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NAVY DEPARTMENT  
BUREAU OF ENGINEERING

FR-1121

Report on

Studies of Grid Alloys  
for  
Submarine Storage Batteries  
(Continuation of Report No. M-1052)

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Date of Test: 15 May 1934 to 31 December 1934.

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## ABSTRACT

This report is a continuation of NRL Report No. M-1052.

Results and conclusions from the life-tests conducted at the Bureau of Standards are presented briefly. The NRL alloys subjected to the above life-test realized the expectation that they would be free from local action and sulphation; but the positive grids disintegrated under oxygen attack. The cause of this action (which prior tests at this Laboratory did not give reason to anticipate) has been found. The steps taken to prevent its future occurrence are described.

Further electrolytic corrosion tests on 29 alloys under controlled conditions are described.

A further modification of the Navy alloys has been developed and is described here. In this alloy it is believed that the strontium has been protected from atmospheric attack during casting -- the main cause of failure of the former grids.

A new life-test series is to be commenced and the program for this test is described.

## AUTHORIZATION

1. This problem was authorized by Bureau of Engineering confidential letter C-SS/S62(2-15-Ds) of 21 February 1933. Other pertinent data are listed as references (a) to (c) inclusive.

- Reference:
- (a) Preliminary Report on Studies of Grid Alloys for Submarine Storage Batteries, dated 27 July 1933.
  - (b) NRL Letter SS/19 of 20 April 1934 to Bureau of Engineering.
  - (c) NRL Report No. M-1052 of 17 May 1934.

## STATEMENT OF PROBLEM

2. The object of this work is to develop an alloy for storage battery grids, particularly the positive grids, which will consist principally of lead and have the desirable properties of lead alloyed with antimony, but without the presence of antimony or any other metal tending to produce sulphation and self-discharge.

3. A further elaboration of the above statement will be found in reference (c).

## KNOWN FACTS AND THEORETICAL CONSIDERATIONS BEARING ON THE PROBLEM

4. The previous report, reference (c), contains a statement of these matters, to which nothing more can be added at this time.

## NARRATIVE OF ORIGINAL WORK DONE AT THIS LABORATORY

5. The work done up to 15 May 1934 is described in reference (c).

6. Since the submission of the above report, the work has followed two main lines: first, a more intensive examination and study of the more promising alloys already developed, together with a few others which it did not seem wise to ignore; and second, the examination of the results of the life-test made at the Bureau of Standards and the extraction of all possible benefit from these results.

7. Preparation of 29 new alloys and a very careful corrosion-test, repeated a second time under modified conditions, consumed the summer and fall.

8. At the same time, the life-tests were progressing and continued until 31 August (cycle 93). At this date, it was apparent that many cells were in bad condition and it was decided to make a "standing-idle" test of 30 days' duration before too much deterioration had taken place. This was done, and cycling was resumed on September 30, continuing for another 8 cycles, thus ending after cycle 101, when it was plain that no good purpose could be served by further cycling.

9. At the conclusion of the cycling, negative elements were removed from selected cells and tested for sulphation by Mr. Snyder, using Dr. Vinal's

method. A separate report on the life-test results is being prepared by the Bureau of Standards. These sulphation tests lasted from 16 October to 22 December 1934.

## METHODS

### Electrolytic Corrosion Studies at this Laboratory

#### (a) Materials

10. Materials were the same as described in reference (c).

#### (b) Experimental Methods

11. Results presented in reference (c) indicated that daily and seasonal temperature changes had a strong influence on electrolytic corrosion. Accordingly, the new corrosion-test cells (similar to those shown in Plate I of reference (c)) were assembled in a long iron box, with an inch of cellotex heat-insulation entirely surrounding it. This box was filled with enough water nearly to submerge the test-cells. Along the sides of the box ran copper tubing through which tap-water was circulated. By this means, the temperature was kept nearly uniform and in the neighborhood of 75°F, thus avoiding the variations in behavior to which attention was called in reference (c), paragraphs 58 to 60.

12. Aside from the above described water-bath, all methods and materials were exactly like those described in reference (c), except as noted below.

13. Corrosion series K consisted of 46 cells comprising 23 different alloys, each alloy being used as the positive in two cells. Some of these alloys represented compositions previously tested; some were of similar composition with the addition of 0.2% sodium. The latter was introduced in order to protect the strontium from oxidation during melting and pouring. Another group of alloys, containing calcium, were taken as representative of alloys being studied by the Bell Telephone Laboratories in an investigation having a similar objective to this one. (It should be noted that the service contemplated by the above organization is that of telephone operation, where batteries are kept "floating" on a d.c. power supply. There is abundant evidence that such service imposes different requirements than does the nearly complete power cycling of naval submarine storage batteries.) Other alloys of miscellaneous composition (corresponding to patented compositions) were included, with the idea of leaving no possibilities, even the most unlikely ones, unexplored. Some alloys were made up with commercial "grade A" pig-lead instead of the high purity lead previously used.

14. Developments in the Bureau of Standards life-test, i.e., the unexpected signs of failure of the positive grids of the Naval alloys, pointed to the suspicion that the difference in behavior was due to the fact that in the Naval Research Laboratory corrosion tests, the current was passed continuously without any period of reversal corresponding to the discharge cycle in the life-test. Accordingly, a new series, L, was set up. The electrodes of this consisted of the same 23 alloys as used in series K. (Each melt having been cast into a mold holding three electrodes, there was a

spare electrode of each.) To these were added five additional alloys containing besides strontium and tin, small additions of sodium, silver or copper. The reason for investigating the behavior of the latter alloys was the known fact that silver in the amount used (0.05%) is supposed to have a highly protective effect against intergranular corrosion of lead antimony, and it was hoped this effect might also be observed in the present alloys.

15. The manner of conducting the corrosion in Series L was to "charge", i.e., pass current in such a direction as to oxidize the positive plate, for about 23 hours a day. The current was then reversed for about one hour, it having been found by experiment that this length of time was sufficient to convert the lead peroxide to sulphate.

#### Discussion of Results of Electrolytic Corrosion Series

16. The results of these two series are presented in Table I. The results of analyzing these data are presented in the order of their importance. In this table, "total oxygen" means the gain in weight of the cell as a whole -- electrodes and deposited residue. "Internal oxygen" means the oxygen in the form of lead oxide within the positive plate.

(a) When the electrolysis is interrupted by daily reversal of sufficient length to convert the surface peroxide to sulphate, the rate of oxidation is much increased. (It will be noted that this was in spite of the fact of lower ambient temperature during the reversal series) However, the relative order of merit of the various alloys remains very much the same, as evidenced by the columns marked "Ratings".

(b) The presence of tin definitely increases corrosion resistance in calcium alloys, reaching an optimum at 2% tin with 0.2% calcium (Alloys Nos. 1 to 5). Even up to 4%, tin increases the resistance of strontium alloys (Alloys Nos. 6 to 8). It has little effect, on the other hand, on magnesium alloys (Alloys Nos. 13 and 14), and even a deleterious influence in sodium alloys (Alloys Nos. 10 and 11).

(c) Sodium in amounts up to 0.2% has a definite protective action on alloys which already contain tin, together with strontium (cf. alloys 6 and 16, 12 and 18, etc.). This is due to the action of sodium as a scavenger during melting and pouring.

(d) Silver, at a percentage of 0.05%, has a protective effect even greater than that of sodium (cf. alloys A and B, A and 12). This effect is due to an entirely different cause than in the case of sodium additions.

(e) Copper has no good influence compared with the other elements mentioned. Neither do magnesium, aluminum or lithium, so far as this limited number of alloys may justify a conclusion.

(f) The use of grade A pig-lead instead of high purity lead has a bad effect on corrosion resistance (cf. Nos. 6, 7, 8 with 19, 20, 21).

(g) Alloys containing 0.2% calcium, protected by the presence of tin, compare favorably with strontium alloys similarly protected. This is contrary to the conclusion reached in reference (a) which related only to alloys from which tin was absent.

TABLE I.

Electrolytic Oxidation Series K and L  
 Series K, 7/19/34 to 8/30/34, 150 ampere hours. Mean temp. 74°F.  
 Series L, Daily Reversals 10/25/34 to 11/27/34, 109 A.H.; Mean temp. 62°F.

Alloy No.	Nominal Composition (Exclusive of Lead)	RESULTS OF ELECTROLYSIS TESTS					
		SERIES K (Continuous)			SERIES L (Daily Reversals)		
		Total Oxygen Milligrams per A.H.	Internal Oxygen Milligrams per A.H.	Rating	Total Oxygen Milligrams per A.H.	Internal Oxygen Milligrams per A.H.	Rating
1	0.2%Ca, 0.2%Sn	5.50	2.85	15	7.88	5.16	17
2	0.2%Ca, 0.4%Sn	5.50	3.05	14	5.48	2.44	6
3	0.2%Ca, 1.0%Sn	4.72	3.05	10	4.62	2.34	5
4	0.2%Ca, 2.0%Sn	2.27	1.42	5	3.93	2.26	2
5	0.2%Ca, 4.0%Sn	5.70	4.37	16	8.40	5.60	19
6	0.4%Sr, 2%Sn	4.70	3.48	9	7.05	5.45	13
7	0.4%Sr, 3%Sn	1.68	0.46	2	6.91	5.36	11
8	0.4%Sr, 4%Sn	0.97	0.00	1	2.75	0.99	1
10	0.7%Na	11.63	6.52	22	12.22	6.10	21
11	0.7%Na, 2.0%Sn	13.42	11.42	23	15.35	13.26	23
12	0.4%Sr, 1.0%Sn	5.85	4.50	17	7.10	4.37	14
13	0.1%Mg, 2.0%Sn	4.05	2.38	7	5.82	3.55	8
14	0.1%Mg	5.40	2.56	13	7.76	2.87	16
15	10% Sb	6.30	2.97	19	14.45	7.20	22
16	0.4%Sr, 0.2Na, 2.0Sn	2.12	1.38	4	4.35	2.55	4
17	0.4Sr, 0.2Mg, 2.0Sn	5.18	4.23	11	8.57	6.69	20
18	0.4Sr, 0.2Na, 1.0Sn	1.97	1.06	3	4.05	2.07	3
19	0.4Sr, 2.0Sn*	3.43	2.28	6	5.69	3.70	7
20	0.4Sr, 3.0Sn*	5.42	4.00	12	7.00	5.40	12
21	0.4Sr, 4.0Sn*	5.96	4.31	18	6.50	3.95	10
22	0.6Ba, 2.0Sn*	4.23	2.91	8	7.97	6.75	18
23	(0.2Li, 0.2Ca, 0.3Sn, 0.5Al	7.53	4.25	21	7.22	5.20	15
24	(0.2Ca, 0.15Mg, 2.0Sn, 0.05Al	7.50	6.36	20	6.07	4.63	9
A	0.4Sr, 1.0Sn, 0.05Ag				3.05	1.63	
B	0.4Sr, 1.0Sn, 0.1Na				4.55	2.29	
C	0.2Sr, 0.2Sn, 0.1Na				4.77	2.49	
D	0.2Sr, 0.2Sn, 0.05Ag				4.93	2.82	
E	0.2Sr, 0.2Sn, 0.05Cu				8.35	5.37	

Ag = silver, Al = aluminum, Ca = calcium, Cu = copper, Li = lithium,  
 Mg = magnesium, Na = sodium, Sn = tin, Sr = strontium, Sb = antimony.

\*Prepared with commercial "Grade A" pig-lead.  
 "Ratings" based on total oxygen absorption.

(h) Most of the alloys represented in this series, which is on the whole a selection of highly resistant compositions, surpass the 10% antimony alloy (No. 15) either in continuous or interrupted attack by nascent oxygen. If this conclusion appears to be contradicted by performances in life-tests, then the blame must be placed elsewhere than on the composition of the alloys.

Physical Properties of the Alloys in Series K and L

17. The only physical property thus far determined for these alloys is the Brinell hardness number, determined in the manner described in reference (c). The results are presented in Table II.

TABLE II.  
(For Compositions See Table I)

<u>Alloy No.</u>	<u>Brinell Hardness</u>	<u>Alloy No.</u>	<u>Brinell Hardness</u>
1	13.6	16	20.9
2	18.6	17	12.0
3	17.7	18	15.9
4	19.0	19	15.4
5	13.1	20	13.2
6	15.5	21	14.6
7	14.4	22	10.2
8	13.9	23	20.4
10	16.8	24	19.1
11	15.9	A	15.6
12	12.3	B	17.1
13	9.1	C	10.4
14	8.7	D	8.1
15	17.7	E	7.4

The Brinell hardness number may be taken as a gage of ultimate strength. It will be noted that there are a number of compositions which receive a very high rating both in hardness and oxidation resistance. The more prominent ones are listed below:

TABLE III.

<u>No.</u>	<u>Composition</u>
16	0.4% Sr, 0.2% Na, 2.0 Sn
4	0.2% Ca, 2.0% Sn
18	0.4% Sr, 0.2% Na, 1.0% Sn
A	0.4% Sr, 0.05% Ag, 1.0% Sn
B	0.4% Sr, 0.1% Na, 1.0% Sn

Conclusions from Life-Test

18. A separate report is being submitted by the Bureau of Standards, in which details of the life-test will be found. It is, however, necessary to state here briefly the more important findings from this very instructive test, in order to present in a unified form the results of the combined investiga-

lug. "B" is a pure lead grid; it shows much buckling and deformation throughout. "C" is an 8% antimony grid. It shows a general deformation somewhat worse than "A", but lacks the pronounced failure in the one side-bar. The explanation of this failure is plain if the manner of casting the grids is considered. In the mold used at the Bureau of Standards, the metal is poured from the top. Thus the metal in the broken side-bar had had more exposure to air and greater oxidation than any other part of the grid. Plainly, (and this is borne out by microscopic examination) the cause of failure is internal films formed in the casting process. The cure is equally plain: grids of such alloys as these must be bottom-poured, or else other precautions taken against this type of metallurgical defect.

23. In support of the above explanation, another observation is pertinent -- that difficulty has been found in welding or "burning" these alloys, due to formation of an oxide film which prevents mutual fusion of the two parts. The penetration of such films into the interior of a grid would form cold-shuts of a fatal kind. Plate II is a photomicrograph of a section of side-bar from a grid cast out of Navy Alloy No. 2. It shows plainly the existence of an intercrystalline oxide film penetrating deeply into the metal. This photograph was taken on a section cut by means of a sharp chisel, unpolished and unetched.

24. In the light of what has been said, the lack of agreement between the Laboratory corrosion-tests and the life-tests is clearly explained. The electrodes used in the Laboratory were solid rectangular plates, and, moreover, they were cast in a bottom-pour mold which allowed minimum exposure to air and minimum surface disturbance. In contrast, the grid-mold used at the Bureau of Standards is top-pouring and the metal splashes down through open air-spaces providing an ideal opportunity for oxidation and partial cold-shuts.

## CONCLUSIONS AND RECOMMENDATIONS

### A. Facts Established

25. The strontium-tin alloys of lead have shown themselves, when cast under ideal conditions, superior to the antimony-lead alloy in strength, electrical conductivity (see reference (c), paragraph 62) and resistance to corrosion. As cast into grids in a mold unsuited to them, they develop an oxide brittleness which is not an inherent defect.

26. Alloys free from antimony seem prone to treeing.

27. Further modifications of the Navy alloys, as described in this report, exhibit still better properties of strength and corrosion resistance than those previously studied.

28. In particular, the addition of 0.1 to 0.2% of sodium is of great benefit, probably mostly because it acts as a "scavenger", protecting the strontium in the molten lead from oxidation, and/or producing a more fusible oxide with less tendency to spread over the surfaces and prevent interfusion.

29. Calcium alloys protected by tin are comparable in properties with strontium alloys.

## B. Future Program

30. It is intended to proceed on life-tests of a new series of alloys. Part of this work is already in progress, i.e. the casting of grids. The make-up of the new series is given in Table V.

TABLE V.

<u>Alloy No.</u>	<u>Composition (Balance Grade A Pig-Lead)</u>
I	0.15% Ca, 0.4% Sn
II	0.15% Ca, 0.4% Sn, 0.15% Na
III	0.15% Ca, 0.4% Sn, 0.15% Na, 0.05% Ag
IV	0.35% Sr, 0.4% Sn, 0.25% Na
V	0.35% Sr, 0.4% Sn, 0.25% Na, 0.05% Ag
VI	0.35% Sr, 0.8% Sn, 0.25% Na
VII	0.35% Sr, 0.8% Sn, 0.25% Na, 0.05% Ag
VIII	4% Sb

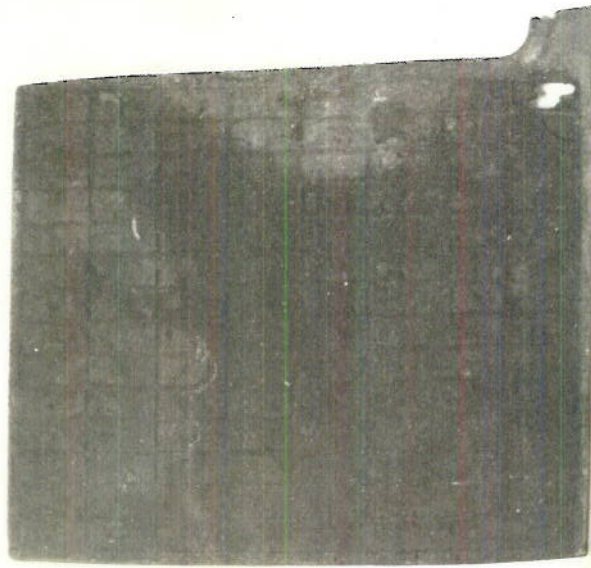
The number of cells used will be 40, 5 cells for each alloy. In every case, both positive and negative plates will be of the same material. The same cycling procedure will be used on these as on the preceding life-test -- self-discharge and sulphation included. No compositions very high in tin are included, due to its being a strategic metal.

31. It is proposed to include also a group of cells with glass containers in order to study "treeing" and other visible phenomena. Means will be used to prevent formation of trees in the other cells.

32. Samples for impact test will be cut from side-bars of specimen grid-castings. If these show that the sodium additions have not eliminated porosity, an attempt will be made to modify the mold so that the casting can be bottom-poured. It is believed that a second life-test series where results were affected by this factor would be useless and misleading.

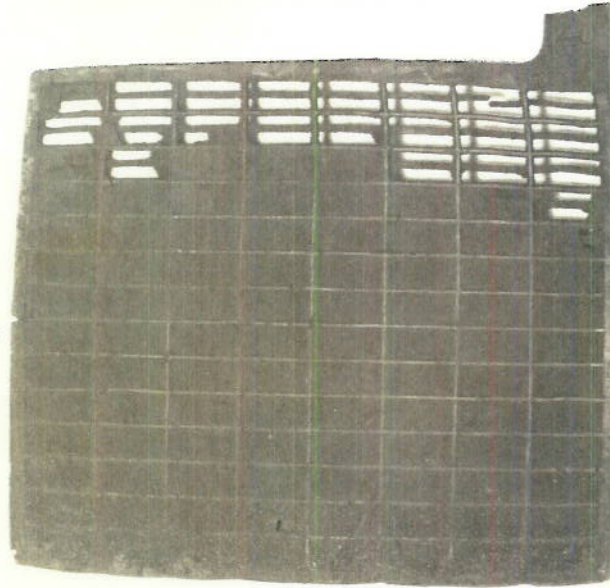
33. The Laboratory is of the opinion that a bottom-pour grid mold and casting equipment should be built, even if not finished in time for the present life-test. Such a molding equipment can be constructed at an estimated cost of \$600.00, including melting-pot, mold, cooling device, and equipment for convenient manipulation. It would serve not only for manufacture of life-test grids, but as a demonstration of the metallurgical technique applicable to these alloys when that stage of development is reached.

C



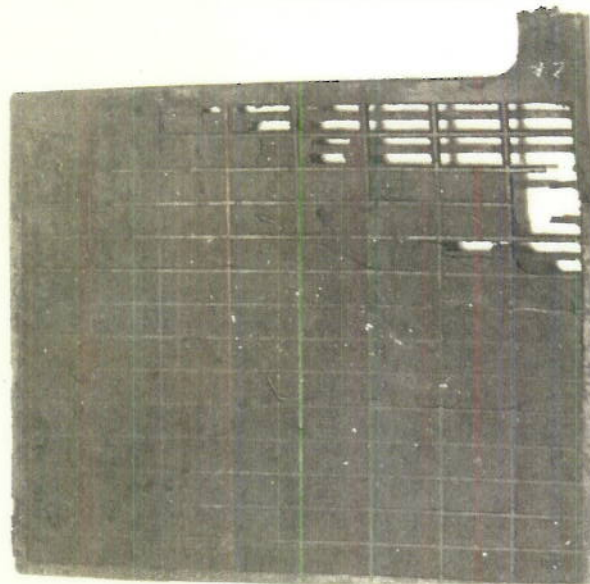
8% Antimony

B



Pure Lead

A



Navy Alloy No. 2.

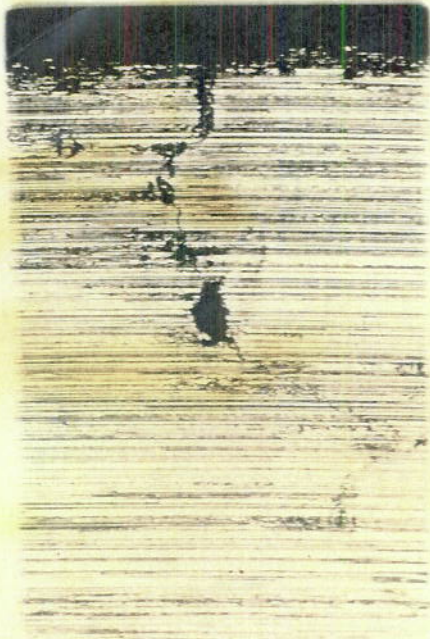


PLATE 2