time	Amperes	Voltage	Air Flow cu.ft./min.	%H ₂	Gassing Current	Cell Temp.	Gravity
0930	500-0	2.22-2.12	2.625	1.50	124	130°	1207
0945	0	2.12	"	1.14	95	-	-
1000	0	2.08	"	1.00	83	129	1207
1030	0	2.06	"	.97	81	129	1207
1100	0	2.04	"	.90	74	128	1206
1200	0	2.04	"	.72	60	128	1206

Test 9. Hydrogen evolution on discharge.
 Temperature approx. 125° F

Cell No. 68
 Gravity: 1205

1230	0-1660	2.04	2.625	.76	63	128	1205
1235	1660	1.93	"	.45	37	-	-
1245	1660	1.93	"	.48	40	-	-
1330	1660	1.90	"	.35	29	127	1191
1430	1660	1.87	"	.25	21	125	1171
1530	1660	1.82	"	.12	10	125	1145
1630	1660	1.75	"	.08	7	125	1124
1730	1660-0	1.60	"	.02	3	124	1104

Test 10. Hydrogen evolution on open circuit.
 Temperature approx. 100° F

Cell No. 68
 Gravity: 1246

1500	500-0	2.30	2.63	1.60	150	102	1246
1500	0	2.22	"	.95	89	101	1246
1530	0	2.16	"	.90	85	101	1246
1600	0	2.14	"	.80	75	101	1246
1700	0	2.12	"	.70	65	101	1246
1800	0	2.10	"	.65	61	101	1246
1900	0	2.08	"	.58	55	96	1243
2000	0	2.08	"	.50	47	96	1243
2030	0	2.08	"	.50	47	96	1243

Test 11. Hydrogen evolution on open circuit.
 Temperature approx. 90° F

Cell No. 68
 Gravity: 1280

1730	500	2.36	2.63	1.45	139	89	1279
1800	500-0	2.36-2.28	"	1.60-1.00	154-96	90	1279
1815	0	2.22	"	.75	72	-	-
1900	0	2.18	"	.70	67	-	-
2000	0	2.16	"	.65	62	88	1279
2100	0	2.14	"	.60	57	-	-
2200	0	2.14	"	.56	54	86	1279
2400	0	2.12	"	.51	49	84	1279
0100	0	2.12	"	.48	46	-	-
0300	0	2.11	"	.45	43	-	-
0500	0	2.11	"	.40	38	-	-

Test 11. (Continued) Hydrogen evolution on open circuit
 Temperature approx. 90 °F

Cell No. 68
 Gravity: 1280

Time	Amperes	Voltage	Air Flow cu.ft./min.	%H ₂	Gassing Current	Cell Temp.	Gravity
0700	0	2.10	2.63	.38	36	-	-
1000	0	2.10	"	.38	36	81	1277
1300	0	2.10	"	.38	36	-	-
1600	0	2.10	"	.31	30	80	1275
0900	0	2.09	"	.25	24	78	1271

Test 12. Hydrogen evolution during discharge.
 Temperature approx. 90° F

Cell No. 68
 Gravity: 1280

2000	500-0	2.38-2.31	2.60	1.60-1.40	155-133	85	1280
2005	0	2.26	"	.90	86	85	1280
2015	0	2.22	"	.85	81	-	-
2030	0-2230	2.21-1.96	"	.80-.55	76-52	85	1280
2045	2230	1.95	"	.53	51	-	-
2100	2230	1.94	"	.50	48	-	-
2130	2230	1.92	"	.35	33	87	1265
2200	2230	1.89	"	.25	24	88	1253
2230	2230	1.86	"	.13	12	89	1238
2300	2230	1.83	"	.08	8	90	1224
2330	2230-0	1.78	"	.05	5	91	1211

Test 13. Hydrogen evolution on open circuit.
 Temperature approx. 100° F

Cell No. 68
 Gravity: 1274

2200	500-0	2.32-2.27	2.60	2.05-2.00	189-184	105	1274
2205	0	2.23	"	1.60	147	-	-
2215	0	2.20	"	1.55	143	-	-
2230	0	2.18	"	1.45	133	-	-
2300	0	2.16	"	1.30	120	103	1274
2400	0	2.14	"	1.20	110	101	1274
0100	0	2.12	"	1.00	92	101	1274
0200	0	2.11	"	.95	87	101	1273
0300	0	2.11	"	.90	83	100	1273
0400	0	2.10	"	.85	78	99	1273
0600	0	2.10	"	.80	73	99	1273
0800	0	2.10	"	.70	64	98	1272

Test 14. Hydrogen evolution on discharge.
 Temperature approx. 100° F

Cell No. 68
 Gravity: 1275

2330	500-0	2.34-2.28	2.60	2.00-1.60	184-147	100	1275
2400	0-2230	2.20-2.00	"	1.30-.90	120-83	-	-
0030	2230	1.95	"	.80	74	100	1271
0100	2230	1.93	"	.60	55	101	1260
0130	2230	1.88	"	.45	41	-	-
0200	2230	1.86	"	.30	28	102	1227

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Test 14. (Continued) Hydrogen evolution on discharge.
 Temperature approx. 100° F

Cell No. 68
 Gravity: 1275

Time	Amperes	Voltage	Air Flow cu.ft./min.	%H ₂	Gassing Current	Cell Temp.	Gravity
0230	2230	1.84	2.60	.15	14	-	-
0300	2230	1.79	"	.08	7	104	1216
0330	2230	1.74	"	.04	3	-	-
0340	2230-0	1.70	"	.02	2	104	1185

Test 15. Hydrogen evolution on open circuit.
 Temperature approx. 130° F

Cell No. 68
 Gravity: 1275

2400	200-0	2.22-2.18	2.60	2.30-2.10	202-185	125	1275
0010	0	2.16	"	2.00	176	-	-
0030	0	2.14	"	1.95	172	-	-
0100	0	2.11	"	1.90	167	128	1275
0200	0	2.10	"	1.85	163	129	1274
0300	0	2.10	"	1.80	158	129	1273
0400	0	2.10	"	1.73	152	130	1271
0500	0	2.10	"	1.60	141	129	1269
0600	0	2.10	"	1.60	141	129	1268

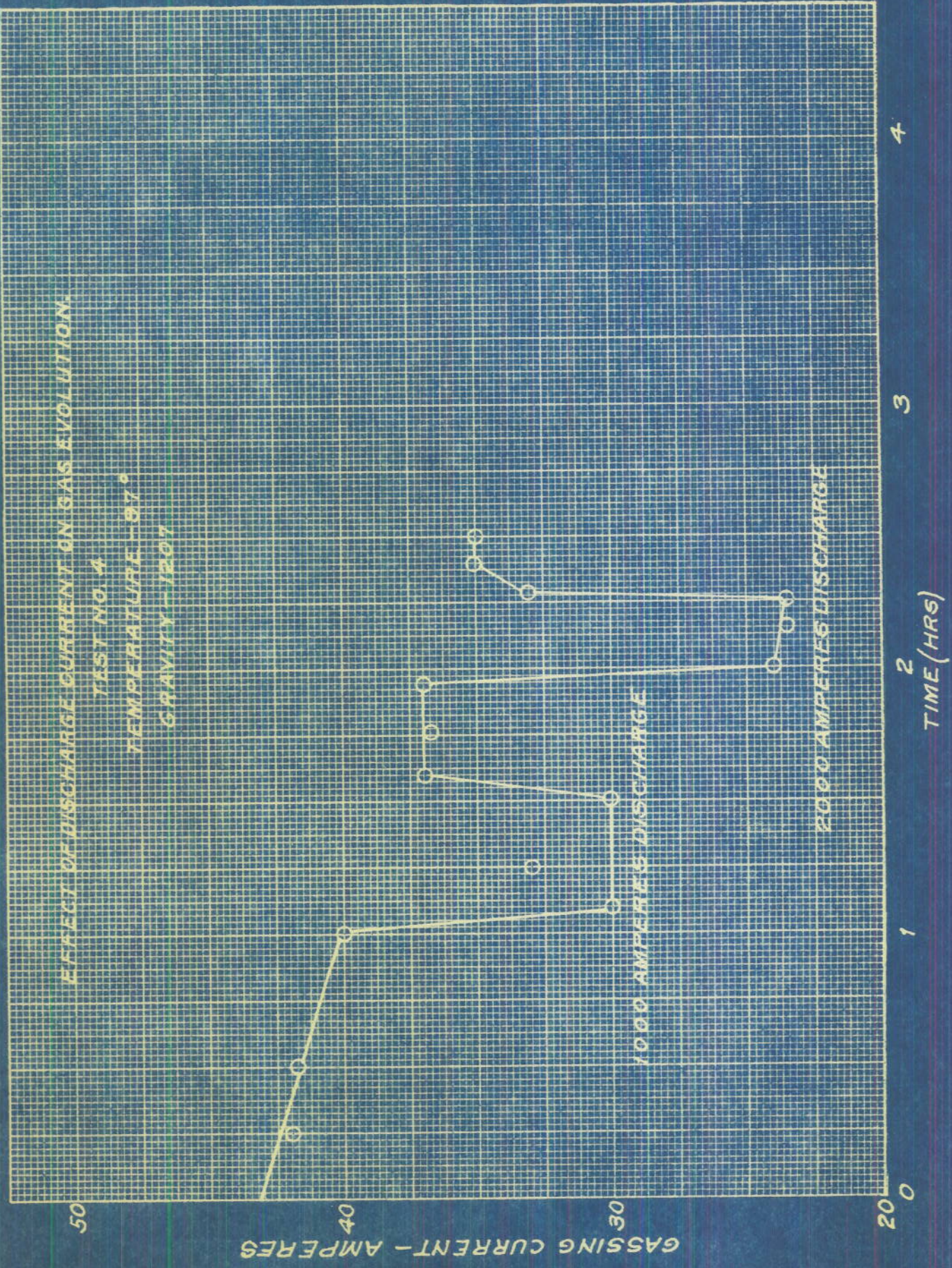
Test 16. Hydrogen evolution on discharge.
 Temperature approx. 130° F

Cell No. 68
 Gravity: 1269

0640	0-2230	2.10-1.95	2.60	1.55	136	129	1267
0645	2230	1.95	"	1.12	99	-	-
0700	2230	1.94	"	1.02	90	-	-
0730	2230	1.91	"	.80	70	129	1244
0800	2230	1.88	"	.50	44	-	-
0830	2230	1.84	"	.30	27	130	1212
0930	2230-0	1.74	"	.10	9	128	1182
1000	0	1.98	"	.30	27	130	-
1100	0	2.00	"	.40	35	129	-
1300	0	2.00	"	.40	35	128	-
1500	0	2.00	"	.40	35	128	-

IF SHEET IS READ THIS WAY (HORIZONTALLY) THIS MUST BE TOP. IF SHEET IS READ THE OTHER WAY (VERTICALLY) THIS MUST BE LEFT HAND SIDE.

N. R. L. 34A



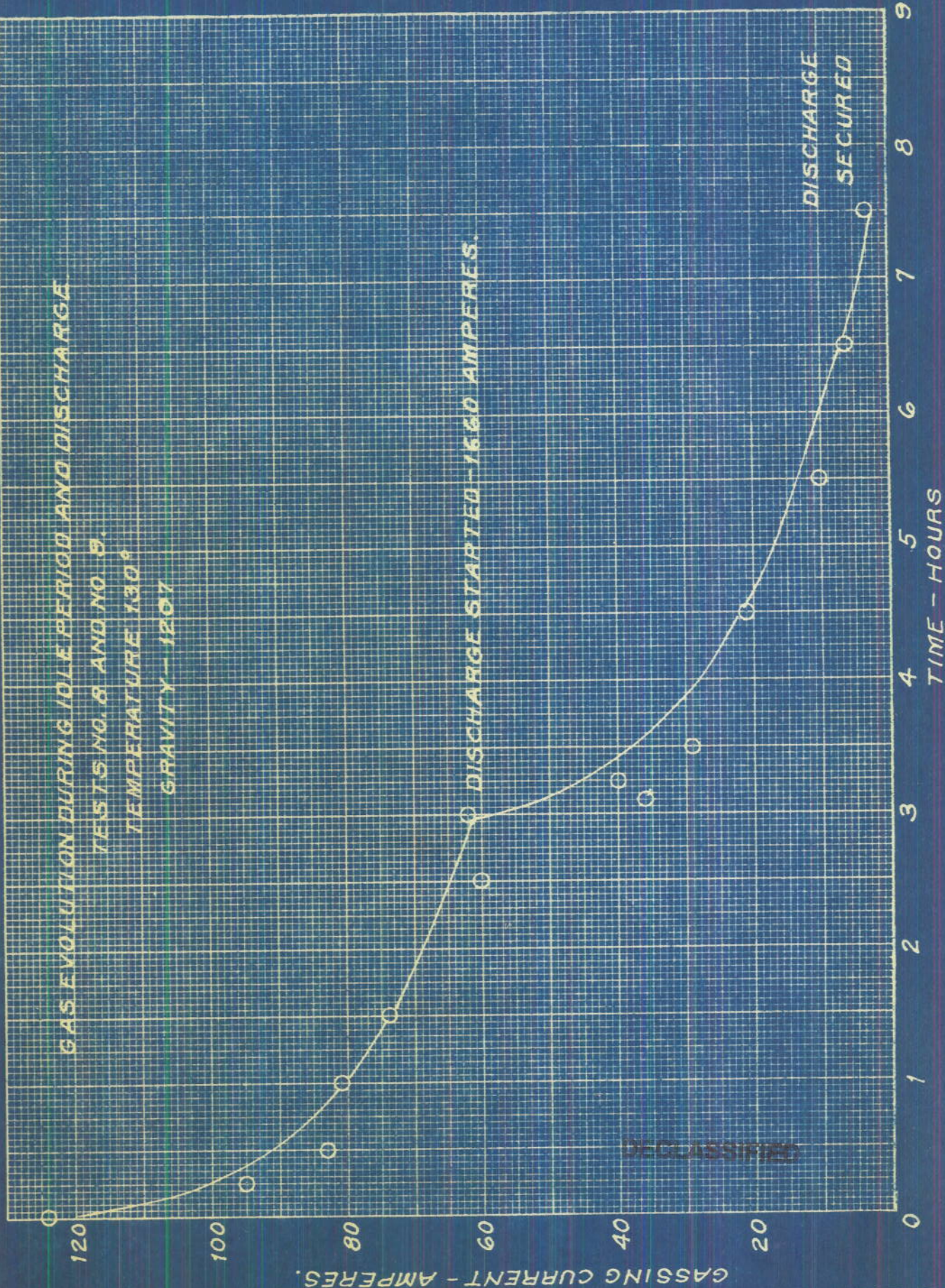
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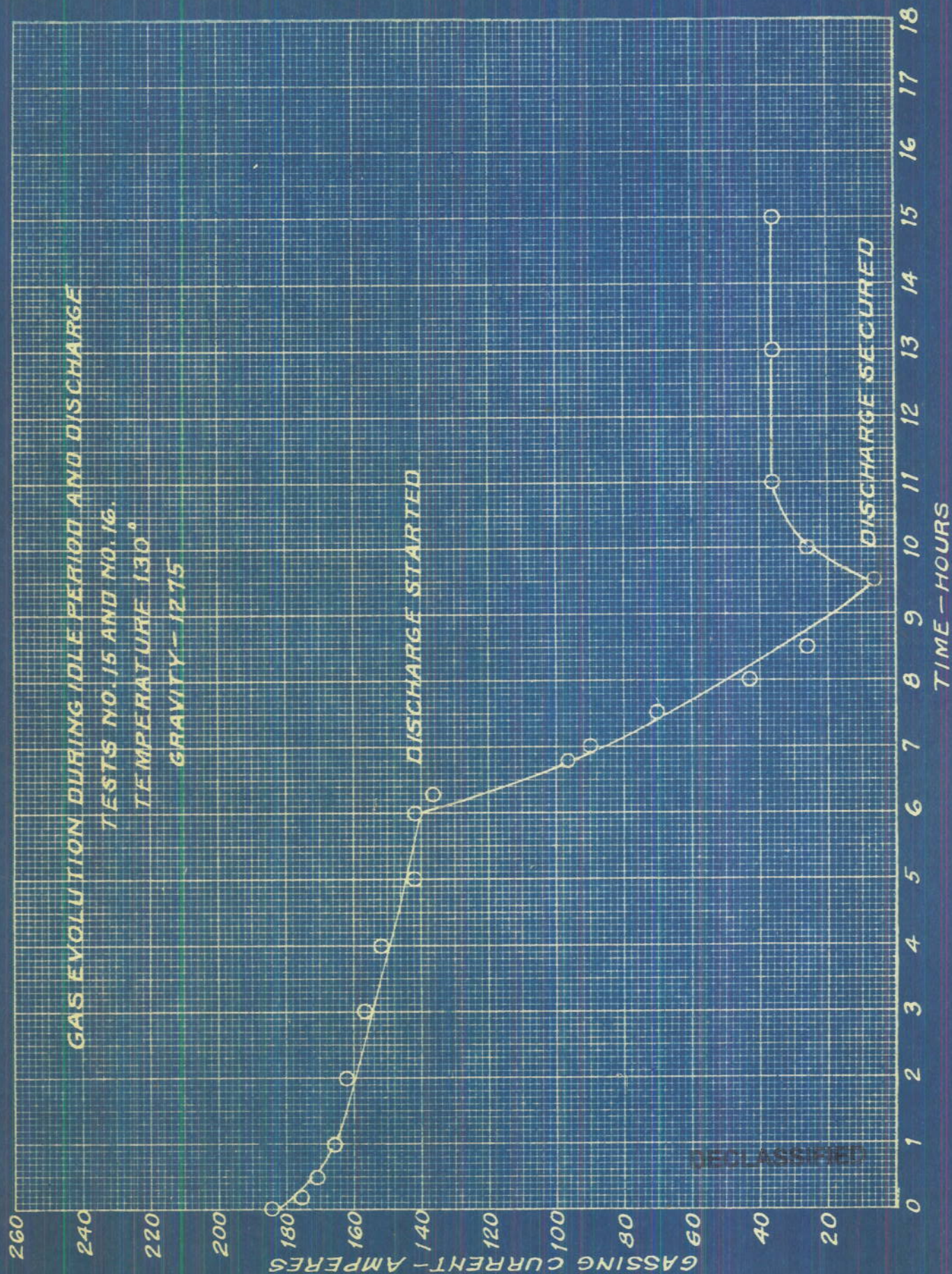
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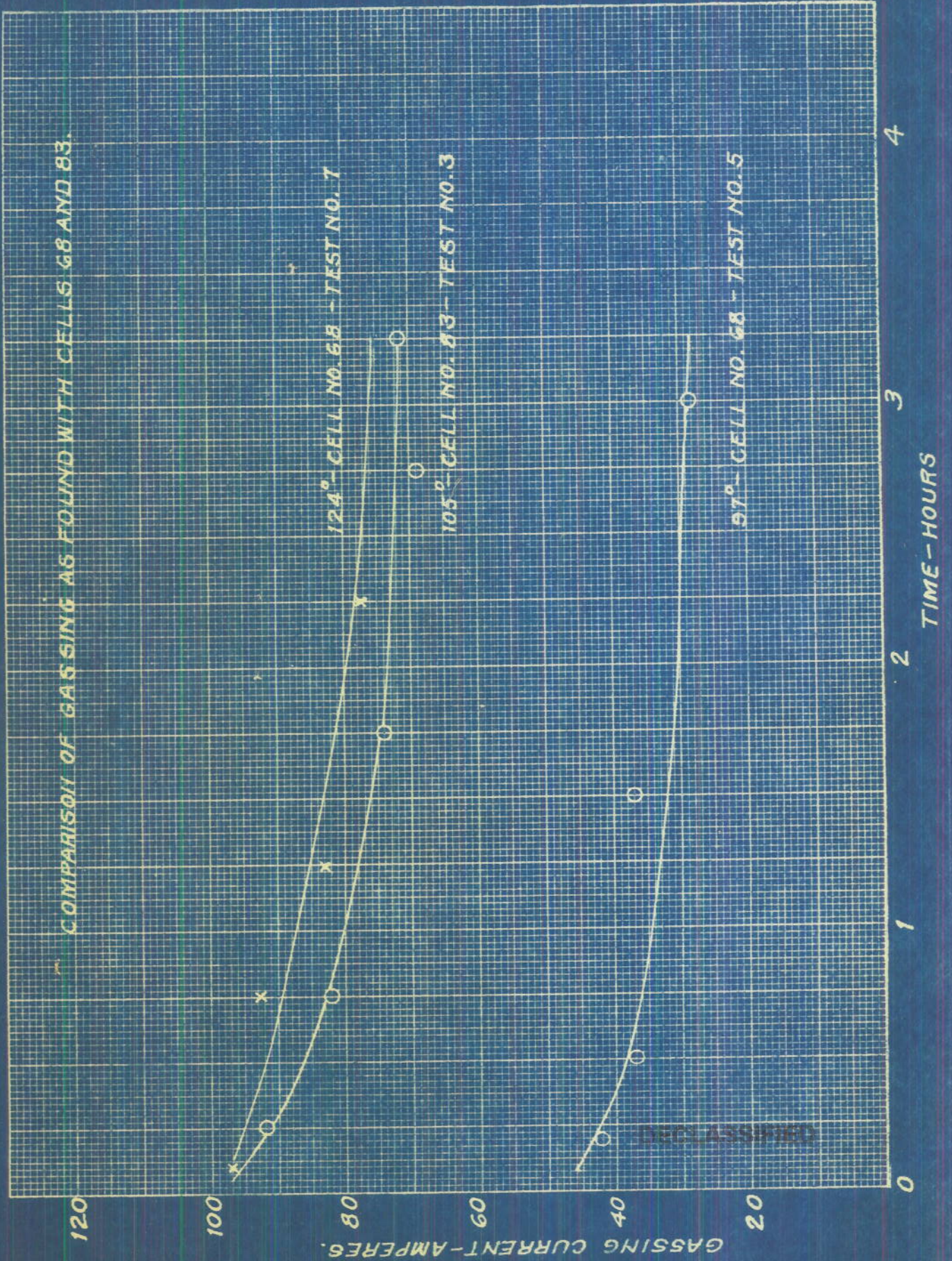
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TEMPERATURE 130°

GRAVITY - 1207

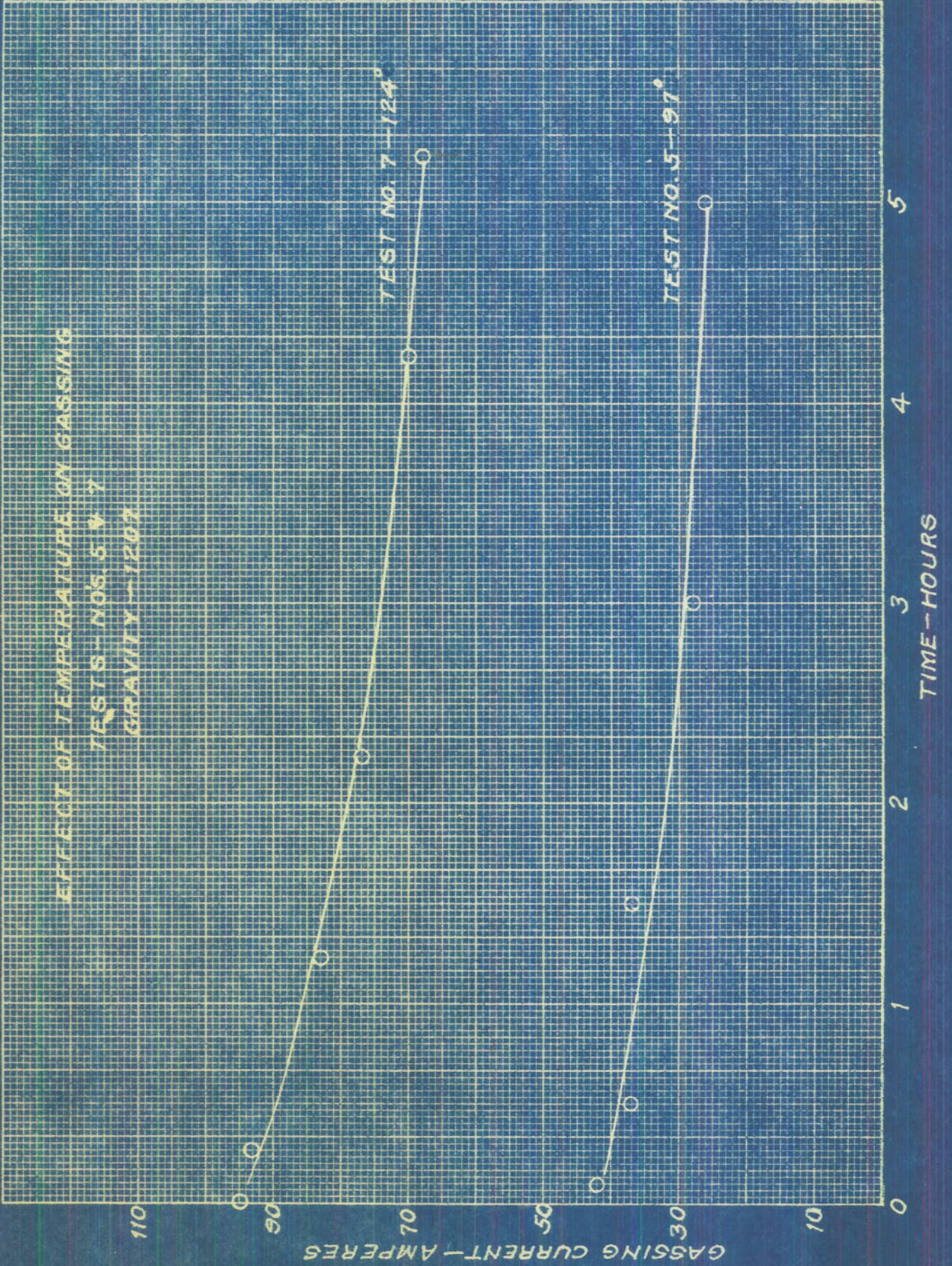






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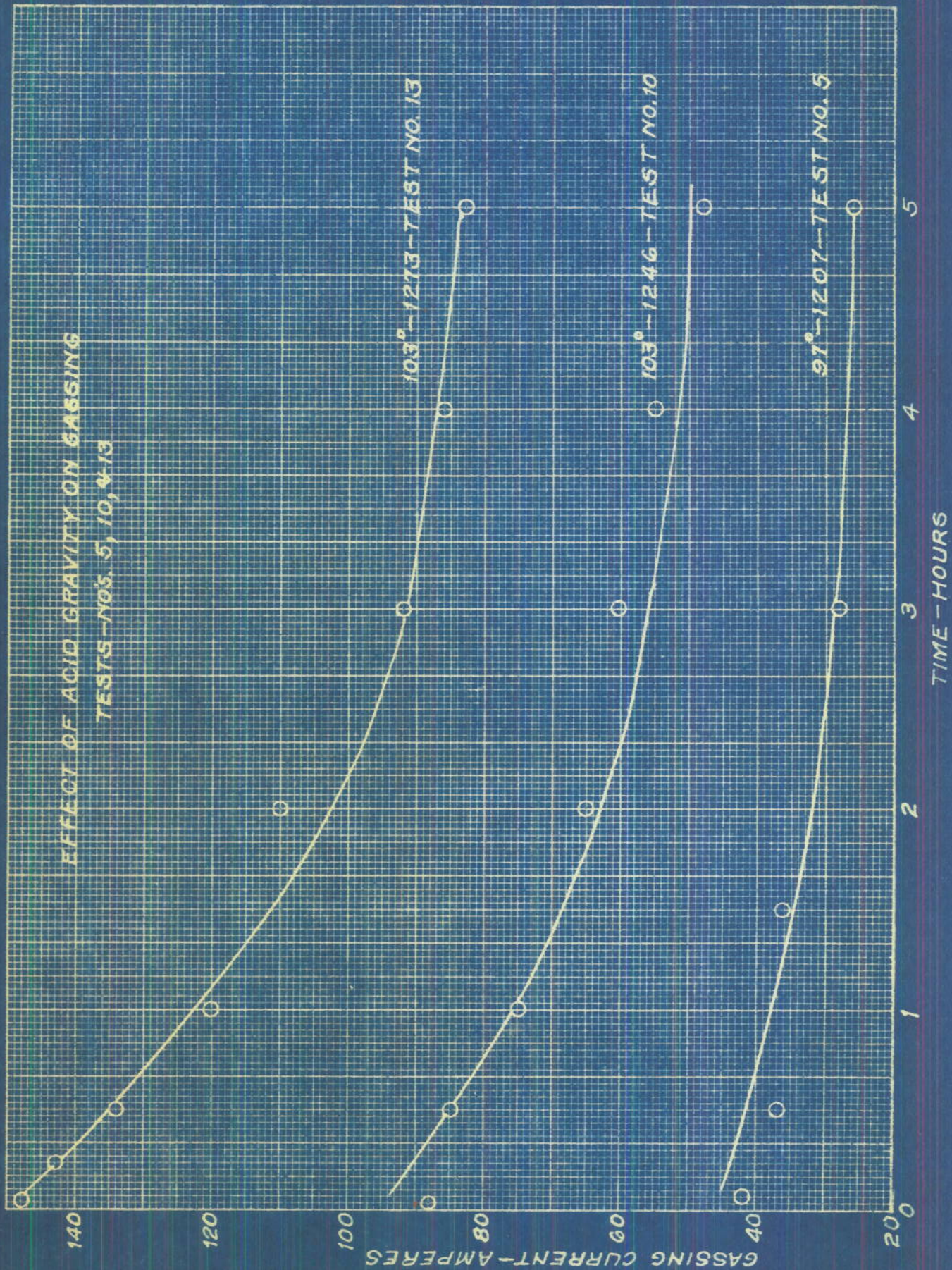
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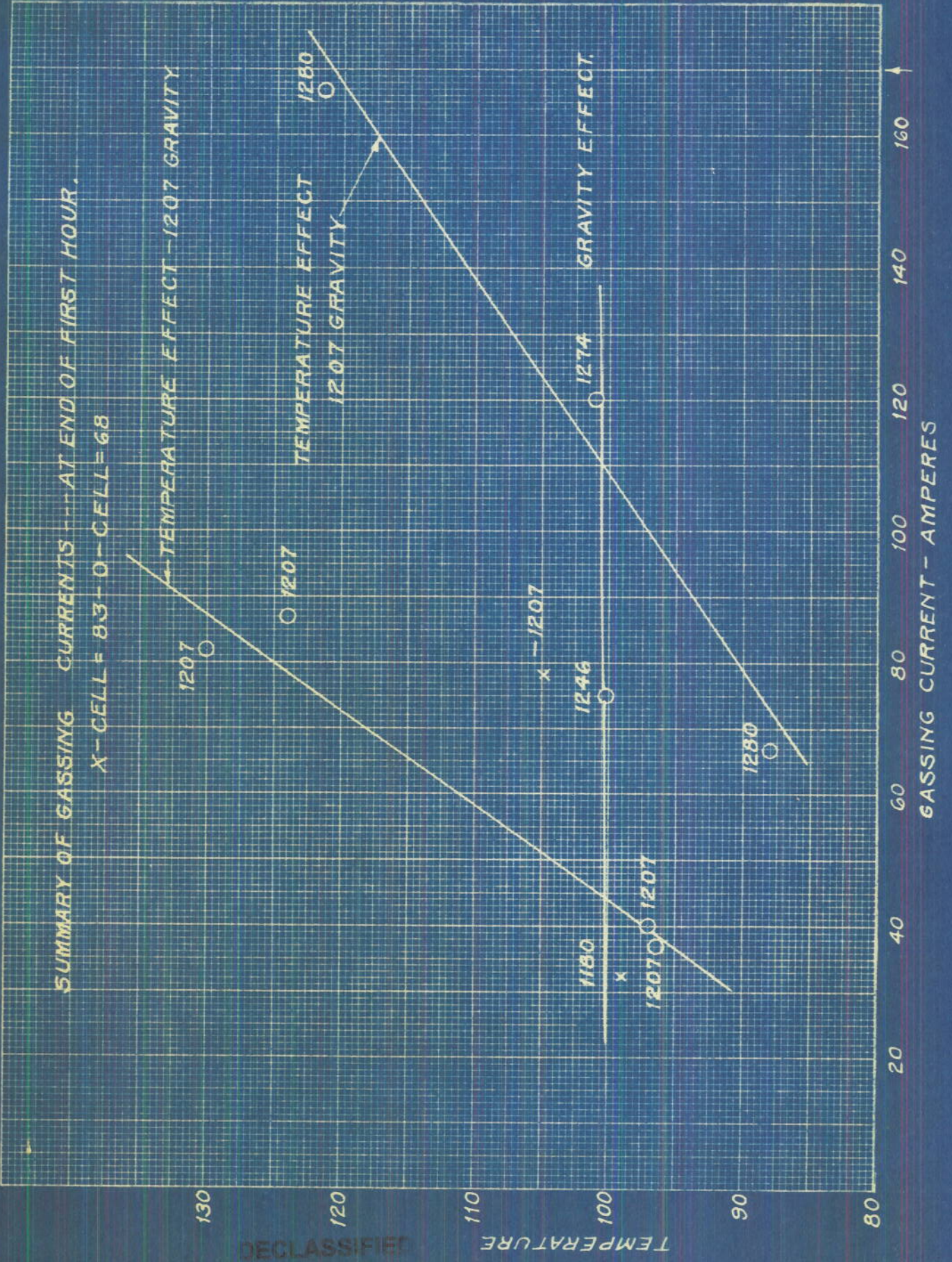
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SUMMARY OF GASSING CURRENTS --- AT END OF FIRST HOUR.

X-CELL = 83-O-CELL=68



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