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SUBJECT

SUBMARINE STORAGE BATTERIES -
STRATIFICATION OF ELECTROLYTE

BY

NAVAL RESEARCH LABORATORY

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NAVY DEPARTMENT

BUREAU OF ENGINEERING

P-1189

Report on

Submarine Storage Batteries -
Stratification of Electrolyte.

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
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A B S T R A C T

This report discusses the effects resulting from the stratification of electrolyte in submarine batteries. These effects are such as to accentuate the deficiencies inherent in the use of tall, narrow storage cells for submarine work.

AUTHORIZATION

1. This problem was authorized by reference (a); other correspondence pertinent to this problem are listed as references (b) and (c).

Reference: (a) Bu.Eng.let.SS/S62(7-30-D1) of 7 August 1935.
(b) CO USS BONITA's let.SS165/S62-4 of 12 July 1935 to Bu.Eng.
(c) Institution of Electrical Engineers, Journal, 66 529 (1928).

STATEMENT OF PROBLEM

2. During the greater portion of the charge of a lead-acid storage cell strong sulphuric acid is generated within the pores of the plates by the action of the charging current. This strong acid tends to fall to the bottom of the cell and stratification results — layers of strong acid at the bottom of the jar, progressively weaker layers above. If the charge is not continued well into the gassing phase, this stratification remains and has certain deleterious effects. In the normal charge of a submarine battery, the charge has to be continued for some time after the active material in the plates has been recharged in order to generate gas to mix up the stratified electrolyte. If this gassing were not required, the charge could be secured before the usual excessive gassing occurs. This would have the following advantages: explosion hazards due to gassing would be minimized, battery temperatures would be kept down, formation of acid spray would be reduced, water loss would be cut down, and wear and tear on engines and electrical plant would be reduced.

KNOWN FACTS BEARING ON THE PROBLEM

3. The effects of stratification are encountered more in Navy submarine cells than elsewhere owing to the narrow, deep cells used and to the small excess electrolyte space provided. In the batteries of telephone and public utility companies, the use of large open cells with a great excess of electrolyte minimizes the amount of stratification, while in industrial and other uses of tall cells, as in traction batteries, vibration and motion tend to reduce stratification.

4. The experience of the Material Laboratory, Navy Yard, New York, in the life testing of submarine cells shows two effects of stratification and its associated phenomena. Cells broken down for inspection at the end of the life-test period often have the lower third of the plates seriously sulphated. Apart from the gassing of the cells on charge, the chief factor in mixing the electrolyte in submarine cells is the rolling, pitching and vibration of the ship. The effect of these upon the electrolyte stratification is well brought out in reference (b) in tests of the N.R.L. battmeter on the U.S.S. BONITA. These tests showed that when the battery was charged while the ship was under way at sea, the hydrometer readings more nearly corresponded to the battmeter readings than was the case when the battery was being charged when the ship was secured to a dock. That is to say, the stratification was less when the ship was under way. This effect finds confirmation in the experience of the Material Laboratory. Formerly submarine cells on life tests were rocked on a tilting machine simulating the rolling of a submarine at sea. Experience showed that cells so rocked had a longer life than those standing quietly in the laboratory.

THEORETICAL CONSIDERATIONS

5. When a storage cell is charged, sulphuric acid is generated within the pores of both the positive and negative plates. This acid mixes with the electrolyte within these pores and makes it more concentrated and therefore of a higher density. As the charge progresses, this concentrated heavy acid is forced out of the plate and there meets the lighter electrolyte near the separators. Being more dense, the concentrated acid tends to fall to the bottom of the jar, just as honey poured into a glass of water falls to the bottom, even though it is soluble in water. If the charge were secured at this point, there would be a condition of stratification with strong electrolyte at the bottom of the cell, progressively weaker electrolyte in layers toward the top.

Open Circuit Effects

6. With the negative plates of the cell now in contact with strong electrolyte at the bottom of the cell, and at the same time in contact with weak electrolyte at the top, there results what is known as a "concentration cell", as illustrated in Plate 1. That is to say, owing to the higher potential of the Pb-$PbSO_4$ electrode in concentrated sulphuric acid than in weak, a cell is set up such that the bottom of the plate tends to charge the top of the plate. Similarly, the positive plates constitute a concentration cell which tends to result in a charging of the top of the positive plates at the expense of the bottom. If, therefore, this stratified condition is present on an open-circuit, the net result is for the bottom of the element to become further discharged.

7. If subsequent charges were not carried fully to completion, the ultimate result of this would be an unhealthy sulphation of the bottom of the plate. To illustrate, if a submarine cell with 1.280 specific gravity electrolyte were cycled repeatedly without sufficient gassing to stir up the electrolyte completely (even if the plates were fully charged), the concentration of the electrolyte at the bottom of the element would gradually increase and at the end of the charge would become greater than 1.280. It is well known that unhealthy sulphation and corrosion of grids is much more rapid in electrolyte greater than 1.280 specific gravity. Hence, this stratification condition would result in hastening this type of corrosion and sulphation. Recent work by the Bell Telephone Laboratories shows that corrosion and sulphation of this type are much greater in alloys and storage battery plates containing antimony than in pure lead or lead alloys other than of antimony.

Charge Effects

8. This "concentration cell" effect also has an influence on the charge. The work of the British Admiralty Research Laboratory on the current distribution in tall submarine cells (reference (c)) shows that the upper portion of tall elements takes a charge better than the lower. As the upper portion becomes charged, the sulphuric acid there formed streams down to the lower part and thereby increases the electrode potentials of the lower portions of the plates. This increased potential opposes the charging current and thus tends to confine the charge even more to the top of the element. Were it not for the polarization resulting from gassing, the bottom of the element might remain uncharged.

Discharge Effects

9. If now a stratified cell is discharged, the fact that the lower portion of the cell has a higher electrode potential than the upper tends to cause the lower portion to discharge first, whereas, as the British Admiralty work shows, in a normal cell the upper portion discharges first. One effect of this maldistribution of discharge current is to reduce the capacity of a normal unstratified cell, and it might be expected that with a stratified cell the increased discharge from the lower portion would tend to increase the overall capacity of the cell. However, this increase in the capacity of the lower portion due to the "concentration cell" effect is at the expense of the capacity of the upper portion, and hence little or no gain results.

10. In open-circuit, charge, and discharge conditions alike, the effect of stratification is to accentuate the deficiencies in electrical and other characteristics inherent in the use of tall, narrow cells.

METHODS OF TEST

11. The experimental work discussed in this report was incidental to other problems which have been reported on previously.

DATA OBTAINED

12. The amount of stratification in submarine cells is illustrated by Plate 2 taken with a USS CACHALOT cell (WLH-29), while the effect of stratification and the attendant phenomena on the capacity and hydrometer readings in a cell is shown in Plate 3, which records the data of a test by the Electric Storage Battery Company on a UL-49 Ironclad.

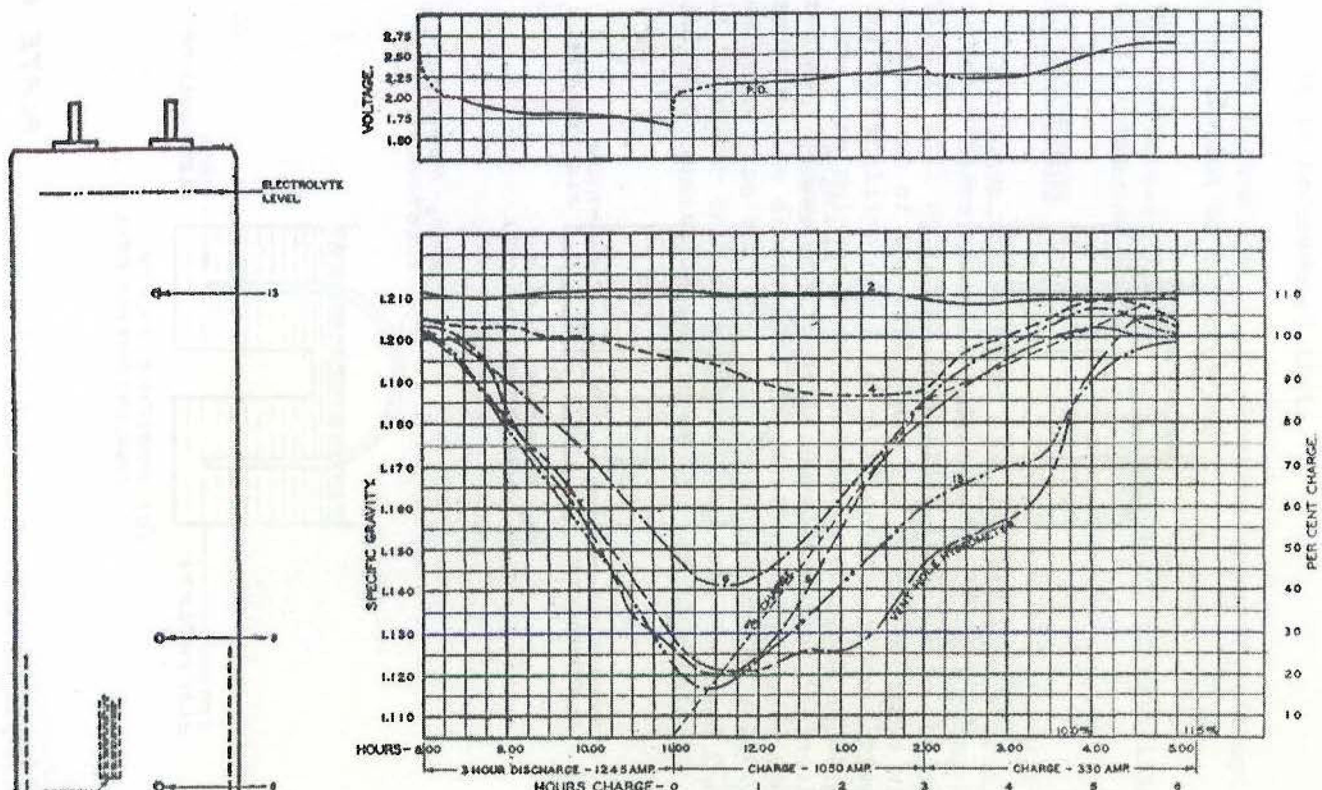
CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

13. From the above discussion it follows that in the present design submarine cells with their tall, narrow elements, stratification tends to cause the following effects: on open-circuit it would sulphate the lower portion of the plates, corrode the grids and negative material of this portion, and thereby shorten life and reduce capacity; on discharge it would reduce the capacity of the cell; and on charge it would favor the upper portion of the element in taking the charge. In short, the effects of stratification are to increase the deficiencies already inherent in tall, narrow elements. In the present design cells gassing with all its attendant evils must therefore be resorted to in order to mix up the electrolyte at the end of charge.

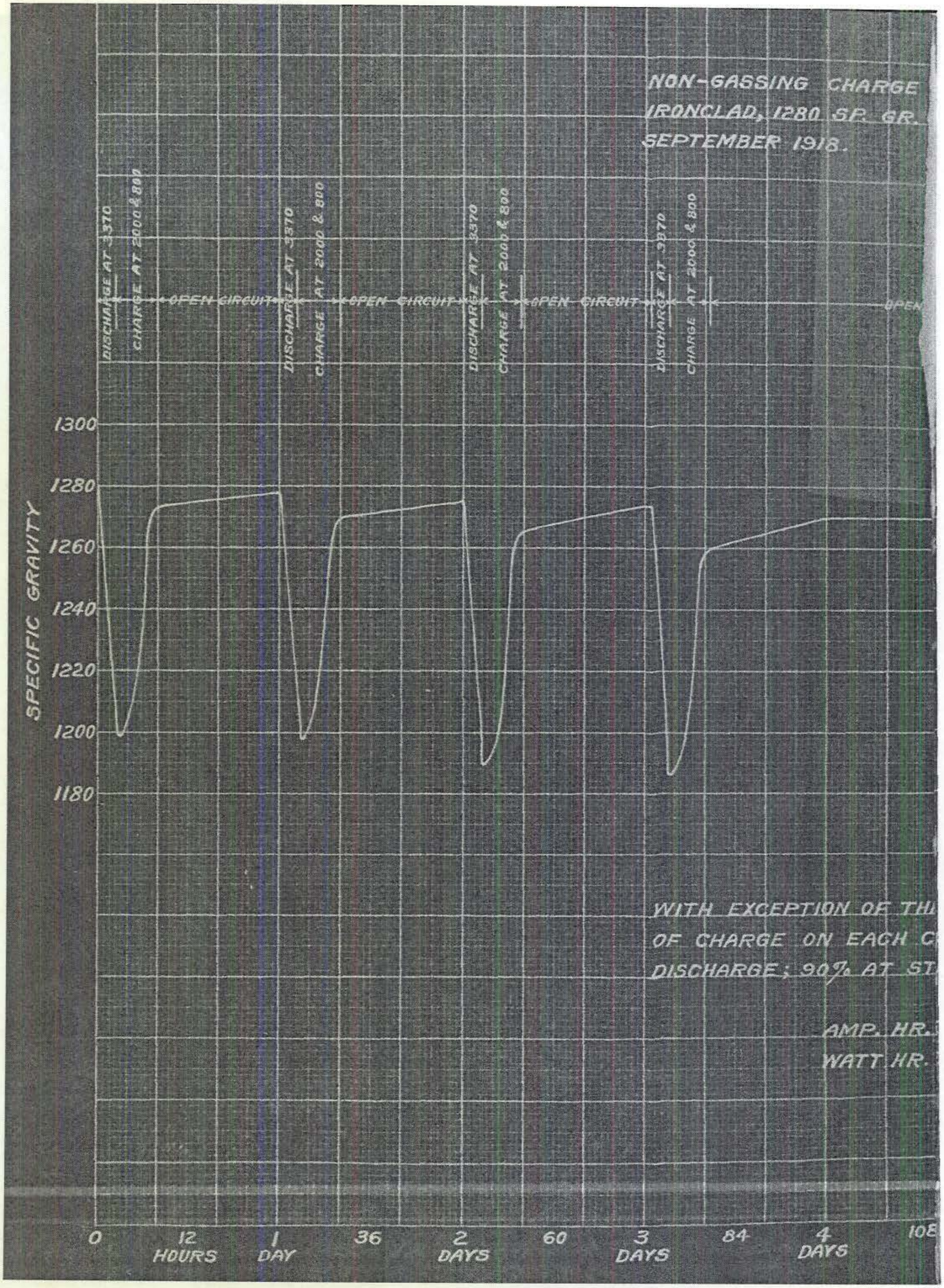
(b) Opinions

14. To minimize the effects due to stratification and to increase the discharge capacity of submarine cells, several engineers have suggested that artificial means be used to circulate the electrolyte. For example, it has been suggested that each cell in a battery be fitted with an electrically driven stirrer (Plate IV) or a compressed gas lift. The complexity introduced by such a device makes this Laboratory hesitate to recommend its adoption, but the Bureau might well consider its feasibility. Another suggestion which has been made is to invert the negative plate assembly so that the negative bus bar



SPECIFIC GRAVITY OF ELECTOLYTE AT VARIOUS LOCATIONS FROM BOTTOM TO TOP OF WLH-29 LC. SUBMARINE CELL ON DISCHARGE AT 3 HOUR SERVICE RATE FOLLOWED BY CHARGE. TEST Nº 7226. THE ELECTRIC STORAGE BATTERY CO. PHILADELPHIA, PENNA.-U.S.A.

Plate 2.



NON-GASSING CHARGE
IRONCLAD, 1280 SP. GR.
SEPTEMBER 1918.
DISCHARGE AT 3370
CHARGE AT 2000 & 800
OPEN CIRCUIT
DISCHARGE AT 3370
CHARGE AT 2000 & 800
OPEN CIRCUIT
DISCHARGE AT 3370
CHARGE AT 2000 & 800
OPEN CIRCUIT
DISCHARGE AT 3370
CHARGE AT 2000 & 800
SPECIFIC GRAVITY
1300
1280
1260
1240
1220
1200
1180
WITH EXCEPTION OF TH
OF CHARGE ON EACH C
DISCHARGE; 90% AT ST
AMP. HR.
WATT HR.
0
12 HOURS
1 DAY
36
2 DAYS
60
3 DAYS
84
4 DAYS
108

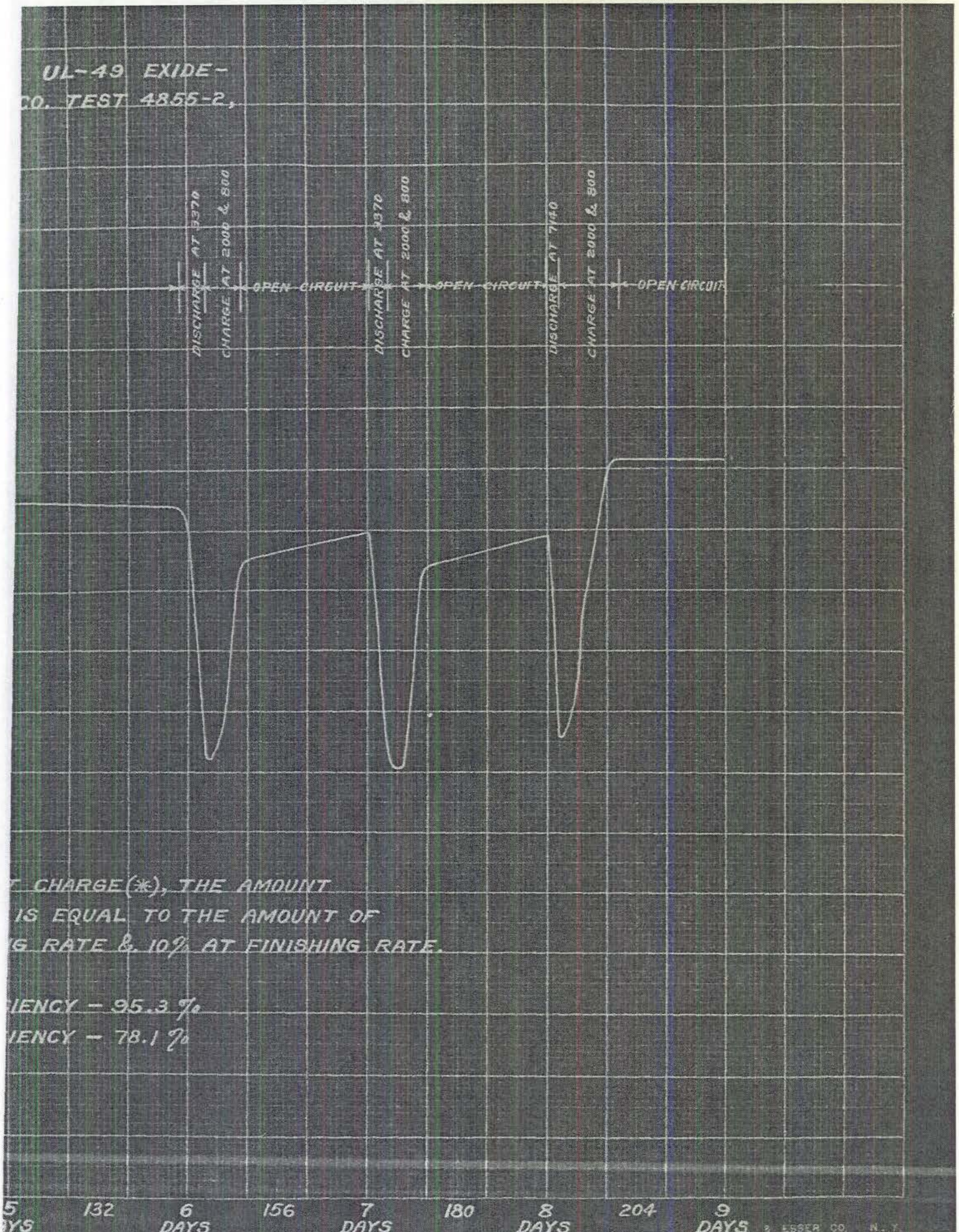
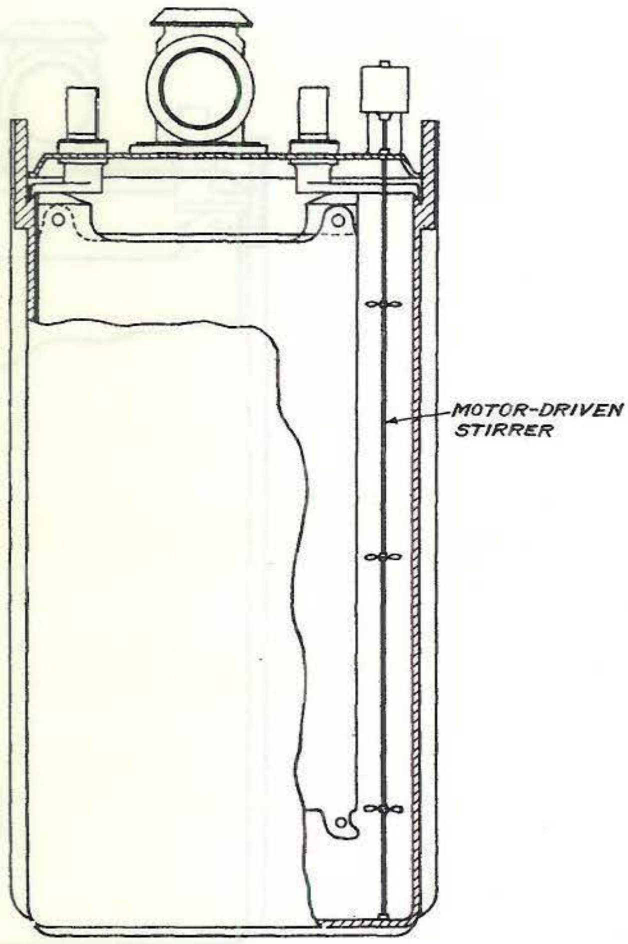
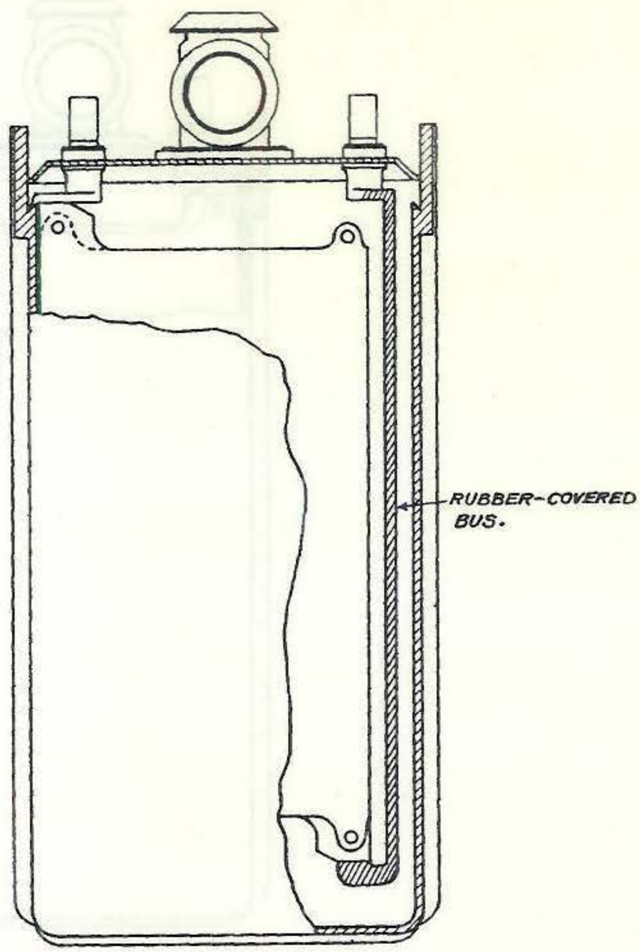

UL-49 EXIDE-
CO. TEST 4855-2,
DISCHARGE AT 3370
CHARGE AT 2000 & 800
OPEN CIRCUIT
DISCHARGE AT 3370
CHARGE AT 2000 & 800
OPEN CIRCUIT
DISCHARGE AT 7140
CHARGE AT 2000 & 800
OPEN CIRCUIT
T CHARGE(*), THE AMOUNT
IS EQUAL TO THE AMOUNT OF
IG RATE & 10% AT FINISHING RATE.
IENCY — 95.3 %
IENCY — 78.1 %
5
YS
132
6
DAYS
156
7
DAYS
180
8
DAYS
204
9
DAYS

PLATE 3



S/M CELL WITH ELECTROLYTE CIRCULATOR

PLATE 4



S/M CELL WITH BOTTOM COLLECTOR BUS.

PLATE 5