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INVESTIGATIONS OF METHODS OF INCREAS-
ING LIFE AND CAPACITY OF LEAD ACID
STORAGE BATTERIES. I. PRELIMINARY
STUDY OF METHODS FOR EVALUATING THE
CORROSION RESISTANCE OF POSITIVE GRID
MATERIAL

BY

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- Report P-2908 -

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ABSTRACT

Theoretical considerations are given to the causes of corrosion of the positive grid, nature of the corrosion film, cause of gassing, overvoltage of hydrogen and oxygen, and contamination of the negative plate by transfer of antimony from the positive grid. Desirable grid and plate characteristics are discussed.

Methods of evaluating positive grid alloys are enumerated and experimental data given to allow correlation between laboratory tests and the behavior of the positive grid in service. The limitations of laboratory tests, particularly of short duration, to evaluate alloys are discussed.

The corrosion resistance of positive grid alloys is believed to be related to the character of the oxide layer formed by anodizing in sulfuric acid. A compact and adhering coating is necessary to protect underlying metal from further attack, while a flocculent layer allows continued attack of the grid.

The effects of heat treating and cold working antimonial lead alloys and the introduction of a small quantity of silver upon their physical properties and corrosion resistance are demonstrated. Although the particular heat treatment used enlarged the grain size of the alloys, it was beneficial in improving tensile strength. Corrosion resistance of low antimony alloys was adversely affected by the heat treatment. 1/10% silver was found to reduce grain size, improve tensile strength, and promote the formation of a compact and adherent corrosion film. A theory is presented to explain the behavior of silver and antimony as inhibitors of anodic corrosion of lead.

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I INTRODUCTION

A. Authorization

1. This study was authorized by Bureau of Ships letter S62-4 (660s-330) of 23 December 1942.

B. Statement of Problem

2. To investigate the possibility of improving the lead-acid storage battery. The present study has been specifically concerned with the improvement of the positive grid alloy.

C. Known Facts Bearing on the Problem

3. Among the possibilities of improvement of the lead-acid storage battery, increasing the corrosion resistance of the positive grid is among the most promising. Positive grids are subjected to severe anodic attack during the entire life of the battery and eventually disintegrate sufficiently so that the members are not continuous, active material is not held in place, and conductivity is not satisfactory. A second source of battery failure traceable to the positive grid is self-discharge of the negative plate (1, 2, 3). Antimony, which is usually added in quantities from 7 to 12% to inhibit positive grid corrosion and to give suitable strength, stiffness, and casting qualities, is transferred electrochemically to solution and redeposited on the negative surface. This antimony deposit eventually lowers the hydrogen overvoltage on the negative plate sufficiently to increase self-discharge of hydrogen. Self-discharge presents two serious problems with batteries used in submarines. First, self-discharge reduces battery capacity, and second, hydrogen is spontaneously eliminated which presents an explosion hazard. High self-discharge is usually accompanied by excessive hydrogen gassing during charging.

4. Ordnance applications of storage batteries require the highest weight and volume efficiencies compatible with other characteristics such as suitable life of the battery, high discharge and low self-discharge rates. The most obvious method of increasing battery efficiency is to design cells to contain more active material and less grid weight. Recent trends in battery requirements (4) point to higher one-hour rates. Higher discharge rates require the use of thinner grids so that more plates may be used per cell. Reducing the size of the supporting grid metal makes the plate more susceptible to failure by corrosion, buckling, or creep of the grid members.

5. Positive grid materials should possess the following characteristics:

(a) Positive grid material should not be appreciably attacked under operating conditions. Unless some commercially available inert metal or alloy can be found, which is not likely under the severe conditions mentioned, the positive grid will probably resist corrosion by the formation of an adherent, compact, conducting corrosion product on the metal surface. Only lead alloys have met this requirement.

(b) The positive grid alloy should contain no ingredients which would adversely affect the behavior of the positive or negative active

materials. This requirement eliminates appreciable quantities of metal less active than lead, since the extreme anodic conditions at the positive plate would cause them to dissolve. Once in solution, they would be reduced upon contact with the lead surface. Such impurities on the lead surface would probably ruin the voltage and capacity of the battery and permit excessive self-discharge. The presence of traces of such metals in the grid, however, may not be objectionable from this standpoint. In fact, a solution of the grid problem at this time seems to lie in finding an alloy containing small quantities of alloying metals which give the metal corrosion resistance but do not harm the battery performance.

(c) The grid must have such adequate physical properties as tensile strength, stiffness, conductivity, resistance to warping and creeping, and suitable casting characteristics. High antimony content facilitates casting, while lead alloys low in antimony are generally difficult to cast. If an alloy having satisfactory properties other than casting should be found, special methods such as pressure casting should be investigated. If satisfactory castings are not possible, it may be feasible to punch the grids from rolled metal or to weave grids from wire. Cold working of grid metal may have beneficial effects such as reducing grain size, reducing casting defects, improving physical properties, and increasing uniformity of composition. A second plan of attacking the grid corrosion problem lies in physical manipulation of the grid metal to create homogeneity of the alloy and to eliminate casting defects.

(d) The grid should be as light in weight and occupy as little volume as possible in order to attain maximum battery output per unit weight or volume. The high density of lead materials is unfavorable, but no grid made from lighter materials has been found which will withstand the corrosive action. A lighter weight grid metal which would withstand corrosion would be welcomed by the battery industry. Some chance of improving weight characteristics exists by using such light conductors as copper or aluminum for the grid core with a lead or lead alloy plating. Practical difficulties with such a scheme are all too obvious, however. One pin hole or imperfection in the lead coating would expose the copper or aluminum to the anodic corrosion, disintegrate the positive grid, and in the case of copper would ruin the negative plate by deposition of metallic copper on its surface. The admirable characteristic of the lead alloy grid of "self-healing" any break in the protective oxide coating is lacking in the case of the lead-coated copper grid. Lead plating lighter base metals may be applicable for preparing a primary one-shot or short life lead-acid batteries with maximum weight efficiency.

(e) The cost of the grid material must not be unreasonable. For ordnance requirements, cost increase might be justified if properties of the alloy were improved. The use of precious metals in appreciable quantities for grid alloys would not be justified, although from a standpoint of inertness some might have great corrosion resistance. However, traces of noble metals, such as platinum, on the negative plate would cause excessive gassing. In fact, introducing a trace of platinum into a cell is a most effective means of sabotage.

6. Previous investigations (5 to 9) are not entirely consistent regarding the type of alloy which would best serve as a positive grid material. All alloys which have shown promise during laboratory electrolytic and steam tests have not proven to be satisfactory when made into grids and tested in batteries. The difficulty of correlating arbitrarily designed laboratory tests with service conditions must be constantly kept in mind when reviewing this work and formulating new experiments. On the other hand, it is essential to devise techniques for studying suggested alloys under accelerated conditions, since the construction of hundreds of batteries with many alloy combinations and cycling them for several hundred cycles until failure occurs is an overwhelming task for any laboratory with a limited staff. An effort was made in this investigation, therefore, to study techniques of evaluating grid materials so as to be able to correlate these preliminary tests with behavior of the same grid alloys in storage batteries. Such experiments have a two-fold purpose of enabling one to accept or reject the significance of a laboratory test and to establish data which might shed light on the mechanism of grid alloying and treatment upon resistance to anodic attack. Also, preliminary experiments will expose obviously undesirable grid alloy properties and make it unnecessary to perform the time-consuming task of assembling storage batteries from them.

7. The latest NRL report on grid corrosion, (5) summarizes the results of life tests on storage batteries with grids made from 14 different alloys. This report states that grids made of lead containing 2-1/2% antimony and .05 to .10% silver resist attack better than standard grids made of 8 to 11% antimony and at the same time produce negligible sulfation and self-discharge of the negative plates. Reference (11) also indicates the beneficial effect of small percentages of silver upon corrosion resistance of lead alloys.

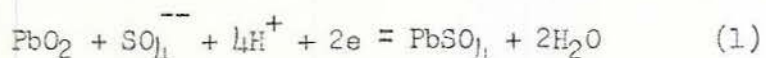
8. 2% antimony alloys have another interest from the standpoint of physical properties. If lead with antimony content of 2 to 3% is heat treated slightly below the eutectic temperature, 252°C, and quenched, a maximum in tensile strength is obtained which is even higher than that of 9 to 12% alloys (12,13). This heat treatment essentially creates a solid solution by allowing the alloy to attain equilibrium in the α area of Plate 3 (14,15). After quenching, the antimony-rich phase separates in the form of microscopic particles which impart excellent tensile strength to the alloy. In general, single phases are less susceptible to corrosion than multi-phase alloys, so at the start of this study it was thought possible that 2% heat treated alloys might have superior corrosion resistance and physical properties to the conventional 9% antimony grids.

D. Theoretical Considerations

9. While the immediate problem has been stated as grid improvement, the overall characteristics and requirements of a storage cell must be kept in mind when considering new materials. Much has been written regarding the nature and conditions affecting the reversible voltage of an electrode, but little has been offered to explain the behavior of an electrode subjected to current drain. Such behavior is complex and depends not only on such factors as the nature of the electrode, concentration and temperature of the electrolyte, but also on other conditions which will be discussed briefly.

10. On Plate 1, reversible solution potentials of lead - lead sulfate and lead sulfate - lead dioxide couples are plotted in order of increasing positive potential. These values (16) are positive or negative to the mercurous sulfate

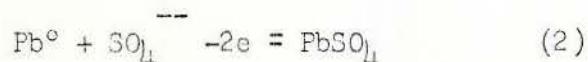
electrode which is arbitrarily assigned zero potential. Potentials may be displaced from these equilibrium values by connecting the electrodes to sources of higher or lower potential. Forceably displacing potentials will be resisted by the electrodes, however, by release or absorption of electrons by the circuit which tends to overcome the potential shift and return it to its open-cell value. Displacing an electrode negatively from its equilibrium potential causes it to act as a cathode (the pole of reduction), while displacing the equilibrium potential positively causes the electrode to act as an anode (the pole of oxidation). These considerations are valid for either an electrolytic cell operating from an external voltage source, or for a spontaneously operating system as the discharging storage cell. For instance, the reversible potential of the lead sulfate-lead dioxide electrode is +1.11 volts (referred to the mercurous sulfate electrode in 1.260 specific gravity sulfuric acid). This potential can be forced to some slightly more negative value, +1.10 volts, by connecting through a resistor to an electrode of more negative potential, i.e., the lead-lead sulfate system. The negative electrode would force electrons to the positive electrode which would immediately resist this disturbance by reduction of lead dioxide to lead sulfate with a consequent absorption of electrons,



This reduction would continue until the acid concentration corresponded to an open cell value of +1.10 volts for the positive pole or until all of the lead dioxide is exhausted.

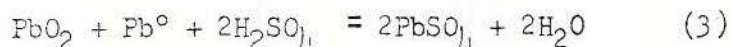
11. The behavior of the cathode electrode mentioned would be independent of the nature of the anode. It might be mercury-mercurous sulfate, or hydroxyl-oxygen as well as lead-lead sulfate. The potential behavior of the lead sulfate-lead dioxide plate would be the same with any companion electrode as long as the current density and electrolyte concentration and composition remained unchanged. Cell voltages, as contrasted to electrode potentials, however, would be very different for the three cases. In the case of the oxygen anode, an external voltage source would be necessary since the dioxide electrode would be negative to the gassing electrode. Referring to Plate 1, the cell voltages would be approximately 1.1, -0.4 and 2.0 volts, respectively. The dioxide plate potential could be followed in any case independently of the anode by referring it to a third reference electrode from which no current is being drawn to polarize it. The mercurous sulfate or cadmium electrodes are references commonly used.

12. An analagous situation would take place at the negative electrode connected to a cathode as described above. Forcing a lead-lead sulfate plate to a more positive potential than its equilibrium value would cause a liberation of electrons by that plate to the external circuit in order to resist the potential shift. Such a loss of electrons would initiate an oxidation of lead to lead sulfate.



13. The above two processes account for current produced when the poles of a lead-acid storage cell are connected. Each pole attempts to change the potential of the other, but if the current drain is not more than can be counter-balanced by the above mentioned oxidation and reduction processes, the potentials will remain only slightly displaced from their equilibrium values and the reaction of

equation (3) will result.



(See Figure A, Plate 2). If capacities of the plates are exceeded, or if a deficiency of either active material or electrolyte exists, electron production cannot keep up with the potential change, and the electrodes will attain the same potential, and the cell voltage will be zero.

14. The distance which a metal or metal ion is removed from its open cell potential is a measure of its tendency to be oxidized or reduced, provided that some rate limiting process is not governing the speed of oxidation or reduction such as an insoluble or slightly soluble surface film, a deficiency of electrolyte, or some overvoltage phenomenon.

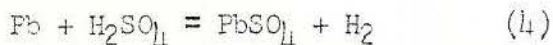
15. Following this same line of reasoning, it is easy to see why any metallic positive grid would be subjected to severe corrosive conditions. The grid would be forced to a potential much higher than its reversible value and would therefore be subjected to oxidation. If metallic lead is used for the grid material, the lead dioxide-lead couple would react as indicated by equation (3).

16. One may wonder why the grid is not entirely converted to lead sulfate. This process would occur if it were not for the fact that an adherent, non-permeable corrosion product must be formed on the lead surface which protects the underlying lead from further attack. The resistance of lead alloys to anodic attack in sulfuric acid is probably closely associated with the character of this surface film. Studies of corrosion of grid alloys should consider the chemical and physical nature of this film separating the potent lead-lead dioxide couples. The effect of alloying ingredients on the film is probably closely associated with an alloy's anodic corrosion resistance.

Spontaneous Gassing

17. Since the spontaneous gassing of hydrogen is one of the most formidable problems in the lead-acid battery, this reaction will be considered in detail. If a hydrogen electrode composed of hydrogen gas bubbling over a platinized platinum surface in 1.250 specific gravity sulfuric acid is allowed to attain its equilibrium potential, it will be 0.57 volts more negative than the mercurous sulfate electrode (Plate 1). If the potential of the same electrode were fixed at 0.91 volts more negative than the reference by shorting to a lead negative plate of high capacity, hydrogen gas would be vigorously liberated from the platinum surface. If a reversible oxygen electrode were fixed at a potential 1.11 volts more positive than the reference by shorting to a lead dioxide plate, oxygen gas would be liberated.

18. From the above, it might be expected that hydrogen gas would be formed at any lead surface in sulfuric acid and oxygen at any lead dioxide surface according to the equations:



19. If these processes did take place at any appreciable rate, however, the lead storage battery would be worthless, since its plates would spontaneously decompose in sulfuric acid. It is here that the unusually high overvoltage of hydrogen on lead and oxygen on lead dioxide save the situation. Even though potentials of lead plates are more negative than the hydrogen reversible potential, hydrogen is not reduced until the potential is approximately 1.3 volts more negative than mercurous sulfate due to the abnormally high overvoltage of hydrogen on pure metallic lead. A parallel situation exists at the positive electrode between lead dioxide and oxygen. This fortunate situation at the negative plate exists only if the lead is uncontaminated. If only a trace of platinum were deposited on a negative plate, the battery would become worthless due to the fact that hydrogen would be eliminated in preference to reduction of lead sulfate to lead. Other metals have the same effect as platinum, unfortunately, including antimony although the degree is less pronounced. It will be noticed by reference to Plate 1 that the positive plate is above the oxidation potential of antimony, which causes antimony metal to leach from the positive grid and enter solution as the antimonous ion. The negative plate is below the antimony reduction potential, so antimonous ion is reduced to metallic antimony on the lead surface. The "antimony black" has a much lower hydrogen overvoltage than does metallic lead, so hydrogen gassing can now take place at the lead potential. If this process is continued to excess, the battery would become worthless due to its inability to take and to hold a charge.

20. Gassing potentials of submarine cells in good condition (low self-discharge) and in poor condition (high self-discharge) are indicated on Plate 1. Open circles indicate hydrogen gassing potentials measured when charging a 9300 ampere hour battery at 300 amperes. The cell was in good condition with only seven cycles and a low self-discharge rate. The hydrogen gassing voltage of -1.40 volts indicates an overvoltage of 0.83. Solid circles indicate the gassing potentials of an old cell of 7450 ampere-hours capacity and a high self-discharge rate. Its hydrogen gassing voltage of -1.04 at 425 amperes was probably due to an accumulation of antimony on the negative surface which lowered the overvoltage of hydrogen to 0.47. Since the gassing potential at lower current densities would be more positive, hydrogen would be eliminated when the battery was on open cell or even when it was being discharged.

21. The higher positive gassing potential of the old cell is probably due to greater current density on the positive surface. The negative gassing potential of the old cell is more positive than that of the good cell in spite of its higher current density. It should be noted that cell gassing voltages can be misleading as an index of a cell's condition. In this case the voltages of the poor and good cell are almost identical (2.5 and 2.6 volts, respectively).

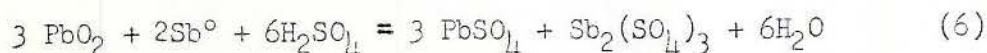
22. Electrode and electrolyte properties which are of practical interest when designing batteries are enumerated below:

- (a) The electrodes should resist excessive "polarization" when any appreciable current is drawn from them. Polarization may be due to lack of reducible or oxidizable compounds at the electrode surface, lack of sufficient electrolyte, excessive accumulation of reaction products, or the formation of an impervious reaction product at the surface which shuts out electrolyte. The last mentioned condition, while undesirable for active material, explains the corrosion resistance of lead in sulfuric acid.

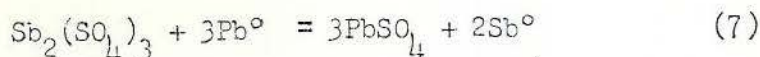
- (b) The electrode should not react spontaneously with the electrolyte. Most of the "active" metals which might otherwise be obvious choices of negative materials are eliminated by this stipulation. Magnesium, for instance, would be an excellent light-weight, high-potential negative if it did not react spontaneously with aqueous electrolytes to form hydrogen gas. Any metal more electronegative than hydrogen may displace the gas. Lead will generate hydrogen if coupled to a metal of low overvoltage, i.e., platinum or antimony.
- (c) Electrodes should have suitable potential characteristics. A low cell voltage might be permissible if the cell would deliver large currents without appreciable loss of voltage. The watt-hour capacity per unit weight or volume is a better index of a cell's efficiency than ampere-hour capacity.
- (d) The resistance of the electrode should not be large. Too large resistance would itself limit a cell's capacity in addition to causing unequal current distribution at high rates. To avoid high resistance it is desirable that both solid reactants and products at an electrode surface be conducting materials.
- (e) Electrolyte resistivity should be sufficiently low to permit passage of current without excessive IR drop. This factor prevents the use of most non-aqueous liquids for electrolyte solvents. Decreasing electrolyte resistance during high-rate discharge is another reason for increasing the number of plates per cell.
- (f) Electrolyte viscosity should be sufficiently low to permit rapid diffusion of spent electrolyte from the electrode surface.
- (g) The specific volume per unit of cell capacity for the positive, negative, and electrolyte should be sufficiently low to permit compact cell design. Dozens of combinations of electrodes could be used to make a battery if it could be of unlimited size. However, the volumes and weights of cells per unit capacity are too large in most cases to be practical.
- (h) Electrodes for storage cells have the additional requirements that after discharge the cell can be recharged by current reversal. After recharging, the electrode and electrolyte should be returned to their original condition and distribution. This stipulation permits only electrodes whose oxidized and reduced forms are both insoluble in the electrolyte to be used in reversible cells. Redeposition of soluble products by charging is generally not satisfactory for more than a few cycles because of uneven distribution on the grids and unsatisfactory physical form. It is this repeated cycling of a storage battery that promotes the disintegration of the positive grid. A loose, non-adherent corrosion film will not protect underlying metal, and will probably become dislodged from the grid metal during gassing of the positive plate at the end of a charge. Positive

grids with self-healing corrosion film would be necessary for long life.

23. Plate 2 shows three conditions which may be expected when two systems are connected to form a couple. Figure A supposes the anodic and cathodic sections to have equal capacity. When connected through a resistance, each is drawn from its open cell potential an equal amount, and when shorted the final potential is midway between the open cell potentials. This might represent a perfectly balanced lead-acid cell in a condition of open cell, discharge and dead short. Figure B represents systems in which the cathodic capacity is larger than the anodic capacity. The potential of the cathode is undisturbed by connecting the weak anodic area, either through a resistance or a short. This condition is realized when a speck of antimony is in direct contact with a large surface of lead dioxide in sulfuric acid. It is seen that the antimony speck held at the potential much more positive than its reversible value is subjected to a terrific oxidizing atmosphere.



24. Figure C represents systems where the anode has more capacity than the cathode and so is undisturbed when connected to a weak cathodic system. This is illustrated by antimony ion in contact with a large metallic lead surface in sulfuric acid. Here, the potential of the antimony ion in contact with lead is forced to a much lower potential than its reversible value and is accordingly reduced:



Processes B and C are the reactions by which antimony is transferred from the positive grid (B) to the negative plate (C).

II METHODS OF EVALUATING PROPERTIES OF GRID ALLOYS

A. Physical Properties

25. (a) Tensile Strength. Although grid alloys do not require great strength, they should have suitable stability to withstand normal handling and pasting and to resist deformation after cell assembly. The large submarine grids have an enormous total weight supported by the grid members, but the entire compact assembly is in turn supported by a heavy case. In some cases, pure lead negative grids have been used in submarine batteries. Considerable care must be exercised while pasting and handling these grids, but they apparently have sufficient strength. Since pure lead has a very low tensile value, it seems that this property is a desirable but not strictly necessary property of grid alloys.

Procedure A Tensile Strength Determination

26. Specimens were cast into 1/4 inch strips or into cylinders approximately 3 inches in diameter by 4 inches long. If the alloy was cold-worked, the cylinder was compressed to a slab approximately 1/2 inch thick by a 150-ton hydraulic press and rolled to approximately 1/4 inch thickness in a rubber calender. The 1/4 inch slabs were cut into pieces approximately 1/4 inch square by 3 inches long. A 2-inch center section was turned to a diameter of

0.20 inches. The specimens were heat treated in a thermostatically controlled oven and quenched in a dry ice acetone mixture or in ice water. A Dillon dynamometer and tensile machine was used to rupture the samples. A gear-reduced motor assured a constant rate of pull of 0.135 inches per minute. Elongation was measured by counting the gear revolutions after start of stress and until rupture.

27. The Dillon machine gives only approximate results since it was designed for much higher tensile specimens. For this reason, the following method has superseded Procedure A.

Procedure B Tensile Strength Determination, Improved Method

28. Specimens were cast into cylinders $3/8$ inches in diameter by 6 inches long. A section of the specimen was turned to 0.25 inches diameter as indicated by Figure B, Plate 6. Heat treatment was conducted in a electrically controlled constant temperature oven. Quenching was done in a dry ice bath or ice water bath. Specimens were ruptured by a Riehle Testing Machine operating at 0.2 inch per minute.

29. It is believed that for future work casting tensile specimens directly would be preferable to turning the desired shape on a lathe. Any type of physical treatment after casting will very likely affect the physical nature of an alloy, and properties may be different from those of the original cast specimen.

30. If the sample is to be heat treated or cold worked, this should be deliberately done under controlled conditions and compared with the original cast specimen. This effect of heat treating and cold working has been largely neglected in studies of grid materials.

31. A bothersome feature of casting tensile specimens is the presence of casting defects and "blow-holes" in the interior of a piece. X-ray examination of a reasonably thin specimen (0.070 inches) can be used to detect these casting flaws. Satisfactory conditions for taking X-ray photographs are reported by the Metallurgy Division as follows:

Machine used -	150 KV "Kaleket"
Tube Voltage -	145 KV
Exposure -	3000 ma second
Film -	48" Eastman type "F" between lead screens each .005 inches thick
Filter -	0.010 inch Lead Filter at tube
Development -	Regular X-ray

32. Stiffness, or the ability to resist deformation during charging and cycling of the positive plate is perhaps as vital a property as tensile strength.

33. (b) Hardness. Hardness is one of the physical properties of alloys which is probably not directly related to over-all battery behavior but has been found to correlate with tensile strength. Hardness of alloys change with composition, heat treatment and aging. (13)

34. Hardness measurements were made with the Knoop Hardness Tester which has found applicability in the determination of the hardness of individual grains

and segregations in metallurgical specimens because of the small area of the indentation. The load on the diamond indenting surface can be varied from approximately 100 to 1000 grams. The time of application of the load is fixed automatically at 20 seconds by a motor-switch arrangement.

35. To use the Knoop tester for lead and its alloys, it is advisable to use a load of approximately 200 to 500 grams to obtain an indentation which is not restricted to too small an area. Several measurements must be made, the average being used to evaluate the Knoop number. If several phases of rather large grain size of varying hardness are present in the specimen, it is necessary to recognize these phases before hardness measurements are made. The specimen must be approximately 1/4 inches thick and highly polished without inducing strains which will alter the hardness of the specimen. The length of the indentation is measured using a traveling microscope or a microscope with a Pilar micrometer eyepiece. Measurements made using the Knoop tester for pure lead and approximately 4% antimony-lead alloys have been reproducible.

36. (c) Conductivity. Conductivity is one of the important grid characteristics. The production of current by a battery requires the presence of a conducting medium to connect the active materials with the external circuit. Poor conduction would cause poor current distribution at high rates, and consequent loss of efficiency at high rates. Lead is not a particularly good conductor of electricity, but, as stated before, it is the only known available substance which can withstand the corrosive action to which the positive grid is subjected. Cell design for highest efficiency requires the use of optimum grid weights and cross sections. Too much grid will add unnecessary inert weight to the battery, while insufficient grid or faulty distribution of conducting members would cause poor current distribution or excess heating at high current rates. Conductivity of the corrosion product of a grid is essential to promote electrical contact between grid and active material.

37. Metallic conductivity can be accurately determined by passing a direct current through a standard resistance in series with the metal of unknown resistance. Measuring the voltage drop across a section of known length and cross section of the unknown will give the IR value of Ohm's law. The current, I, can be calculated by measuring the IR drop across the standard resistance, and the resistance of the unknown calculated. The use of low current and a sensitive potentiometer for the voltage drop measurement minimizes heating effects. The wire may be immersed in a water or oil bath for temperature control.

38. Lead alloy wire is extruded by pressing the heated metal through a die by means of a hydraulic press. Such extrusion naturally exposes the alloy to severe working and strain, the effects of which may be reduced by heat treatment. Conductivity has been used to study solid solubility of antimony in lead (17).

39. (d) Casting Properties. Casting qualities of alloys must be considered in the over-all problem. It must be expected that newly developed alloys may not have the admirable casting characteristics possessed by commercial antimony-tin-lead alloys. In order to evaluate the casting characteristics and to establish techniques for forming the metal, a study should be made covering such variables as mold and melt temperatures, mold venting, and design, surface coating, and other variables, correlated with the quality of the casting. Proper casting technique is an art which must be carefully considered. The presence of

casting flaws, blow holes, or alloy segregation may cause failure of a grid that might possess good properties if a more refined casting procedure were used,

40. It seems to be difficult if not impossible to perfect lead castings in which flaws can not be detected by means of X-ray examination. It is entirely possible that grid failures in some cases are due to casting flaws. It is characteristic of positive grids which have been in service to have local pits and cavities which may be exposed blow holes. This angle of establishing the best casting conditions from a standpoint of grid quality rather than from the standpoint of speed of production has probably received little attention from manufacturers and should be carefully investigated. The problem of obtaining good castings as the antimony content of alloys decreases will probably become increasingly acute. In general, pure lead and 9 to 12% antimony alloys are easy to cast, but low antimony alloys can be cast only with difficulty.

41. The problem of evaluating casting conditions is a complex one and should be treated both from the metallurgical and electrochemical standpoints. The grain size of a lead alloy casting, the mode of arrangement of the different phases present, the effect of traces of minor constituents in the lead alloy, which the metallurgist can evaluate physically, may be related to electrochemical behavior of the alloy when subjected to anodic attack. The latter problem is apparently little understood in the case of lead alloys. The role which antimony or other alloying constituents play in inhibiting anodic corrosion, for example, is not clear.

42. Metallurgical methods for studying the character of cast lead specimens are:

- (a) The use of photomicrographs. (18,19)
- (b) The use of radioactive antimony which would register an "autoradiograph" on photographic film. (20)
- (c) The use of "microradiography" transmission methods. (21)
- (d) The use of the "microanalyzer", and X-ray diffraction. (22)
- (e) Relating physical properties as tensile strength, conductivity, or hardness, to alloy structure. (18, 29, 30)

Electrochemical methods which might be used for studying the characteristics of castings are:

- (a) A study of potential gradients between different alloy phases. (23,24)
- (b) Studies of the open cell potentials and potentials of alloys when made anodes. (25)
- (c) The process of corrosion itself is essentially electrochemical in nature. An attempt should be made to relate casting conditions, alloy composition, including the effect of trace elements, and the corrosion characteristics.

Methods of evaluating corrosion properties of alloys will be considered in following sections.

B. Change of Resistance During Corrosion.

43. The corrosion of lead wire in acid vapors has been followed by resistance

measurement (26). Since the measurement of resistance of a wire is a simple and precise technique, such a method was thought to be a possible method of evaluating the corrosion resistance of an alloy. As the metal wire corroded, its resistance would increase and be a measurable record of the rate of attack.

Procedure C Resistance Method of Corrosion Evaluation

44. Wires approximately .038 inches in diameter were extruded from lead alloys containing 0, 2, 4 and 9% antimony by an electrically heated press. Eleven such wires were arranged in parallel around a central pure lead wire in a vertical tube and potentiometer connections made at the ends of each wire. Suitable connections were provided for connecting the cell to a 110 d.c. source with resistances to limit the charging current to 0.126 amperes. After an eight-minute charge, the cell was shorted through a 125 ohm resistance by an automatic time cycler, and the samples discharged for an eight-minute period. A diagrammatic sketch of the apparatus is shown by Plate 5.

45. Resistances of the wires were determined by interrupting the charging current and connecting each wire in series with a storage battery, standard resistance, and controlling resistance. The voltage drops across the standard resistance and corroding wires were measured by a sensitive potentiometer and the resistance of the lead wire calculated.

46. Resistances of the lead wires were measured before and after the introduction of 1.300 specific gravity sulfuric acid into the vertical cylinder. Since practically the same resistances were obtained for the two conditions, it was concluded that the presence of the slightly conducting acid did not affect the resistance of the wire conductor appreciably.

47. In addition to following resistances, the distribution of the charging current among the competing samples connected in parallel could be determined by measuring the voltage drop across each wire while the cell was carrying the total current. It can be shown mathematically that the total IR drop across the wire serving as anode is one-half the value that would be measured if the entire current leaving the wire were passing between the potentiometer contacts. Therefore, the IR drop of the anode multiplied by two and divided by the resistance of the wire gives the current leaving each anode.

C. Change of Weight of Specimen and Weight of Residue

48. Much emphasis has been placed in previous investigations upon the weight changes of the specimen being anodically corroded. It appears, however, that such a weight change, particularly during the first stages of corrosion, does not correlate with the ability of an alloy to withstand corrosion when used as a positive grid in a battery. For instance, a 9% antimony alloy has been found to lose more weight of residue than pure lead when anodically attacked during a time of three months. Also, more current is consumed by an antimony alloy during the first stages of corrosion at constant potential than pure lead. Experience has proven, however, that a 9% antimony alloy is superior to pure lead as far as corrosion tendencies of the positive are concerned. The type of attack, uniform, intergranular, intragranular, or penetrating, and the nature of the corrosion product, spongy, flocculent, compact, flakey, is significant in addition to the actual amount of residue or change in weight of the specimen.

49. A better method of conducting preliminary tests would be to run tensile strengths of the corroding specimens along with microscopic examinations to determine how much the corrosion is weakening the member. Also, the volume of the corrosion product is important. If the product is too flocculent as in the case of pure lead, it may cause "mossing", shorting or bucking of the cell sooner than a larger quantity of the compact corrosion product characteristic of 9% antimony. Also the conductivity of the corrosion product and its degree of adherence must be considered. For instance, an alloy which corrodes rapidly initially but which forms a thick compact, conducting corrosion product over the surface of the metal may be a very satisfactory grid material. In this respect, silver-bearing alloys seem to corrode more rapidly at first than pure lead or 9% Sb alloys, but the corrosion product is more compact and has less tendency to flake off, and the type of corrosion is more uniform with little tendency to form pits or intragranular crevices.

D. Evaluation of the Anodic Corrosion of Metals.

50. If a metal is at equilibrium with its ions in a given electrolyte, it exerts a characteristic potential which can be assigned a value as compared with some standard half-cell. Such potentials can be plotted in order of increasing positive potential as in Plates 1 and 2. If metals are forced to potentials more positive than their equilibrium values, they become "anodes" and are subject to electrolytic oxidation. This condition is realized by all metals composing the alloy of the positive grid in a storage battery, and it is of interest to develop controlled test methods to evaluate the tendency of metals to corrode when anodically polarized.

51. Figure A, Plate 4, shows the experimental procedure for studying the corrosion of metals whose potentials are fixed by being shorted to a positive plate. The sample does not have sufficient area to resist complete polarization by the large positive plate. The potential of the sample is therefore fixed at essentially the positive value as illustrated in the shorted condition of Figure B, Plate 2. A small one-ohm resistor is placed in the shorting circuit for measurement of electrolytic current due to the couple.

Procedure D Method of Evaluation of Anodic Oxidation of Various Metals in Sulfuric Acid

52. Metal samples were cut to a cross-sectional area of one square centimeter and polished with grit No. 1 or No. 4/0 emery paper. All metal surface and leads were heavily coated with bees wax to confine currents to the one square centimeter surface. The samples were shorted to a charged positive plate and immersed in a 1.300 specific gravity sulfuric acid as illustrated by Figure A, Plate 4. Currents were measured by a recording General Electric Potentiometer Recorder or a Rubicon Potentiometer. Potentials of the sample were measured with a potentiometer against the mercurous sulfate electrode. The experiment was conducted at room temperature which varied between 18° and 25°C. (Temperature should be controlled by a constant temperature bath in future experiments of this type).

E. Residual Current Method of Corrosion Evaluation

53. When subjected to anodic oxidation in sulfuric acid lead is peculiar in

that its oxidation product is an insoluble sulfate or the dioxide itself which is inert in the absence of reducing agents. After a sufficient coating of the oxidation product has been produced, the base metal will be somewhat protected from further attack due to the absence of electrolyte in direct contact with metal.

54. If the lead dioxide and metallic lead are separated in a beaker of acid and then connected by a shorting wire and ammeter, the rate of oxidation of the lead will be directly proportional to the current reading according to Faraday's Law. As the protecting film forms on the lead surface, the rate of oxidation and consequently the current will become less and less. Finally, after a considerable time, the current should furnish an index of the anodic corrosion resistance of the particular lead or lead alloy used. Initial currents measured by this method probably have little significance as far as corrosion evaluation is concerned, since the protecting film has not yet been formed.

55. Currents measured from competing alloys connected through low resistance shunts to the same source of positive potential should give an index of the relative corrodibility of the alloys, since by this method the potentials of the metals will be the same. (See Plate 9) After a time, the currents will be low and IR drop in the resistance windings will be negligible.

56. The method may be useful for determining the effect of several variables upon the corrosion rate. Such variables may be the composition, heat treatment, and physical working of the alloy, the potential at which the samples are held relative to the positive plate, the cycling sequence, degree of gassing permitted, and possibly physical straining of the metal in order to simulate the jarring action to which a storage battery would be subjected in use.

57. Perhaps the greatest difficulty with the above method is the task of distinguishing currents causing corrosion from other currents which are not related. If the analysis mentioned in section I-D were strictly true; that is, if lead dioxide were completely converted to lead sulfate at a potential slightly more negative than that of the lead dioxide-lead sulfate couple, then the residual current would be due to the oxidation of metallic lead to lead sulfate, the corrosion process which is desired to be measured. If this were the case, lowering the potential slightly would cause, if anything, a slight decrease in the oxidation current. Actually, lowering the potential slightly causes a reversal in sign of the current and a large reducing current to replace the small oxidizing current. This phenomenon is subject to several interpretations and is interesting at least from an academic standpoint. For the purpose of measuring corrodibility, however, sufficient measurements must be made to be assured that the current measured is a corrosion current and not an intermediate oxidation-reduction current. If potentials are held constant for a long period and temperature kept constant, it would be expected that the intermediate oxidation-reduction system would become dissipated and only the lead to lead sulfate current remain.

Procedure E Residual Current Method of Corrosion Evaluation

58. The apparatus used for the corrosion current method is shown diagrammatically by Figures A and B, Plate 9. Alloy samples were cast in 3/8 inch cylinders and turned down for tensile tests as shown by Figure C, Plate 9. A positive plate was used as a control electrode, and the samples of much smaller

capacity arranged at equal distances from the positive in 1.300 specific gravity sulfuric acid. Electrical connections between the samples and the positive plate were made with a variable voltage divider consisting of a 22-ohm, 50-watt rheostat. The variable contact was rotated at the rate of one revolution per hour by a clock motor. Since the center of the winding was tapped and connected to the positive plate, the potential of the samples would vary between more positive and more negative values than the positive plate to assimilate potentials experienced during charge and discharge of a storage cell. Included in the circuit were one-ohm resistors for each sample so that the amount and sign of current flowing from each sample as a result of the potential fluctuation could be measured by a Rubicon potentiometer or a General Electric recording potentiometer. After cycling the specimens for some time to build up an oxide film, the one-ohm resistor was arranged in parallel with a recording potentiometer and the cycling current recorded. After this, the cycling was stopped and the sample held at a fixed potential to allow the sulfate-dioxide current to dissipate and the lead oxidation current to be measured with the Rubicon potentiometer.

F. Photomicrographic Methods.

59. Specimen Preparation. Because of the relative softness of lead and the lead alloys, it is rather difficult to prepare a specimen free from deep scratches and cold worked metal; however, with care the true structure can be revealed. For lead and the lead-antimony alloys up to about 4% antimony, the microtome method has been used successfully (18). This procedure consists of mounting the specimen in a clamp and slicing thin sections of the metal with the microtome blade. To avoid the difficult sharpening of the microtome blade, replaceable blades (Stanley No. 1991) can be used.

60. With an antimony content above 4% it becomes increasingly difficult to prepare a specimen suitable for metallurgical examination by the microtome method because of the hard crystals of segregated antimony. In this case, the specimen is ground successively on No. 1, No. 0, No. 00 emery paper, and finally on No. 000 which has been used previously. The emery papers should be smeared with a solution of paraffin in kerosene.

61. After the sample has been prepared by either of the above methods, the final polishing is done on wet cloth covered with Fisher Polishing Alumina grade No. 3. The specimen is held very lightly against the nap during the final stages of the polishing.

62. After polishing, a thin film of cold worked metal will almost certainly be present. This is removed to a large extent during the etching process. It may be necessary to repeat the polishing and etching several times depending upon the thickness of the cold worked surface. There are several good formulas for etching reagents suitable for lead and lead alloys. One that has been useful is: three parts of glacial acetic acid to one part of hydrogen peroxide. After an etching time of from one to five minutes, the samples are immersed in concentrated nitric acid and rinsed quickly with distilled water. Another etching procedure which is reported to be effective is anodic polishing in perchloric acid solutions (12).

63. The corrosion of lead alloys can be followed microscopically by subjecting microtomed specimens to anodic attack in sulfuric acid to simulate conditions present at the positive grid of a battery. Photomicrographs are taken at various

time intervals to follow the progress of corrosion and to determine which phases of the alloy are resistant and which are attacked. Grain structure and phase distribution can be observed after these anodic etchings.

64. Photomicrographic Technique. It is difficult to specify a set of conditions which will guarantee photomicrographs representing the true character of a variety of specimens, for the conditions such as lighting, exposure time, type of film, etc., vary with the subject.

65. The Palo copying camera has been adapted so that it is capable of yielding good results. A sponge rubber ring adapter has been made which fits over the eyepiece of the microscope thus preventing the fogging of the film because of light leakage. The copying camera is equipped with a plate holder which accommodates a 9 x 12 cm. cut film adapter.

66. The copying camera is mounted on the vertical support and is adjusted so that the lower end of the bellows just rests on the rubber ring adapter. The bellows are then extended until the proper size field is obtained. The final adjustment of the focus is made using the microscope and the ground glass plate.

67. The proper illumination of the subject will require some experimentation. Blue light often results in greater resolution and proper filters may be used if it is desired to give contrast to the specimen. A text of photomicrographic procedures has been prepared by Shillaber (19).

G. Decrease of Tensile Strength During Corrosion.

68. One of the most popular means of evaluating corrosion resistance is to compare the tensile strength of a corroded and uncorroded control specimen. This test is a significant one in the case of grid alloys, since it uncovers defects that might otherwise escape notice. With deep intragranular attack, the alloy might have a good external appearance but would crumble if placed under stress. Examination of the broken section might give clues as to the cause of failure (i.e.) (intragranular attack or casting imperfections). This effect would cause a positive grid to fail in service by physical disintegration and by loss of conductance.

Procedure F. Tensile Strength Method of Corrosion Evaluation

69. Lead-antimony alloys were prepared by melting pure lead and commercial 4 and 9% antimonial lead alloys in desired proportions in a graphite crucible. Heating was accomplished in an electric furnace controlled by a glass encased iron-constantan thermocouple immersed in the melt and a Tagliabue potentiometer controller. Melt surfaces were covered by powdered graphite to reduce oxidation, and the liquid metal was stirred by means of a graphite rod to assure uniformity.

70. In case silver was used in the alloy, weighed silver foil was fused in a small lead button on the bottom of a graphite crucible by means of an oxygen gas torch. Lead was gradually added to the button until it weighed about 200 grams. This large button was then melted with the lead-antimony alloys as described above.

71. A thermocouple was inserted in one mold section before casting in order to secure time-temperature records during the solidification of the casting. All

specimens were turned on a lathe to resemble Figure B., Plate 6. Two samples from each casting were heat treated in a constant temperature oven held at 235°C for 16 hours and then quenched in ice water. This treatment was chosen, since it gave a maximum tensile strength with the 2% antimony alloy. Two untreated specimens from each batch and two heat treated specimens were mounted in a 4 oz. glass jar, 2 inches diameter by 2 inches high (Figures A and D, Plate 6) with a sheet lead cathode. The assemblies were filled with 1.30 specific gravity sulfuric acid, the 28 cells arranged in series and charged at .380 amperes continuously. (Figure C, Plate 6) Since 26.8 sq. cm. of anode area was exposed, this rate corresponded to a current density of 1.4 amperes per sq. cm. The specimens were discharged twice daily by shorting the cells through a resistance.

72. Charging potentials with a mercurous sulfate reference electrode were recorded. After the corrosion period the cells were disassembled and the anodes, cathodes, and residue in the cell bottoms examined and weighed. The specimens were photographed and they and the controls broken by a Thiele tensile machine, operating at a speed of 0.2 in. per minute.

73. As previously stated, it is now believed that more significant results can be obtained by using cast tensile specimens, X-rayed to detect casting flaws. If samples are altered in any manner after casting they should be treated under controlled conditions and compared with untreated specimens.

H. Effect of Alloying Constituents upon Cathode.

74. A requirement of a satisfactory positive grid alloy is that it not only possesses resistance to corrosion but also in no way adversely affect the negative plate. High antimony content positive grids have good corrosion resistance, but the antimony leaching from the grids deposits upon the metallic lead surface at the negative plate and causes hydrogen gassing.

75. Methods of checking the effect of an anode upon the lead cathode include measuring the gassing and open cell potentials of the negative plate, chemical analysis of the negative, and spontaneous gassing of the negative plate. The voltage of the gassing specimen as taken against a standard mercurous sulfate or cadmium electrode serves as an indication of a healthy or contaminated negative plate.

76. Time-potential behavior of a lead specimen can be correlated with lead purity. Reference (25) points out that pure lead will hold its potential in sulfuric acid for 10 hours, while 9% antimonial lead becomes sulfated in one hour, after which the potential fails.

77. Surface impurities may impart their characteristic potential to a metal or may cause inflections in the voltage-time curve when a small current is carried by an electrode. The presence of impurities on a negative plate can, of course, be detected by usual procedures of spectrochemical, or polarographic analysis.

78. The quantity of gas liberated per unit time per unit capacity of a given acid concentration and constant temperature is a measure of the self-discharge of the negative plate. Reference (27) also describes a method for following self-discharge by the change of weight of a negative plate. Allowing a charged battery to remain on open cell for a week or so and comparing its capacity after that time with the capacity immediately after charge is a practical test of the ability of a battery to hold its charge.

I. Properties of Storage Batteries Made from Grids of Varying Composition

79. The ultimate test of battery design is to assemble complete cells and to cycle them competitively with suitable control cells until failure occurs. This practice is avoided as much as possible in preliminary work due to the overwhelming task of manually constructing the cells and following them for as long as one to two years during a life test. This procedure is unavoidable, once factors are fairly well established by preliminary tests.

80. Extensive work on fabrication of storage cells has not as yet been done by the Laboratory. Methods used to date are described in this section, however, as a matter of record.

81. Grid Casting. One of the most highly skilled arts in battery fabrication is casting the lead alloy grid. Battery grids have rather intricate forms involving a large number of fine members. High antimony alloys are much more easily cast than low antimony, probably due to the eutectic properties and low melt viscosity (28). One of the practical advantages of high antimony alloys in addition to corrosion resistance is the ease of casting. As the antimony content is decreased to approach values around 2%, the eutectic solidification temperature is still maintained at a temperature of 252°C, but the melt must be held at a temperature considerably above the usual temperature when 9% antimony is used, probably to compensate for the higher viscosity values of the low antimony alloys. This requires that melt temperatures for low antimony alloys be high and mold temperatures be low, a rather unsatisfactory casting combination. Evaluation of casting characteristics up to this time has been to vary melt and mold temperatures until full grids are obtained. The study of casting technique involves many factors in addition to melt and mold temperature. The mold design is very critical. Battery engineers indicate that only a few men in the country have had sufficient experience to design grid molds. Venting of the mold is important as well as the surface coating and method of application. Powdered cork suspended in water is reported to be an excellent mold coating. Timing of the cycle of operation of continuously operating molds is critical. Working out best casting procedures for an alloy is hence a difficult job but must be considered in the over-all problem of making battery grids. The most corrosion resistant alloy in the world would be worthless as a grid material unless some means can be found to fabricate it to the desired grid form.

Procedure G. Method of Casting Grids.

82. Casting temperatures for S.L.I. Grids were as follows:

<u>% Antimony</u>	<u>Melt</u>	<u>Temperature</u> <u>Mold</u>	<u>Comments</u>
0	420-430°C	250-270°C	
2	510°C	215-220°C	Imperfect grids due to shrinkage cracks.
4	480-490°C	215-220°C	
9	440-460°C	220°C	

83. The above table correlates melt and mold temperatures that have been used for grid casting at various antimony concentrations. This has not been an extensive study, but temperatures at which full castings have been obtained are indicated. At times the quality of the casting has not been good. For instance

in the case of 2% antimony alloys shrinkage cracks were present in all grids. There is always a possibility that with different conditions or a more skillfull mold operator that better grids could be cast from this alloy.

84. A mold purchased from the Aljon Speciality Company was used for all grid casting. A description of the mold and of grids cast is given in reference (6). The mold was equipped with four 600 watt, 230 volt cartridge heaters imbedded in the mold faces. Voltage applied to the heaters was controlled by a variable transformer which was operated by a reversing motor controlled by a Leeds and Northrup potentiometer-controller. Chromel-alumel thermocouples imbedded in the mold faces were thus used to control mold temperature. Wide temperature variation would be experienced if the reversing motor were allowed to turn the transformer from one extreme range to the other (0 to 230 volts), but much more sensitive control could be experienced if a range of only a few volts is set, the lower voltage being just insufficient to keep the mold at the desired temperature, and the higher voltage a bit more than necessary to hold that temperature. Both mold faces were coated with "Molspray" by means of an air-sprayer. Antimony alloys were prepared by mixing commercial 9 and 4-1/2% antimony-lead alloys with pure lead to secure the desired antimony content. All heating was done over gas burners in a graphite crucible. Molten metal surfaces were covered with powdered graphite to inhibit oxidation. Silver alloys were prepared by fusing silver foil with a small lead button by a oxygen-gas torch, and gradually diluting the button with lead-antimony alloy in the graphite crucible. Melt temperature was controlled by manually regulating the gas heaters and were measured by a glass-covered chromel-alumel thermocouple and millivoltmeter pyrometer, or recording millivoltmeter.

85. After mold and melt were conditioned to the desired temperatures, the alloy was manually poured from the graphite bottom-pour crucible into the mold. Sufficient time was allowed for the gate to solidify or, if the mold temperature tended to rise during continuous casting, water was squirted on the gate to hasten solidification and to bring the mold down to the desired temperature.

Procedure H Evaluation of Alloy Corrosion Resistance by Use in Storage Cells.

86. Pasting grids with active materials was done manually. Large batches of active material were mixed by a Readco mixer, while smaller quantities were mixed by hand, using glass apparatus and plastic spatulas.

87. Preparation of Positive Active Material. The following formula was used in preparing the positive active material:

Eagle-Pitcher 18-F-W oxide	4.33 lbs.
Water	273 cc.
Acid (1.327 specific gravity)	138 cc.

The dry oxide was first mixed manually with 250 cc. of distilled water until a smooth paste was obtained. The acid was gradually mixed with the paste. 1.327 specific gravity acid was chosen, since this strength does not change the consistency of the paste appreciably. After all of the acid was added, the additional water was added to thin the paste to a workable consistency.

88. Preparation of Negative Active Material. The following formula was used

in preparing the negative active material:

Eagle-Pitcher-1-F oxide	8 lbs.
Water	400 cc.
Acid (1.327 specific gravity)	240 cc.

The dry oxide was added to the "Readco" mixer and about 370 cc. of distilled water added. The acid was then added and additional water until the consistency was correct.

89. Density of the paste was determined by filling a small porcelain casserole of known volume (approximately 2.5 cu.in.) with paste, scraping off level, and weighing.

90. Paste was applied to the weighed grids by laying the latter horizontally on a plastic sheet and newspaper. Paste was worked into the grid by a flat plastic spatula and the excess removed by scraping the grid surface. Newspaper and plastic sheet were laid on top and the plate reversed, the newspaper removed from the unfinished side, and the process repeated until a smooth, flush surface was obtained. The plates were removed from the paper, loose active material scraped from the edges and the plates weighed. The plates were dipped in 1.100 specific gravity sulfuric acid for two seconds to set the paste and inhibit cracking, and then air dried at room temperature for several days.

91. Both positive and negative plates were formed in 1.050 specific gravity acid against pure lead dummy grids at 1.5 amperes per plate for 48 hours. After formation, the plates were burned in groups of two positives and three negatives with 0.55 inch centers. Positive plates were wrapped with 0.030 inch glass retainers held in place by 0.015 inch hard rubber retainers. Wood submarine separators with .120 inch ribs and .048 inch webs were placed between the hard rubber retainers and the negative plates.

92. The assembled cells were placed in a hard rubber case with inside dimensions 5-7/8 inch x 1-5/8 inch x 7-1/8 inch deep with 3/4 inch sediment space, acid added to the cells and the specific gravity adjusted to 1.260 during the first two cycles of charge and discharge. Routine cycling was done by an automatically controlled system which charged and discharged the cells four times a day.

93. An analysis of the six-hour cycles is as follows:

	<u>Rate in Amperes</u>	<u>Time</u>	<u>Ampere Hours</u>
Charge (high rate)	0.75	1.77	15.5
Charge (low rate)	1.60	2.52	4.04
TOTAL CHARGE		4.29	19.54
Discharge (constant current)	10.9	1.65	18.0

The high rate charge was calculated to replace 86% of the discharge during the 1.77 hour period and an additional 22% of the discharge replaced at a low rate to avoid vigorous gassing and over-heating. Cells were placed in a water bath kept at a constant temperature of 77°F during their life cycling.

94. Capacity discharges were run every 25 cycles to check the condition of each

cell. Current was controlled by placing the cell in series with the 110 volt d.c. line. Capacity discharges were conducted as follows:

- (a) Equalizing charge of 1.5 amperes for 16 hours after a low rate charge.
- (b) Six hours on open circuit before capacity discharge.
- (c) Capacity discharge at 5.0 amperes to 1.70 volts per cell.
- (d) Charge at 2.0 amperes for 12 to 16 hours before cycling.

95. Single plate potentials during charge and discharge were determined by measuring the voltage between the negative plate and a cadmium stick which had previously been soaking in sulfuric acid, using a voltmeter having a resistance of 1000 ohms per volt. Readings were checked with a potentiometer to be sure that the cadmium electrode was not being polarized.

96. Gassing of the cells was measured by displacement of water in inverted burettes. To check for leaks which would give an erroneous gassing rate, a slight vacuum was applied to each cell and manometer readings recorded. An unchanging manometer reading indicates tight connections. Leaks in cells were sealed with battery sealing compound or beeswax. To check cells for leaks and shorting, they were charged at 1.00 amperes after a long charge and the volume of gas measured until it reached a constant value. The theoretical volume of oxygen and hydrogen at 0°C and 1 atmosphere pressure should be 10.46 milliliters per ampere-minute.

J. Constant Current - Voltage Relations

97. A simple technique of obtaining electrochemical data for metals in contact with electrolyte is to record their potential under different conditions of constant current between the metals and a companion electrode. The method has been used to determine relative rates of self-discharge of lead and its alloys. (25)

98. The sample of known area and with a surface prepared by some reproducible method, i.e. metallographically polished (12), is made either anode or cathode by means of a high voltage d.c. source with suitable resistance to limit the current to the desired value. A recording voltmeter is then used to plot the potential of the specimen against a standard inert electrode, i.e., the mercurous sulfate electrode in sulfuric acid.

99. The recording voltmeter must possess several characteristics not commonly found in commercial instruments. It must be suitably sensitive, fast, stable, and of high input impedance in order to record all potentials and inflections without polarizing the reference electrode or the specimen. Conventional self-balancing potentiometers are not satisfactory for this purpose, since they draw appreciable current when off-balance and would polarize the cell. Some electronic system similar to the L & N "Glass Electrode Recorder", or L & N "Thermionic Amplifier" used with a recorder as the "Micromax" are perhaps the best known commercial instruments which might meet some of the requirements. This Laboratory has used the R.C.A. "Volt-Ohmyst, Jr." in conjunction with a "Micromax" or a "Brown" potentiometer recorder to record potentials of storage cell plates.

III THE PHYSICAL EFFECTS OF HEAT TREATMENT AND AGING LEAD-ANTIMONY ALLOYS

100. The effect of heat treatment and aging on the physical properties of lead-antimony alloys was studied in an effort to obtain a positive grid material which has the necessary strength but does not permit antimony to leach into the electrolyte in large enough quantities to interfere with desirable negative plate characteristics. It was thought that if the antimony content were reduced to approximately 2% so as to exist in the form of a solid solution with lead, this single phase might be more resistant to chemical attack and yet possess the necessary strength. 2% antimony-lead alloys have been of considerable interest as material for telephone cable (12), and much work has been done by Dean (12) in the direction of producing a strong alloy with 2 to 3% antimony content. It was thought expedient to duplicate some of this work to establish techniques, tie in with the literature (12) and then to test the corrosion resistance of the low-antimony alloys.

Procedure 101. Alloys were prepared by diluting commercial 4% antimonial lead with refined lead. Silver alloys were prepared by heating a button of the antimonial lead alloys with a weighed quantity of silver foil on charcoal and dissolving the antimony-silver-lead button in the desired quantity of antimonial lead. Specimens were prepared and treated as described in Procedure A of Section II-A.

TABLE I

Effect of Aging on Tensile Strength and Elongation of 2% Sb-Pb Alloy (Cold rolled, 95% reduction, heat treated for 92 hours at 240°C, dry ice quench)

	<u>Aging Period</u>	<u>Tensile Strength</u> (lbs. Sq. In.)	<u>Elongation</u>
Control	No Heat treatment	3500	45%
	24 hours	7550	--
	7 days	9250	5
	14 days	7800	4
	22 days	7050	7

These results are plotted on Plate 7.

Conclusions 102. (a) The tensile strength of 2% antimonial lead increases very rapidly after the specimen is removed from the oven and quenched.

(b) The tensile strength is not constant but rather reaches a maximum and then tapers off. After 22 days the tensile was twice that of the unheat-treated specimen.

(c) The maximum tensile strength was observed after 7 days, and this value exceeds that of the unheat-treated 10% antimonial lead alloy.

(d) The elongation decreases as the tensile strength increases.

(e) This behavior is well explained by the theory of "precipitation hardening" (13). The antimony is taken into solution by long heating at 240°C, (See Plate 3), and is uniformly precipitated in a micro form from a supersaturated solution during a long period after quenching. The resulting finer-grained alloy has different properties than the original alloy with macro crystals of antimony.

TABLE II

Effect of Length of Heat Treatment on the Tensile Strength of the 2% Sb-Pb Cast and the 95% Reduced Specimens. (Heated to 240°C, pulled after aging 24 hours, ice quench)

<u>Time at 240°C</u>	<u>Cast</u> Tensile Strength (Lbs. / Sq. In.)	<u>95% Reduced</u> Tensile Strength (Lbs. / Sq. In.)
0	3580	3550
1 hour	6960	6120
2 hours	6820	7660
8 hours	7200	7585
16 hours	7600	8170
48 hours	6550	8500
3 days	7300	7665

These results are plotted on Plate 8.

Conclusions 103. (a) A heat treatment of one hour was sufficient to nearly double the tensile strength of both cast and reduced samples. Little change was observed after one hour's heating.

(b) The optimum time for heat treatment is about 16 hours for maximum tensile of unreduced 2% antimonial lead alloys.

(c) Reduced specimens were slightly stronger than unreduced alloys.

TABLE III

Effect of Heat Treatment at 232°C, on Tensile Strength of the 1% Sb-Pb 95% Reduced Alloys. Aged one week.

<u>Time at 232°C</u>	<u>Tensile Strength</u> (Lbs. / Sq. In.)
1/2 hour	3430
1 hour	3590
4 hours	3230
8 hours	3210
24 hours	3000
48 hours	3000
1 week	3130

These results are plotted on Plate 8.

Conclusions 104. (a) No pronounced increase in tensile was noted after heat treatment of the 1% antimonial lead alloy.

(b) The tensile strength varied very little from 1/2 hour of heating to 1 week at 232°C.

(c) Apparently most of the 1% antimony remains in solution. The small amount precipitating from saturated solution does not effect the physical properties of the alloy.

TABLE IV

Effect of Heat Treatment at 232°C on the Tensile Strength of 2% Sb-0.1% Ag-Pb Alloys. Aged one week.

<u>Time at 232°C</u>	<u>Tensile Strength (Lbs. / Sq. In.)</u>
1/2 hour	6090
1 hour	8750
4 hours	10200
8 hours	8730
24 hours	8425
48 hours	8900
1 week	8690

These results are Plotted on Plate 8

Conclusions 105. (a) The incorporation of silver (0.1%) gave a higher tensile strength than the alloy without it.

(b) The maximum tensile was obtained after 4 hours at 232°C.

Summary 106. The above results confirm and augment the work of Dean (12). It is apparent that physical properties of lead are affected not only by composition but also by the history of the sample, particularly its heat treatment and aging. Improvements in tensile strength of lead alloys may or may not be accompanied by improvements in corrosion characteristics. The latter property will be considered in following sections.

107. It must be realized that precise tensile measurements are very difficult to make. It is almost impossible to cast perfect specimens in which blow holes cannot be detected. When turning a specimen, it is likely that this working will affect its properties. The above results must be taken only as orienting experiments. If significant results are desired, sufficient quantities of each type of treated alloy must be tested in order to provide statistical data to which significant tests could be applied.

IV EVALUATION OF ANODIC CORROSION OF METALS BY THE FIXED POTENTIAL METHOD

A. Electrolytic Oxidation of Various Metals.

108. Samples of various metals were prepared as described by Procedure D in Section II. Specimens were shorted to a positive plate through a one-ohm resistor and immersed in 1.300 specific gravity sulfuric acid. The corrosion

current was measured immediately after immersion and for a period of 5 days unless otherwise noted. Table V gives the corrosion currents at the end of 10 minutes and after 5 days. Samples denoted by asterisk disintegrated before the longer period was reached.

TABLE V

Corrosion Currents from Anodic Oxidation of Various Metals
Coupled to a Lead Dioxide Plate in Sulfuric Acid

Element	Corrosion Current in Milliampères		
	10 minutes	5 days	
Si	0.22	0.004	
Se	0.00	0.012	
Pb	0.02	0.014	
Ag	0.89		0.051 *Stopped at 43 1/2 hrs.
Ta	0.00	0.14	
Sb	1.53	0.17	
Fe	0.36	0.22	
Bi	0.37	0.32	
Sn	1.27	0.59	
Te	22.80	1.89	
Cu	9.01	7.39	
Al	1.85	11.40	
Co	7.10		20.00 *Stopped at 6 1/2 hrs. Gassed
Ni	50.60		61.40 *Stopped at 26 1/2 hrs.
Mn	62.70		92.00 *Stopped at 6 1/2 hrs. Gassed
Cr	160.0		156.0 *Stopped at 6 1/2 hrs.

109. The magnitudes of residual currents show the unusual property of lead of sealing its surface to allow little oxidation of the base metal. Antimony, used as an alloying ingredient, has a residual current over 10 times that of lead, so it is understandable why antimony leaches from a positive grid into solution. Attempts to correlate change in weight of the samples with theoretical values obtained by the application of Faraday's Laws were not generally successful. In some cases as in the case of cobalt and manganese, a large deviation from calculated weight changes showed that other reactions were taking place other than electrolytic oxidation.

B. Electrolytic Oxidation of Lead Alloys.

110. The measurement of the electrolytic current produced by shorting a lead alloy to a positive plate is believed to be a simple and effective manner of evaluating corrosion resistance of the alloy. Precautions must be taken to be sure that currents are due only to corrosion of the surface being investigated, the leads and other surfaces of the metal being protected by some good non-conducting and adherent film. Considerable trouble was experienced with corrosion of copper leads during initial experiments, so it was finally decided to make the lead material from the alloy being investigated and to coat

all except an exposed area of 6 sq. cm. with vinylite and paraffin. After one day or so, acid worked under the protective coating and increased the effective surface, so the results are given for 10 minutes and 3 hours time to demonstrate the method. Four to six samples of each alloy were studied in order to obtain some idea of reproducibility. Voltages of samples were made positive to a lead dioxide plate by the device shown by Figure B, Plate 4, and the results given in Table VI.

TABLE VI

Corrosion Currents from Anodic Oxidation of Antimony-Silver-Lead Alloys when Made Positive to a Lead Dioxide Plate in Sulfuric Acid

Current in Milliampères

	<u>10 Minutes</u>		<u>3 Hours</u>		<u>Voltages</u>	
	<u>%Sb</u>	<u>1/10% Ag No Ag</u>	<u>1/10% Ag</u>	<u>No Ag</u>	<u>Positive Plate</u>	<u>Samples</u>
0	.38±.06	.20±.02	.35±.02	.14±.03	1.22	1.35
1	.37±.02	.42±.01	.20±.02	.13±.02	1.21	1.34
2	.20±.03	.22±.03	.20±.03	.16±.03	1.23	1.36
3	.21±.03	.19±.01	.23±.01	.16±.01	1.23	1.36
4	.21±.12	.18±.04	.17±.04	.20±.04	1.20	1.37
9	.19±.03	.29±.06	.27±.03	.24±.04	1.25	1.34
12	.22±.01	.30±.06	.24±.01	.25±.03	1.24	1.37

111. There seems to be a general trend for silver-containing alloys to corrode more rapidly during the first three hours than those without silver. In order to have significance, this type of test should be continued for a period of months to obtain a true "residual current", that is, the current after a heavy corrosion film has formed on the sample's surface.

C. Electrolytic Oxidation and Reduction by Controlled Potential Cycling.

112. This technique of evaluating the corrosion resistance of grid alloys consists in measuring the current consumed or released as specimens of uniform surface area were competitively cycled at identical potentials. (See Section II-D) The purpose of such cycling was two-fold: First, the alloys are subjected to the same potential variation in sulfuric acid as the grid of the positive plate. Second, the oxidizing or reducing currents exhibited when each specimen was held at potentials more or less positive than the equilibrium lead dioxide potential would give information regarding how rapidly the alloy was developing Planté capacity. The rate at which an alloy developed capacity was at first thought to be inversely correlated with its corrosion resistance, but after investigating many samples, it appeared that the reverse situation was more nearly true,-- that is, the formation of a heavy corrosion layer of lead dioxide upon the metal surface is favorable toward corrosion resistance provided that this coating is compact and adherent. Eventually, perhaps after several months corrosion, the heavy, compact, adherent coating of lead dioxide would prevent further attack upon the metal beneath the oxide coating. If the

oxide coating was non-adherent or flocculent in nature, however, fresh metal would continually become exposed, and the base metal would eventually be consumed by the corroding current, particularly if the sample were gassing all or part of the time.

113. Parts A and B of this section describe techniques of measuring anodic currents when samples are held at fixed potentials relative to a positive plate. By a slight modification, the sample can be made to cycle between potentials more negative and more positive than the positive plate to simulate potential changes actually experienced by a pasted grid. A 22-ohm rheostat was altered so that the rotor could be continuously revolved by a clock mechanism operating at one r.p.h. By tapping the center of the rheostat and using the windings as a voltage divider, it was possible to change sample potentials to more positive or negative values than the positive plate as shown by Plate 9. Procedure E, Section II, described the experimental procedure.

114. When the specimens were cycling, a General Electric Potentiometer Recorder was attached to the one-ohm resistor to measure the charge and discharge characteristics of the active surface. The currents were of much larger magnitude than the residual currents due to metallic lead oxidation. Typical charge and discharge cycles are plotted on Plate 10 for pure lead with and without 1/10% silver. For two types of cycling procedures (Figures A and B, Plate 10), the silver alloy gave more capacity on discharge and absorbed more current on charge. This type of experiment might be used to test active materials, their relative capacities, potential characteristics, adherence to the grid, or effect of traces of metals other than lead or of organic addition agents.

115. Table VII lists the charge and discharge capacities represented by areas under plots similar to Plate 10 for all alloy compositions investigated.

TABLE VII

Charge and Discharge Capacities of Antimony-Silver-Lead Alloys

Alloy		Cycle "A"				Cycle "B"			
		Charge		Discharge		Charge		Discharge	
		Sq. In.	Amp. Min.	Sq. In.	Amp. Min.	Sq. In.	Amp. Min.	Sq. In.	Amp. Min.
Sb% Ag									
Pure Lead		3.0	10.7	2.8	10.0	3.3	11.7	2.8	10.0
0	1/10	3.6	12.8	3.1	11.0	3.7	13.2	3.5	12.5
2	0	3.0	10.7	2.5	8.9	2.9	10.3	1.9	6.8
2	1/10	3.3	11.7	2.6	9.3	3.1	11.0	2.0	7.1
4	0	2.4	8.6	2.0	7.1	2.3	8.2	1.6	5.7
4	1/10	3.0	10.7	2.9	10.4	2.8	10.0	1.9	6.8
9	0	3.2	11.4	2.8	10.0				
9	1/10			3.1	11.0				

116. To determine if lead dioxide could be formed at potentials less than the accepted equilibrium value, a fresh piece of metallic lead was connected to the eight alloy specimens and held for a period of several days at a potential of 0.963 or below. Suddenly lowering the potential to 0.817 changed the current from oxidizing to reducing (623 to -170 microamperes). Here, the lead surface had no chance to reach the potential of the accepted equilibrium value of 1.135.

This indicated that some higher oxidation state than PbSO_4 was formed at potentials considerably lower than the accepted equilibrium value for $\text{PbSO}_4 - \text{PbO}_2$. It may be possible that with careful potential and temperature control, such measurements of residual current may be used to evaluate corrosion rate, but the measurements must be more refined than included in this exploratory study. The difficulty is that the "residual current", that is the electrolytic attack on the metallic lead beneath the lead sulfate-lead dioxide coating, may be only a small fraction of the current due to lead sulfate-lead dioxide oxidation or reduction or possibly intermediate oxidation-reductions. The latter sources of current must therefore be reduced to zero before the oxidation of lead can be measured, and no method is apparent at present for separating currents from two such electrolytic processes occurring at the same electrode.

117. Such measurements may possibly be used for a different purpose, however. In order to charge a positive plate, excess current is usually used, and the cell gassed to assure complete charge. Holding the positive plates at fixed potentials and correlating them with capacities obtained on discharge and with capacities after giving the conventional overcharge with gas elimination, would show whether a battery could be charged satisfactorily without gas evolution and consequently without associated attack of the positive material and grid.

Conclusion 118. It is believed that the method described is applicable for evaluating metal electrolytic corrosion if the following conditions are met:

119. (a) The chemical action must be related by Faraday's Laws to the current flowing through the external circuit. Spontaneous reaction of the electrolyte with the metal will not be measured by this method. Since all oxidation reactions can be said to be electrolytic in nature -- that is, requiring separate anode and cathode reactions, the method will work provided that the anodic and cathodic areas can be separated. This, of course, is not simple to completely realize, since the most common cathodic reaction, the reduction of oxygen on the metal surface, may cause oxidation in excess of that equivalent to the current flow in the external circuit.

120. (b) Specimens must not gas. Any gas elimination by the electrodes, hydrogen, oxygen, ozone, will be connected with electrolytic current, and if quantities of gas are very small, it may be difficult to determine if current is due to gassing or to metal oxidation. Hydrogen gassing can be eliminated by fixing the potential more positive than the reversible hydrogen voltage.

121. (c) Tests must be evaluated for a long enough period of time to register a significant evaluation of corrodibility. There is evidence that there is no correlation between the initial rate of corrosion and the average corrosion rate over a long time period. Long-time corrosion resistance is probably due to the formation of an adherent non-porous oxidation film which eventually protects the underlying metal from further attack. Data as obtained by this method is of interest in establishing this fact. Data taken over a long time period, say one year, would be even more useful. Extreme care must be taken that only the specimen surfaces are available for oxidation. Failure of insulating films protecting metal surfaces other than those being studied, or attack of lead wires would render results worthless.

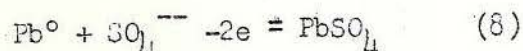
122. Incidentally this method might be a good one for rapidly exploring the field of possible positive or negative materials for use as battery plates in a

given electrolyte. For instance, the high currents given by cobalt, nickel, manganese and chromium in sulfuric acid solution make one wonder if they would not make good negatives in a primary battery. Other factors, of course, might prohibit their use, but their extremely high current capacities may have significance.

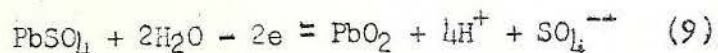
V CONSTANT CURRENT - VOLTAGE RELATIONS

123. Extensive work has not been done using this technique, nor have precise or fast voltage recording instruments been used in this connection. However, two representative voltage curves obtained during electrolysis of pure lead in sulfuric acid at 70°C and -35°C are given on Plate 30 in order to illustrate the method.

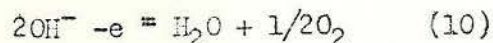
124. At point A in Figure A, Plate 30, the lead specimen had just been made anode with a current in the magnitude of a few millamperes per sq. cm. of electrode area, supplied from a 110-volt d.c. source. The potential of the oxidizing lead specimen was polarized slightly positively, but was stable until point B due to the oxidation process,



125. At point B, the lead surface area was insufficient to consume the oxidizing current and the potential rose sharply in the positive direction until point C was reached. At point C, the chemical action holding the potential constant was possibly,



126. The exact nature of the chemical action here was not as definite as it was at the potential of -1.0. The potential of +1.3 volts is considerably more positive than the reversible lead dioxide-lead sulfate potential of +1.1 volts, and instead of remaining constant or rising, it tends to become more negative. The potential finally become more positive and was gassing at D where the oxygen electrode was holding the potential fixed:



127. At point D, the specimen was released from the polarizing current, and the voltage fell abruptly to the approximate reversible value of 1.1. At E a negative polarizing current was applied which caused a sharp decrease in potential until point F was reached. The significance of this inflection is not at all clear. It may be an intermediate state between lead dioxide and lead sulfate, or it may be a displaced oxygen reduction potential. However, this type of inflection is the kind of data that might be gained by use of this technique. It would be of interest to identify the significance of the "F-G" inflection. At point G, reduction of lead sulfate to metallic lead started, and at point I, the reduced lead surface was gassing hydrogen.

128. Analogous inflections are shown by Figure B at -35°C. As would be expected the lead to lead sulfate capacity was smaller at the lower temperature. The C inflection was much higher than at 70°C, and the "F-G" inflection is entirely absent. The hydrogen gassing potential was more negative than at 70°C.

Conclusions 129. (a) The constant current-voltage technique is a simple and rapid method of exploring electrode behavior under a variety of conditions. A number of variables might be studied by this method including alloy composition, physical treatment, heat treatment, electrolyte composition, temperature, and impurities or presence of dissolved gasses.

130. (b) Refining the method by the adaption of sensitive, stable, high impedance, and fast potential recording devices might yield data regarding undiscovered equilibriums or mechanisms. The "C" inflection, for instance, may possibly be evidence of an intermediate oxidation product between lead sulfate and lead dioxide. The "F-G" inflection has already been mentioned.

VI EVALUATION OF ANODIC CORROSION BY THE RESISTANCE METHOD

131. Since the conductivity of metallic lead and its oxidation product are of different magnitude, that property was thought to be a good index of corrosion rate. Samples were drawn into 0.030 inch wire and arranged as described by Procedure C, Section II. A diagram of the apparatus is given by Plate 5.

132. Changes of resistance of the 0 to 9% antimonial lead samples of two independent runs are shown by Plates 11 and 12. Both runs showed the same general increase in resistance of all alloys during the 60 to 60 day periods. The surprising feature of these experiments was that the pure lead wire held up as well as the antimonial lead alloys. At the end of the test period, the pure lead, 2% and 4% antimonial lead wires had small piles of black flakes accumulated on the bottom of the tubes. The 9% specimen had a smaller gray mound, indicating a more adherent corrosion deposit and a different composition. Possibly the gray color was caused by antimony oxide. The 2 and 4% antimonial lead wires showed extreme stretching and buckling. Pure lead and 9% antimonial lead showed little twisting or buckling.

Conclusion 133. It is believed that the resistance method is a good one for measuring the corrosion of the wires. Whether it is applicable to grid alloys or not is another question. It has become more and more evident that the corrosion property of the grid material is greatly affected by the manner by which the sample is prepared. Extruded lead wire very possibly has different characteristics than a cast lead grid.

VII EFFECT OF HEAT TREATING 2% ANTIMONIAL LEAD UPON ITS CORROSION RESISTANCE

134. Since excellent physical properties can be incorporated in low-antimony lead alloys, it was thought promising to investigate the corrosion resistance of these compositions and the effect of heat treatment.

135. Cast S.L.I. grids of 2%, 4% and 9% antimonial lead and of pure lead were given various periods of heat treatment at 240°C. These grids were then placed in 280 ml. of 1.280 specific gravity sulfuric acid and charged anodically against a platinum cathode at 100 ma. for one-half of an 80-minute cycle. The grids were discharged for the other half of the cycle at 20 ma. Time-potential relations against a mercurous sulfate electrode were followed during the initial charging of the grids at 20 ma. and are plotted on Plate 28. In general, longer heat treatment lengthened the antimony plateau. Heat treatment had evidently in some way brought more metallic antimony to the grid surface. As would be expected, heat treatment destroyed the lead plateau due to surface oxidation of metallic lead.

136. Antimony contents of the electrolyte were periodically determined by withdrawing a filtered sample, precipitating the antimony with hydrogen sulfide, and determining the amount of precipitate turbidimetrically. Table VIII gives results of this series.

137. Plate 13 shows photographs of the grids after completion of the test. The appearance of the 2% antimonial lead grids without heat treatment may be compared with the disintegrated grids with heat treatment. Photographs of 4 and 9% antimony grids are provided for comparison. The pure lead grid seems to be in remarkably good condition. A considerable amount of loose corrosion product is on the grid surface, but the underlying metal is intact as contrasted to the heat treated 2% grids.

Conclusions 138. (a) The results of this test are negative -- that is, heat treatment which enhances the physical properties of 2% antimonial lead alloys seem to decrease its corrosion resistance. A remarkably small quantity of antimony was leached from 2% grids as compared with 4% and 9% antimonial lead.

139. (b) The 2% antimony grids were extremely difficult to cast. Most of the grids had flaws and cracks after casting which were sealed by a hand torch. It would be interesting to compare the corrosion resistance of low antimony alloys with different modes of formation - casting, rolling, with and without heat treatment. Different types of heat treatment might produce beneficial results.

VIII CORROSION RESISTANCE OF SILVER-ANTIMONY LEAD ALLOYS BY TENSILE STRENGTH AND PHOTOMICROGRAPHIC METHODS

A. Corrosion of Tensile Specimens

140. Previous work and literature references pointed to the beneficial effects of small quantities of silver in conjunction with lead-antimony alloys. Since many claims, some without foundation, have been made during the last 50 years for special grid alloys, it is necessary to check this opinion before proceeding with original investigations. Alloys with antimony content from 0 to 12% with and without 1/10% silver and with and without heat treatment were prepared according to Procedure F, Section II.

141. After the samples had anodically corroded for 33 days in 1.300 specific gravity sulfuric acid, they were removed, washed and examined visually. Plates 14 and 15 show photographs of the specimens at the end of the corrosion period. Table IX compares the diameter of the turned down section of each specimen before and after corrosion. The intragranular etching of the pure lead is striking and characteristic of pure lead. Introducing only 1/10% silver to the lead completely changed its appearance after corrosion. The grain is markedly reduced, and the etching between grains is much less pronounced. As the antimony content is increased, the grain size decreases. Heat treatment seems to have the effect of increasing grain size in specimens below 9% antimony. Rather uniform corrosion is noticed in specimens with antimony content below 3%, but at that concentration and above there is a pronounced tendency to have local pits, some of them nearly severing the specimen. The presence of silver has the effect of eliminating these cavities. The effect of cold working the alloy with a lathe can be seen by comparing the turned-down section with the cast surface of pure lead. In every case samples with 1/10% silver have better appearance.

142. Photomicrographs of the corroded specimens are shown by Plates 16, 17 and 18. In general, three types of attack are apparent: (1) Intragranular attack as shown by pure lead or low-antimony alloys. (2) Intergranular attack in which corrosion within grain boundaries is present. This type of attack may expose alloy structure due to differential corrosion of the two phases (Plate 18, 3% Sb.) (3) Occasional deep pitting which is ruinous to strength and is exhibited by specimens with high antimony content but no silver. The cause of this localized pitting is not clear. It may be simply casting flaws or occluded dirt or oxide. It is quite common that a positive grid in a storage battery will part at a few points, but in other sections be in good condition. This local pitting is probably vitally associated with battery failure.

143. Tensile strengths of the corroded and control specimens are given by Table X and are plotted on Plate 19. There is a general trend for tensile strength to increase as the antimony content increases, but checks between duplicate specimens was not good when silver was not present. This erratic nature may be due to casting defects. In many cases local pitting markedly reduced the cross section of a specimen.

144. The consistency of the increase in strength with the introduction of silver, and the beneficial effects of heat treating the silver alloys upon tensile strength are encouraging. A maximum tensile strength of over 8000 pounds per square inch was obtained in the case of the specimens containing 3% antimony and 1/10% silver which had been heat treated. Heat treatment tended to increase the tensile strength of all samples with or without silver. Apparently heat treatment increased the strength of the low antimony alloys sufficiently to overcome its deleterious effect on particle size.

145. Table XI gives the weights of residues deposited after 18 and 33 days of corrosion and the amount of antimony found in the residue and in the negative plate after 33 days corrosion. Table XII gives the gassing potentials of the specimens after 7 and 24 days of corrosion.

146. Residues of heat treated and un-heat treated specimens were similar. A consistent lowering of amount of residue was noticed, however, with the introduction of silver. No striking differences in weights of residues were noticed with variation of antimony content. If anything, there was a tendency for the residue to increase as the percent antimony increased. This effect does not correlate with the known superiority of 9 to 12% antimonial lead grids over pure lead grids, so the weight of residue by itself cannot be conclusive as a criterion of a good grid alloy. An open mind should be kept for the resistance to corrosion of pure lead, particularly on short time tests. This corrosion resistance of pure lead is not generally recognized in the battery industry. The basic objection to pure lead positive grids is very possibly their lack of resistance to deformation rather than corrosion rate. (See Sections VII and IX) Also, the loose nature of the corrosion product on pure lead might cause "growing" and lead to poor conductivity between grid and active material.

147. Heat treatment did not seem to consistently affect the quantity of antimony leached from the specimens. The amount of leached antimony, however, increased with increase of antimony content of the specimens, as would be expected, with an abrupt increase from 4 to 9% antimony. Also, introducing silver consistently reduced the amount of leached antimony. These relations point out the desirability of using less than 9% antimonial lead in order to decrease contamination of the negative plate.

148. There is little effect of antimony content on the anodic gassing voltage as shown by Table XII. The introduction of 1/10% silver, however, noticeably decreases the gassing potential of pure lead or low antimony alloys. This effect may be of interest for decreasing the charging potential of a cell without lowering the negative potential as nickel does.

149. At the conclusion of the cycling period, the samples were charged positively and then discharged at a low current until the dioxide potential failed. Capacities of the various specimens are plotted on Plate 29. The effect of silver and heat treating on the increase of cathode capacity is very noticeable in the case of antimony contents of 4% or less. The greatly increased capacity of the heat treated 3 to 4% antimonial lead alloys with 1/10% silver together with the tight adhesion of the corrosion product suggests the use of this composition as positive active material. It is probably this same adherent coating of dioxide that enhances the corrosion resistance.

150. The appearance of the cathodes used during the corroding period gives information regarding the properties of the anodes. Plates 20 and 21 show photographs of the lead sheet cathodes used for each alloy composition and heat treatment. The cathode opposite pure lead had a thick spongy deposit of metallic lead on its surface. This deposit was probably caused by the flocculent lead dioxide anode corrosion product being transported to the cathode by convection or cataphoresis and reduced on the cathode surface to metallic lead. This effect can be seen to decrease as the antimony content increases or with the introduction of silver.

151. The fact that the spongy deposit on the cathode surface was caused by fine particles from the anode corrosion was proven by making two identical arrangements of lead electrodes except that one had no separator between the anode and the cathode, while the two electrodes of the other were isolated by a micropore separator. No desposition on the negative was noticed in the case using the separator, but the other cathode had a heavy deposit of lead moss. The darkening of the cathodes as the antimony content of the anode was increased is probably due to deposition of antimony black on the lead surface.

B. Corrosion of Microtomed Specimens

152. One series of experiments was run with the object of following the anodic corrosion process by the microscopic appearance of a microtomed specimen. In addition to the general characteristics of the corrosion process, it was desired to know which were the resistant phases in the antimony-lead alloy, and which were attacked more readily.

153. The test specimens were 3/8 inches in diameter x 3 inches long. They were microtomed on the bottom surface and immersed in 1.300 specific gravity sulfuric acid at an angle to prevent gas bubbles from collecting on the polished surface. The negative consisted of a pure lead electrode the same dimensions as the corrosion specimen. An 8-oz. jar was used as the container. The cells were connected in series and cycled for 2 days. A cycle consisted of 23 1/2 hours charge at 20 ma. (28 ma per sq/in) and 1/2 hour discharge by short circuiting the cells. After 2 days corrosion, the cells were dismantled, the anodes cleaned by shorting directly to a negative plate of greater capacity (which reduced most of the lead dioxide to lead sulfate) and soaking in ammonium

acetate bath to dissolve the PbSO_4 . The remaining PbSO_4 and PbO_2 were removed by brushing gently under a small stream of water. After drying thoroughly, photomicrographs of the etched surfaces were made. Plates 22 and 23 show representative photographs after 48 hours of corrosion. Already in the case of low antimony, the grain boundaries are starting to be attacked and intergranular attack is noticed in the case of 2 and 4% antimony specimens. The presence of 1/10% silver decreases this type of attack. High antimony content specimens were finer grained and had an almost amorphous surface.

154. After examination by microscope, the samples were reassembled in the cells and corrosion continued for 60 days. During this period observations were made regarding voltage characteristics and appearance of the corrosion product. At the end of the 60 day test, photomicrographs were taken after cleaning the specimens in the same manner as previously done. Table XIII gives the weights of residues and the gassing potentials of the specimens. The effects of silver in reducing the quantity of residue and the anodic gassing potential are consistent, as in Part A.

155. Plates 24 and 25 show representative photographs of specimens after the 60-day corrosion period. In general, the low-antimony alloys have been etched deeper in a pattern similar to that begun during the initial 48-hour period, while the specimens with 4 to 9% antimony were etched more evenly. The presence of 1/10% silver made the attack appear less in all cases.

156. In order to ascertain which phase was attacked by the anodic corrosion, Figures B and C of Plates 24 and 25 (2 and 4% antimony with and without silver) were examined. In each case, pits were in the form of "islands" in the matrix. This condition was interpreted to signify that the solid solution, which would occur in the form of "islands" in a eutectic matrix, was attacked preferentially to the eutectic.

157. As noticed in Part A, gassing voltages of antimonial lead specimens were generally uniform and did not seem to change with changing antimony concentration or heat treatment. The presence of 1/10% silver, however, lowered the gassing voltage in each case.

Conclusions 158. (a) Anodic corrosion of pure lead caused pronounced intragranular attack. The corrosion product was light, flocculent and non-adhering. Grain size of the pure lead samples was large. The nature of the corrosion product of pure lead explains the tendency of grids cast from that material to "grow". Such "growing" consists of continual flaking of the oxidation product which eventually extends beyond the grid and separator boundaries and causes buckling and shorting of the cell.

159. (b) Introduction of antimony in amounts of 1% or greater decreased grain size and intragranular corrosion. The corrosion product became more compact and adherent as the per cent antimony was increased to 9%. During one month's test, the samples with 9% antimony corroded more than pure lead. This short test cannot be accepted as evidence that low antimony alloys have better corrosion properties than 9% antimony in long-time service conditions. The fact that the corrosion product of the higher antimony grids was compact rather than flocculent would decrease the tendency for antimonial lead grids to "grow" and thus cause distortion and shorting of the cell.

160. (c) The presence of 1/10% silver in all cases increased corrosion resistance. Silver-containing alloys with antimony contents of 1, 2, 3 and 4% gave promise as satisfactory grid materials. Maximum tensile strength of corroded specimens was obtained in the case of 3% antimony with 1/10% silver which had been heat treated. This opinion, of course, must be verified by repeating the tests for significance, and testing the alloys as pasted grids made into cells and cycled under service conditions. Casting low antimony-content alloys presents a difficult problem.

161. (d) Cathodes opposite metallic lead accumulated thick spongy, metal deposits. This effect, also present in the case of low-antimony alloys, was probably caused by reduction of anode corrosion product on the surface of the cathode. Silver in the anode reduced this effect.

162. (e) 16 hours heat treatment at 235°C with an ice water quench increased surface pitting on all samples without silver. Final tensile strength of the heat treated specimens, however, were better than for unheat-treated alloys. Heat treatment enhanced the strength of silver-containing alloys without adversely affecting corrosion resistance. This is one type of heat treatment out of many dozens of possible combinations. More varieties of heat treatment should be included in future studies.

163. (f) Cathodic capacities of the grid materials studied are not inversely correlated with corrosion resistance; on the contrary, samples with greater capacities often possess greater resistance to disintegration. This behavior seems to indicate that corrosion is prevented primarily by the formation of a tough, adherent corrosion product which will not flake off appreciably on continued anodic charge or gassing. Eventually, this coating should become sufficiently thick and non-porous to protect the underlying metal from further corrosion. Accordingly, attention should be focused on the mode of formation of this protective coating. Initial rates of corrosion are therefore significant in relation to a study of the film formation, but will not necessarily correlate with the ability of the specimen to withstand long-time corrosion.

164. (g) Oxygen gassing potentials were less with the presence of 1/10% silver. This effect possibly should be followed up as a means of reducing charging potentials without adversely affecting the negative plate. Possibly, the lower gassing potential explains in part the decreased corrosion of the samples containing silver.

165. (h) The weight of residue alone after anodic charge cannot be taken as a criterion of corrosion resistance. In the above series, the grid material which is commonly used commercially, 9% antimony, lost more residue than alloys with less antimony. Several factors must be considered along with the shedding of corrosion product, such as:

166. (h-1) Were the test conditions similar to service conditions? The high positive potentials during charging indicate that the current density was higher than would usually be expected during the charging of a storage battery (about 1.35 volts to mercurous sulfate). This high charging and gassing rate may have been unduly severe and chipped off the corrosion product at a much more rapid rate than under operating conditions, and the results of the accelerated test may be misleading.

Specimens which corroded little under the vigorous conditions of this test, however would be expected to have good characteristics under service requirements. The formation of loose flakes of corrosion product similar to those formed on test specimens has been noticed on the lugs of positive plates of old submarine cells.

167. (h-2) What is the physical nature of the corrosion product? A flocculent, non-adherent deposit would be little protection to a corroding surface. Gassing would tear the light product from the surface and expose more lead. Even if the alloy with low antimony were corroding at a less rapid rate during the early life of a battery, the continual shedding of the flocculent oxidation product would not only expose fresh metal but would make the grid "grow".
168. (h-3) What are the electrical characteristics of the corrosion product? The grid must remain conducting in spite of the corrosion film. A loose film might ruin the electrical conductivity between the grid and active material.
169. (h-4) In addition to corrosion resistance, what other qualities are required of a positive grid? Resistance to deformation is probably one property not possessed by pure lead which eliminates it as a possible grid material. (See Section IX)

Theory of the Action of Silver as a Corrosion Inhibitor

170. In the normal process of anodic oxidation of lead sulfate to lead dioxide, there is possibly an intermediate step between the sulfate and the dioxide, as indicated by peculiar voltage inflections of an anodically charged specimen containing no dioxide. This intermediate may be the persulfate, whose lead compound is soluble. Lead dioxide formed by this manner is peculiarly spongy, a property characteristic of Planté formation. The flocculent nature of the product eliminates pure lead as a possible positive grid material. To explain this spongy nature, suppose that the soluble lead persulfate, being unstable in acid solution, exists for a fraction of a second before being hydrolyzed to the insoluble dioxide. This interval of time would allow the lead to migrate a short distance from the parent metal before it solidifies as the dioxide in a spongy form.

171. Silver is known to be a good catalyst for the decomposition of the persulfate. For instance, in weakly acid solution, persulfate will not oxidize KI. After a drop of silver nitrate solution has been added, however, the reduction takes place readily. This is a well known quantitative procedure for persulfate and has even been used for the detection of the presence of silver ion.

172. Therefore, if the presence of silver makes the persulfate decompose more readily, the soluble lead persulfate will have a shorter life period, and the precipitation of lead dioxide will occur a sub-fraction of a second sooner than it would if no silver ion had been present. The dioxide coating should therefore be more compact. The formation potential of lead dioxide should also be less. The more compact coating of dioxide will flake off less readily than the flocculent coating. All of these considerations agree with experimental observations.

173. The catalytic action of silver here, must be one of hydrolysis of the persulfate instead of reduction, in the case of KI. Also there is a possibility of the instantaneous formation of a higher lead valence than four. Silver may catalyze this reduction to lead dioxide. In general, there may be some intermediate reaction which is affected by the presence of silver to make a more compact coating of dioxide. The rate of corrosion of the metal alloy with silver is actually greater, therefore, than without silver, but the compact nature of the corrosion product eventually prevents further excessive oxidation.

174. This same reasoning might be used to explain the role of antimony in making a more compact corrosion product than if formed on pure lead.

IX TESTING GRID ALLOYS IN STORAGE CELLS

175. Previous methods of testing grid alloys by laboratory tests have served as orienting experiments, but final conclusions can only be drawn from actual performance in storage cells.

176. Since the positive grids were of primary interest, the negative grids were cast from pure lead to eliminate the influence of negative contamination from other than the positive grid. All of the grids with the exception of the commercial grid were cast at the Laboratory. The results of previous corrosion tests, tensile strengths, capacities, voltage characteristics, and other observations indicated that the alloys most suitable for lead acid batteries were the 2% and 4% antimonial grids with 1/10% silver. Table XIV tabulates the casting data.

TABLE XIV

Grid Casting Data

Cell No.	Grid		Analysis			Mold Temperature	Melt Temperature
	Nominal	Composition	Sb	Ag	Sn		
	%Sb	%Ag					
4	10	0 (Commercial)	9.99%	-	.18%	unknown	unknown
5	00	0				250-265°C	440-460°C
1	2	1/10	2.18	.09	-	220	505
2	4	1/10	4.55	0.073	-	220	495
3	9	0				210-220	440-460

177. The 2% antimonial lead grids were extremely difficult to cast. Many cracks appeared in the members of the cast grids and were sealed with a hand torch. Many combinations of temperatures for both the mold and melt were tried without success for the 2% alloy. This difficulty was not encountered when casting pure lead or the higher antimonial content alloys. The grids were pasted with a positive mix, and the pure lead grids pasted with a negative mix as described by Procedure H of Section II. Density of the paste was 73.5 grams per cu. in. Table XV gives the positive and negative plate potentials at cycle 21 and 100 while charging at 1.6 amperes.

TABLE XV

Positive and Negative Plate Potentials at Cycles 21
and 100 While Charging at 1.6 Amperes.

Cell	Composition of		Cycle 21			Cycle 100		
	Positive Grid		Cell Volt.	Positive	Negative	Cell V.	Positive	Neg.
	%Sb	%Ag						
1	2	1/10	2.63	2.37	-.25	2.65	2.43	-.23
2	4	1/10	2.62	2.38	-.24	2.64	2.45	-.21
3	9	0	2.61	2.40	-.21	2.62	2.45	-.16
4	10	0	2.63	2.41	-.21	2.63	2.47	-.17
5	0	0	2.66	2.41	-.25	2.68	2.45	-.24

178. It is significant to note the difference between the negative gassing potentials of the test cells, as the values are somewhat indicative of the amount of antimony in the positive. The cell having the most antimony in the positive grids have the most positive negative gassing potential. It is quite obvious that with an increase of antimony present in the positive grid there will be a corresponding increase in the amount of antimony electrolytically deposited upon the negative. This then explains the variation in the negative gassing potential, as antimony decreases the hydrogen overvoltage on lead.

179. Spontaneous gassing of cells was determined by water displacement in an inverted burette. Table XVI gives the gassing rates of each cell at cycle 72 and 200.

TABLE XVI

Spontaneous Gassing of Test Cells at Cycles 75 and
200. Life of Cells in Cycles to 80% Original Capacity

%Sb	% Ag	Gassing, cc, per day (STP)		Cell Life
		at 75 cycles	at 200 cycles	
2	1/10	8	14	200 cycles
4	1/10	34	39	446
9	0	121.0	167	350
10	0	95.8	134	230
0	0	5.4	---	70

180. The number of cycles which each cell could withstand before reaching a capacity as low as 80% of its original discharge is listed in Table XVI. Capacities of these cells are plotted against the number of cycles in Plate 27. Photographs of the positive plates after completion of the cycling test are shown by Plate 26. The following appearance of the plates is noted:

181. Pure Lead. The grid is in good condition from the standpoint of absence of rupture. The frame can be broken only with difficulty, and there appears to be no failures due to forming. The frame is warped badly. This lack of stiffness is perhaps the greatest objection to pure lead as a positive grid material. The grid structure must have a certain amount of stiffness to withstand volume changes during the cycling process. Too much warping causes failure by dislodging the active material.

182. 2% Sb 1/10% Ag. This grid breaks very easily either in the frame or in the cross members. The broken section was crystalline as viewed by a hand lens, and there was considerable forming between the crystals. The behavior of this alloy was disappointing, since it showed up very well in previous laboratory tests. It is felt that the poor casting qualities of this alloy account for its poor behavior as a grid material.

183. 4% Sb 1/10 Ag. The grid was not seriously corroded, although the frame and cross members could be broken more easily than before the test. In general, the grid was in good condition.

184. 9% Sb. The frame was in good condition, perhaps better than the 4% Sb 1/10% Ag grid. The cross members seemed to have been weakened by the life test, probably because they were slightly smaller than originally. However, the frame seemed just as resistant to rupture as before the test.

185. Commercial Grid. This grid was greatly weakened by cycling. Many voids were present in the plate where cross members had been corroded away. The frame of the grid was much more brittle than the original grid.

Conclusions 186. (a) According to the data given by Table XVI and Plate 27, batteries with 4% antimony and 1/10% silver grids gave better performance in a service test than either a 9% antimonial lead or a commercial positive grid. Photographs of the positive plates after completion of the test showed that only the 4% Sb with 1/10% Ag, and 9% Sb grids had remained intact. The members of the pure lead grid had not disintegrated, but the plate was so badly warped that the active material had evidently been forced out of place. Only one cell of each alloy composition was made. It would be necessary to have several duplicate checks before it could be said without question that one battery or type of grid was better than another type.

187. (b) Self-discharge of the cell whose positive grid alloy contained 4% Sb and 1/10% Ag was very much less than that of cells with 9 to 10% antimonial lead positive grids. Here there would be a definite advantage to using the first mentioned alloy even if its corrosion resistance were no better than commercial alloys.

188. (c) The results of this practical test check previous laboratory tests in all cases except alloys with 2% Sb and 1/10% Ag which gave good laboratory tests, yet failed when made into actual cells. The reason for this variation is probably due to the great difficulty in obtaining satisfactory castings of the 2% antimony.

189. (d) It is felt that practical tests of the type mentioned here should be run in cooperation with the battery manufacturers. When promising alloys are developed, they must be accepted by manufacturers before use, and they in turn must try them by their own methods. The over-all picture includes the casting technique used, of course, and this may be critically associated with the corrosion resistance of the alloy.

X CONCLUSIONS AND RECOMMENDATIONS

A. General Conclusions Based on Present Study

190. The requirements of positive grid alloys are much too complex to be evaluated by a single test. Some popular methods of corrosion evaluation, i.e., weight of residue for a short-time test or the steam test, may have no correlation whatever with behavior of the alloy under service conditions. It is possible, however, that a well coordinated series of tests would greatly facilitate the selection of the best alloys out of the thousands of combinations of possible alloys.

191. Preliminary tests which seem to be most significant at this time are the reduction of tensile strength during corrosion (II-G) combined with weighing and examination of the corrosion product (II-C), microscopic examination of the corroded specimen and fracture after rupture, together with a study of the effect of grid impurities upon the cathode (II-H). Such preliminary tests must, of course, be confirmed by actually incorporating the alloy in storage cells and cycling the cells under controlled conditions until failure occurs. Control cells using standard materials should be always present in test series. Also, sufficient tests should be made to enable a statistical evaluation of the significance of the results.

192. The mode of grid formation, its physical treatment and heat treatment are all vitally associated with the physical properties of the metal as well as its corrosion resistance. For example, 2% antimonial lead with 1/10% silver had excellent corrosion resistance in one series of tests (VIII-A) and poor corrosion resistance in another series (II). Casting conditions were different for the two tests.

193. The effect of 1/10% silver upon the corrosion properties of lead and lead-antimony alloys was in every case beneficial. The silver reduced the grain size, increased tensile strength, increased cathode capacity of the specimen, and made a more compact and adherent dioxide coating. Local pitting was also absent in corrosion specimens containing silver, although the reason is not apparent.

194. Although the use of low-antimony alloys with a trace of silver for grid materials was indicated by preliminary experiments, no method was devised for casting grids from this composition. High melt temperature, high metal viscosity, and a relatively low eutectic temperature combined to make a difficult casting combination.

195. 4% antimonial lead alloys with 1/10% silver could be satisfactorily cast. This composition shows promise of being a more satisfactory grid material than commercial 9% antimonial lead. Corrosion resistance was similar to that of commercial alloy, and contamination of the negative plate was much less.

B. Recommendations for Future Work

196. The most obvious promise of an improved grid material lies in low antimonial lead with traces of silver or possibly related metals such as copper. Many alloys with silver and antimony contents in the region of the most promising alloy of 1/10% silver and 4% antimony must be checked.

197. In this connection ultra-pure lead, such as prepared by the Betts electrolytic process with 99.995% lead content, should be used in conjunction with chemically pure alloying ingredients in order to properly evaluate the effect of traces of added metal.

198. If the "Decrease of Tensile Strength Method" is used to evaluate corrosion resistance, the tensile specimens should be cast under carefully controlled conditions in the finished tensile form. If the specimens are worked or heat-treated after casting, this should be done under controlled conditions, and unworked or unheat-treated specimens run in the same series as controls. A variety of casting conditions, heat treatments, and reductions should be employed with each alloy composition. A large number of each type of alloy and treatment should be tested in order to be able to test the data for significance.

199. Tensile specimens should be X-rayed before corrosion and before rupture to locate points of weakness and to help locate the cause of failure. Such examination would be helpful to evaluate different casting conditions.

200. Corrosion tests should be conducted for sufficiently long periods to be significant. It is believed that any type of alloy corrosion test conducted for only a few days or weeks will not correlate with service behavior. Significant results can be obtained only after at least a month's electrolytic corrosion. Longer time would even be better. Initial corrosion rates are often inversely related to long-time corrosion tests.

201. It would be of considerable interest to interpret the role of antimony and silver in reducing lead corrosion. Experimentally, both elements seem to reduce grain size and make a more compact and adherent corrosion product. Explaining why these elements make the corrosion product more dense would possibly involve a detailed study of the mechanism of electrolytic formation of lead dioxide and the catalytic effect of antimony or silver upon the rates of processes intermediate between lead sulfate and lead dioxide.

202. The effect of silver in increasing the cathode capacity of lead is interesting from another standpoint than grid alloys. It is possible that a trace of silver in the positive active material would have beneficial results in keeping the lead dioxide intact and improving the conductivity of the active material. A high-capacity primary battery might be devised by tightly packing thin silver-lead sheet between thin separators and cycling to develop capacity. The adherence of the dioxide to the positive plate would lessen the chance of shorting through the thin separator as would be anticipated if pure lead sheet were used.

TABLE VIII

Effect of Heat Treatment Upon Anodic Corrosion
of 2% Antimonial Lead Grids

% Sb	Heat Treatment	Mg. Sb per Cell at end of 28 days	Gassing Potential	Condition of Grid at end of 28 days	Weight of Residue gms.
2	None	3.2	1.373	Good	9.0
2	1 hr. at 240°C	3.3	1.343	Poor - Numerous Cracks	12.4
2	2 hrs. at 240°C	4.5	1.331	Good - One crack in frame	9.7
2	16 hrs. at 240°C	3.2	1.363	Very poor	11.3
2	5 days at 240°C	6.4	1.335	Very poor	10.3
2	7 days at 240°C	3.7	1.353	Very poor	7.0
2	9 days at 240°C	4.7	1.342	Cracked - Voids	9.0
2	14 days at 240°C	3.9	1.362	Poor	8.3
2	19 days at 240°C	7.0	1.344	Poor - Voids - Buckling	12.3
2	28 days at 240°C	4.1	1.350	Poor	10.1
0	None	0	1.364	Fair	6.7
4	None	23	1.294	Very Good	8.0
9	None	91	1.298	Very Good	5.9

TABLE IX

Casting Conditions and Diameters of Tensile Specimens
Before and After Corrosion

% Sb	% Ag	Casting Temp.		Diameter Before Corrosion		Diameter after Corrosion		Change in Diameter	
		Melt	Hold	N.H.T.*	H.T.**	N.H.T.	H.T.	N.H.T.	H.T.
0	0	350°C	255°C	.250	.251	.234	.235	.016	.016
				.251	.251	.235	.235	.016	.016
0	1/10	350	250	.252	.250	.243	.239	.009	.011
				.252	.249	.243	.239	.009	.010
1	0	350	250	.250	.248	.236	.237	.014	.011
				.250	.252	.235	.237	.015	.015
1	1/10	350	250	.250	.250	.244	.245	.006	.005
				.250	.250	.242	.244	.008	.006
2	0	350	250	.251	.250	.236	.239	.015	.011
				.251	.249	.237	.238	.014	.011
2	1/10	350	250	.251	.246	.243	.244	.008	.002
				.251	.247	.242	.246	.009	.001
3	0	350	250	.251	.251	.236	.237	.015	.014
				.251	.251	.236	.237	.015	.014
3	1/10	350	250	.251	.252	.246	.248	.015	.004
				.252	.252	.247	.249	.015	.003
4	0	350	250	.251	.251	.234	.237	.017	.014
				.251	.251	.232	.238	.019	.013
4	1/10	350	235	.250	.251	.243	.245	.007	.006
				.252	.249	.245	.244	.007	.005
9	0	350	225	.251	.251	.227	.226	.024	.025
				.251	.250	.226	.226	.025	.024
9	1/10	350	225	.251	.251	.232	.241	.019	.010
				.250	.248	.235	.237	.015	.011
12	0	350	225	.251	.250	.223	.224	.028	.026
				.250	.252	.222	.225	.028	.027
12	1/10	350	225	.250	.251	.235	.240	.015	.011
				.250	.249	.236	.238	.014	.011

* N.H.T. - Not heat treated

** H.T. - Heat Treated

TABLE X

Comparison of Tensile Strength of Corroded
and Uncorroded Specimens

Tensile Strength in Pounds Per Square Inch

% Sb	% Ag	Control	Corroded	Corroded Heat Treated
0	0	1960	1520	1490
		2040	1720	1510
0	1/10	2940	2720	2590
		2960	2520	2620
1	0	3780	2750	4280
		5190	3000	3760
1	1/10	3900	4690	4930
		5010	4600	4850
2	0	4290	2980	4640
		4270	2730	4400
2	1/10	5290	4950	4330
		5570	4980	6480
3	0	4480	2940	5650
		2390	2060	5400
3	1/10	7380	6280	8530
		6510	6510	8360
4	0	6450	2620	2700
		4960	3175	3520
4	1/10	6830	4950	5180
		5790	5400	5900
9	0	7430	2220	2670
		6370	3790	4160
9	1/10	5240	5650	7280
		6580	6370	8260
12	0	5540	3670	1480
		4500	5220	4660
12	1/10	7420	5600	7800
		7050	5000	8240

TABLE XI

Weights of Residues and of Leached Antimony in
Corrosion Test of Lead Alloy Tensile Specimens

Alloying Elements (Percent)	Weight in Grams of Residue Deposited after:-				Weight in Milligrams			
	18 days corrosion		33 days corrosion		Antimony in Residue		Antimony in Residue and negative plate	
	N.H.T.*	H.T.**	N.H.T.	H.T.	N.H.T.	H.T.	N.H.T.	H.T.
0	3.59 g.	3.47 g.	4.55 g.	5.08 g.	-- mg.	-- mg.	-- mg.	-- mg.
0.1 Ag	2.14	2.23	3.41	3.46	--	--	--	--
1 Sb	3.74	3.47	5.62	5.10	33	34	41	38
1Sb-0.1 Ag	3.63	2.11	3.08	3.37	23	26	23	28
2 Sb	3.49	2.85	5.72	5.66	52	75	59	80
2Sb-0.1 Ag	2.27	1.81	2.64	3.22	24	36	32	39
3 Sb	3.71	3.84	6.11	5.33	92	70	97	78
3Sb-0.1 Ag	1.67	1.76	2.45	2.77	10	47	16	50
4 Sb	3.65	4.00	6.17	3.96	86	66	92	69
4Sb-0.1 Ag	1.74	1.76	3.24	2.99	15	55	23	56
9 Sb	4.90	4.94	7.64	7.33	68	150	216	247
9Sb-0.1 Ag	2.55	2.69	5.02	3.21	55	77	274	--
12 Sb	5.34	5.14	7.98	7.36	82	147	--	--
12Sb-0.1 Ag	2.42	2.86	4.09	3.02	53	92	--	--

* N.H.T. - Not heat treated

** H.T. - Heat treated

TABLE XII

Gassing Potentials and Cathode Capacities of Corroded
Lead Alloy Tensile Specimens

Alloying Elements (Percent)	Gassing Potentials at 1.4 amps/dm ² **				Capacities of Corroded Specimens in Ampere Minutes			
	7 days corrosion		24 days corrosion		18 days corrosion		33 days corrosion	
	N.H.T.*	H.T.***	N.H.T.	H.T.	N.H.T.	H.T.	N.H.T.	H.T.
0	1.588	1.571	1.586	1.576	1.1	0.5	0.8	3.8
0.1 Ag	1.531	1.525	1.405	1.407	4.5	1.2	1.8	4.4
1 Sb	1.588	1.564	1.584	1.583	1.5	1.1	1.0	2.3
1Sb - 0.1 Ag	1.541	1.526	1.422	1.466	2.4	2.3	2.0	4.7
2 Sb	1.585	1.558	1.554	1.577	2.2	3.2	1.7	2.9
2Sb - 0.1 Ag	1.552	1.524	1.447	1.509	1.8	3.0	2.0	4.3
3 Sb	1.555	1.564	1.557	1.574	2.4	3.1	1.8	1.8
3Sb - 0.1 Ag	1.507	1.521	1.411	1.436	3.7	4.4	2.8	5.6
4 Sb	1.545	1.552	1.565	1.563	2.6	2.6	2.1	2.4
4Sb - 0.1 Ag	1.510	1.553	1.496	1.478	4.1	3.6	3.1	5.0
9 Sb	1.549	1.553	1.577	1.575	1.8	1.9	1.8	1.8
9Sb - 0.1 Ag	1.530	1.508	1.521	1.519	1.8	2.0	1.7	1.9
12 Sb	1.536	1.554	1.573	1.578	1.7	1.8	1.8	1.8
12Sb - 0.1 Ag	1.535	1.482	1.528	1.470	1.7	1.9	1.8	2.1

* N.H.T. - Not heat treated

** Mercurous Sulfate Reference Electrode

*** H.T. - Heat treated

TABLE XIII

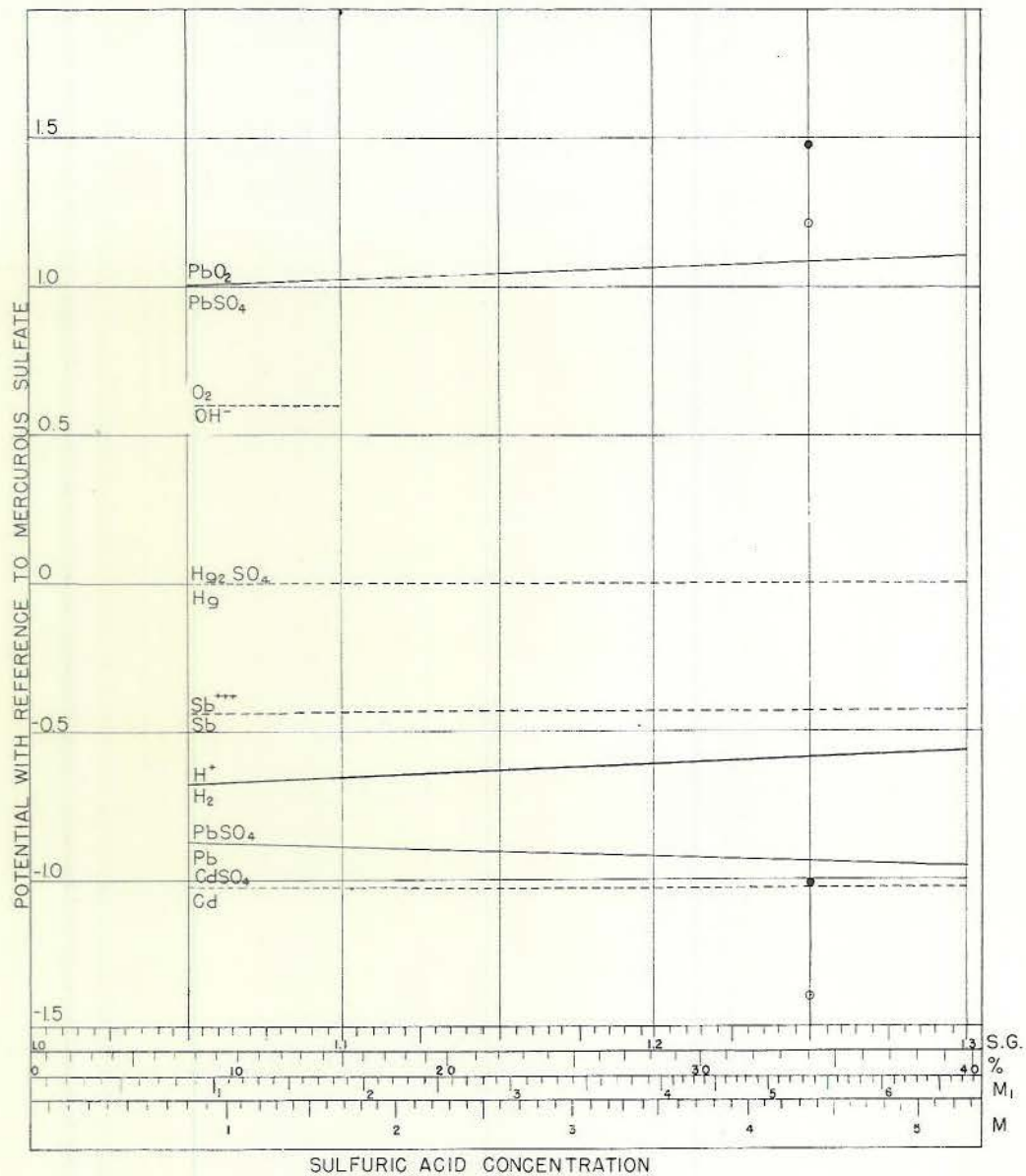
Corrosion of Microtomed Specimens, Weights of Resi-
due and Gassing Potentials

% Sb	% Ag	Weight of Residue		Gassing Potentials at 28ma/sq.in. Hg ₂ SO ₄ Reference	
		Not Heat Treated	Heat Treated	Not Heat Treated	Heat Treated
0	0	1.074	1.088	1.49	1.51
0	1/10	.189	.298	1.41	1.41
2	0	.888	.952	1.51	1.50
2	1/10	.084	.145	1.40	1.44
4	0	1.072	.925	1.50	1.49
4	1/10	.182	.230	1.47	1.49
9	0	1.195	1.136	1.48	1.46
9	1/10	.309	.405	1.46	1.45
11	0	1.235	1.368	1.49	1.51

REFERENCES

1. G. W. Vinal and G. N. Schramm, J. Am. Inst. Elec. Engrs., 44, 128-132 (1925).
2. J. T. Crennell and A. G. Milligan, Trans. Faraday Soc., 27, 103 (1931).
3. G. W. Vinal, D. N. Craig, and C. L. Snyder, J. Research, Nat. Bur. Stds., 10, 795-808 (1933).
4. N.R.L. Letter S62-4 (822-WHP-CHM), 822-25/46 dated 26 April 1946.
5. N.R.L. Report No. M-1698, 18 February 1941.
6. N.R.L. Report No. M-1443, 6 June 1938.
7. N.R.L. Report No. M-1121, 30 January 1935.
8. N.R.L. Report No. M-1052; 117-M-1052, 1934.
9. National Bureau of Standards Report on Project No. 197, 5 September 1936.
10. G. W. Vinal, D. N. Craig, and C. L. Snyder, Bureau of Standards Report, "Composition of Grids for Positive Plates of Storage Batteries as a factor Influencing the Sulfation of Negative Plates", 6 April 1933.
11. C. G. Fink and A. J. Dornblatt, Trans. Elect. Soc., 79, 269 (1941).
12. Metals Handbook, Am. Soc. for Metals, 1939.
13. R. S. Dean, Lyall Zickrick and F. C. Nix, Trans. AIME Inst. Metals (1926).
14. W. S. Pellini and F. N. Rhines, Trans. AIME, 65 (1942).
15. B. Blumenthal, Trans AIME Inst. Metals, Tech. Pub No. 1634, October 1943.
16. H. S. Harned and W. J. Hamer, NRL Report No. P-1071, 14 September 1934.
17. E. E. Schumacher and G. M. Bouton, J.A.C.S. 49, 1667 (1927).
18. F. F. Lucas, Proc. AIME, Inst. Metals, 75, 481 (1927).
19. C. P. Shillaber, "Photomicrography", John Wiley and Sons, (1944).
20. J. H. Lawrence, Am. J. Roentgenology, 48, 382 (1942).
21. M. W. Greenwood, Light Metals, p. 8, January 1939.
22. Hamos, Nature, 140, 30 (1937).
23. E. H. Dix, AIME Inst. Metals, 137 (1940).
24. Evans and Agar, J. Iron & Steel Ind., 141, 219 (1940).
25. H. E. Haring and V. B. Thomas, Trans. Electrochem. Soc., 68, 163, (1935).
26. R. H. Burns and W. E. Campbell, Trans. Electrochem. Soc., 55, 271, (1929).
27. Vinal and Ritchie, Bur. Stds. Tech Paper 225 (1922).
28. Grosheim and Krisko, Z. Metallkunde, 34, 102 (1942).
29. Dean, Hudson and Fogler, Ind. Eng. Chem., 17, No. 12, 1246 (1925).
30. E. E. Schumacher and Ferguson, Metals and Alloys, p. 150, June 1935.

POTENTIALS OF ELECTROCHEMICAL SYSTEMS
OF INTEREST IN LEAD-ACID BATTERIES



S.G. - SPECIFIC GRAVITY 25°C/25°C.

% - PERCENT BY WEIGHT

M_1 - MOLALITY

M - MOLALITY

○ - CHARGE VOLTAGE OF GOOD CELL (GASSING)

• - CHARGE VOLTAGE OF BAD CELL (GASSING)

TYPES OF ELECTROCHEMICAL COUPLES



Open Cell Voltage (OCV)

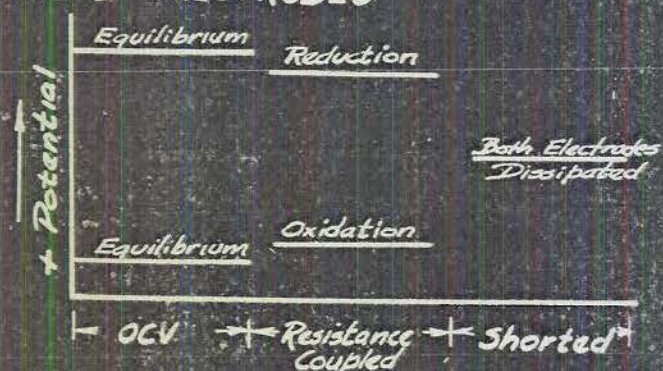


Resistance Coupled

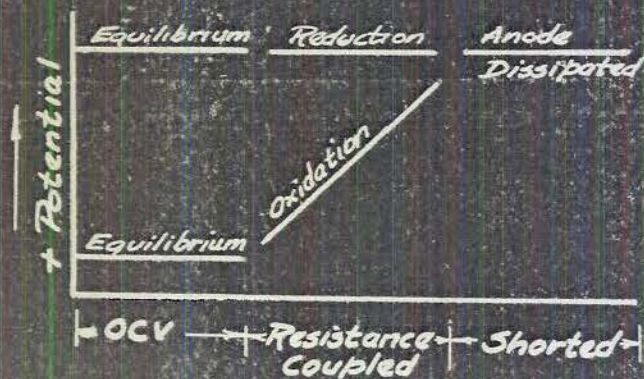


Shorted

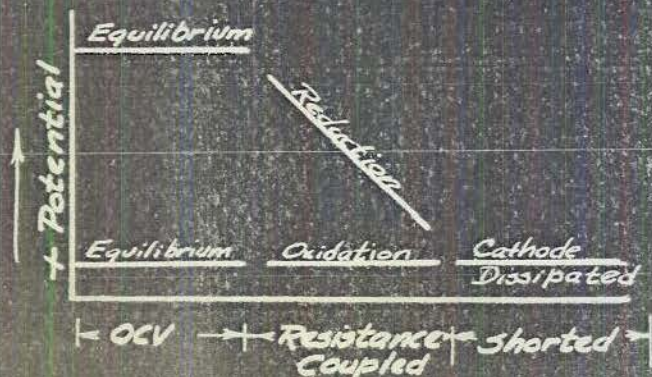
A. BALANCED ELECTRODES



B. MORE CATHODE THAN ANODE CAPACITY



C. MORE ANODE THAN CATHODE CAPACITY



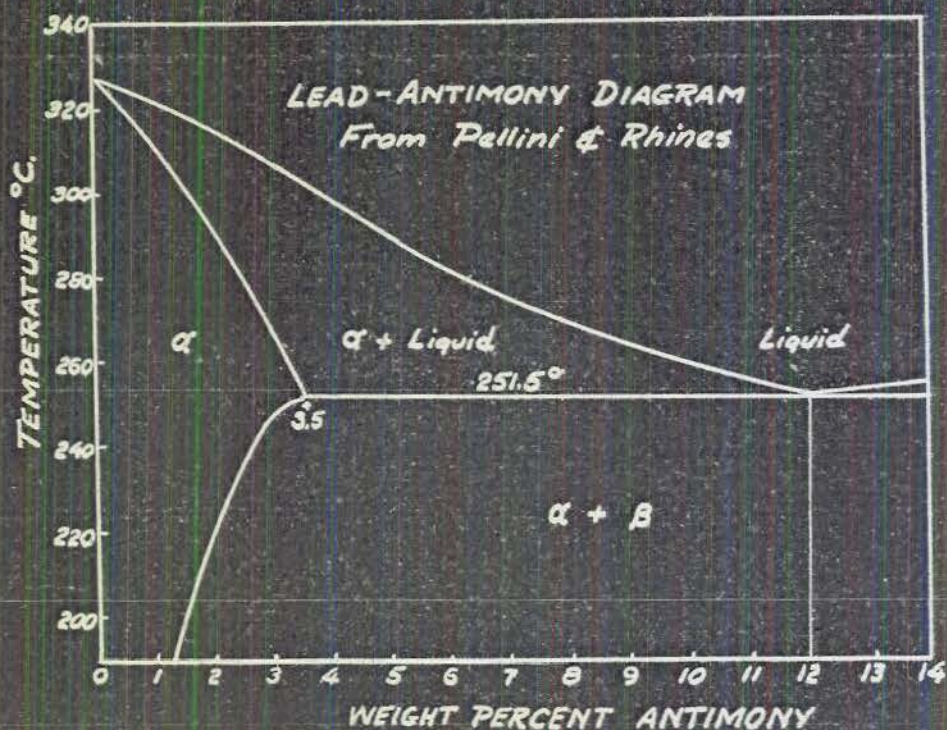
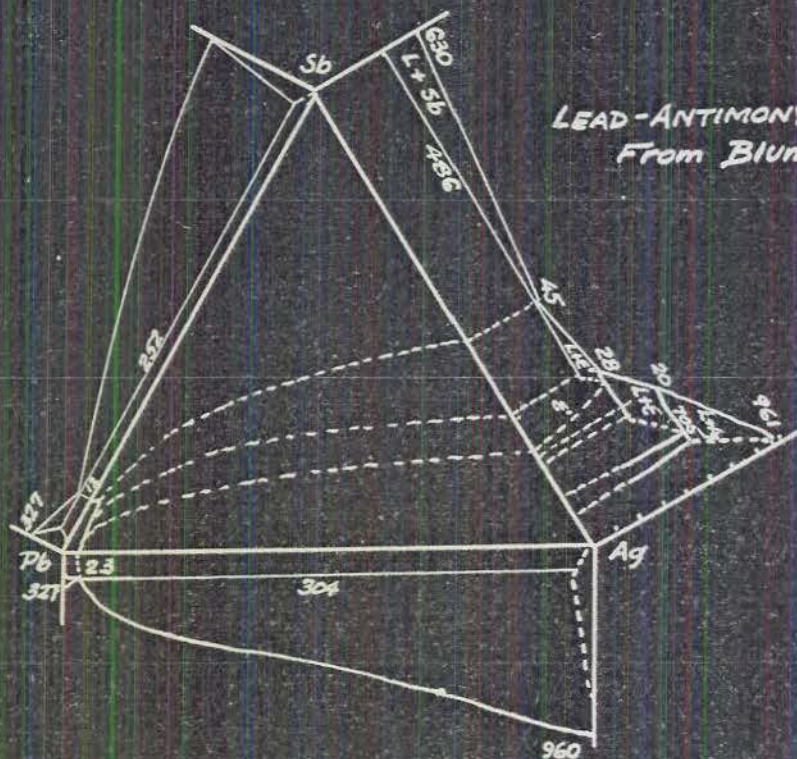


FIG. A
METHOD OF EVALUATING ANODIC CORROSION OF METALS
AT POSITIVE PLATE POTENTIAL

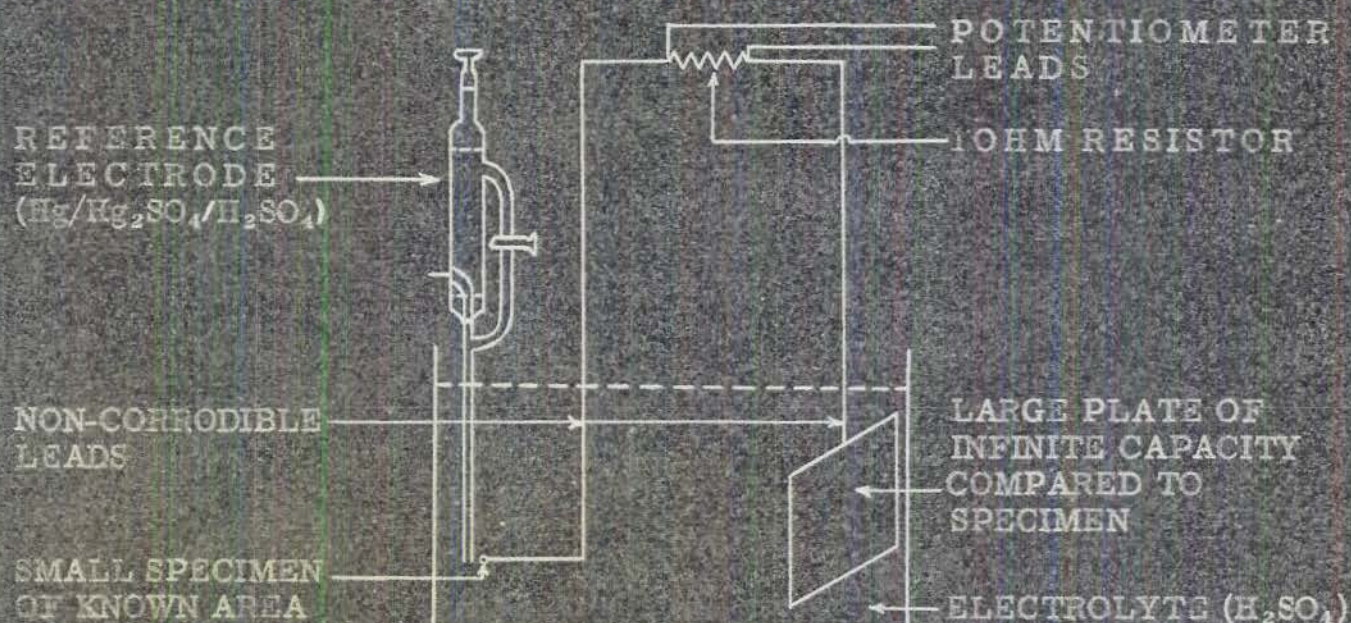
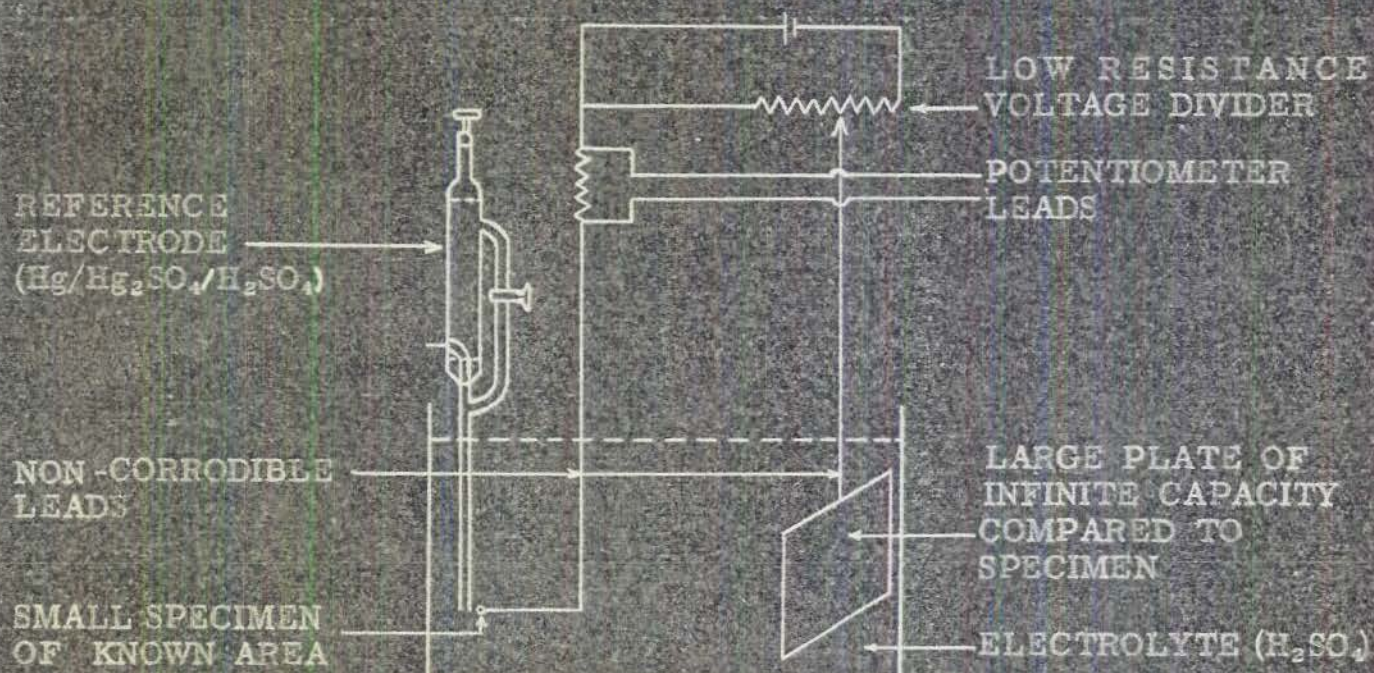
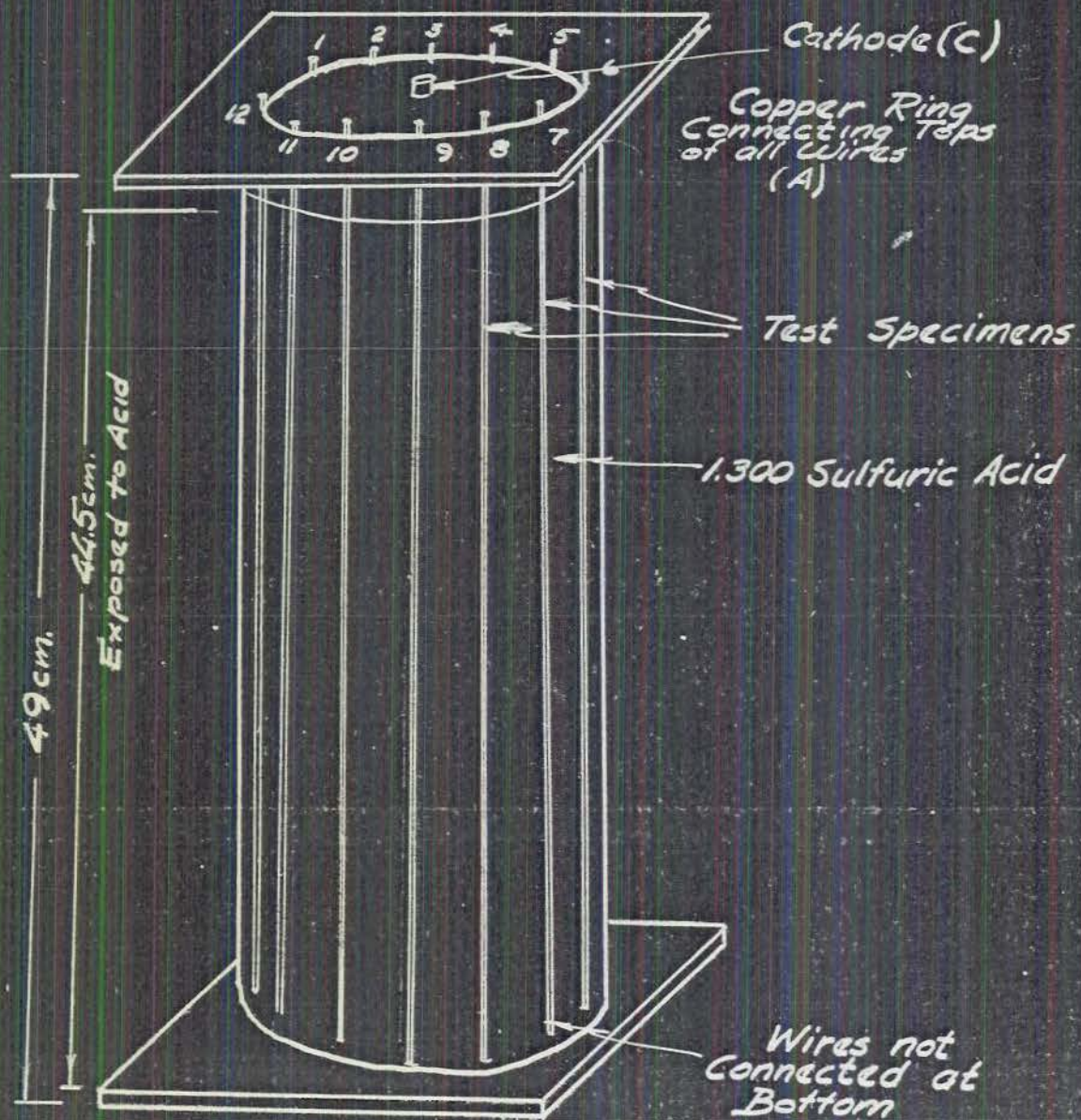


FIG. B
METHOD OF CONTROLLING POTENTIAL OF A SPECIMEN IN
ELECTROLYTE

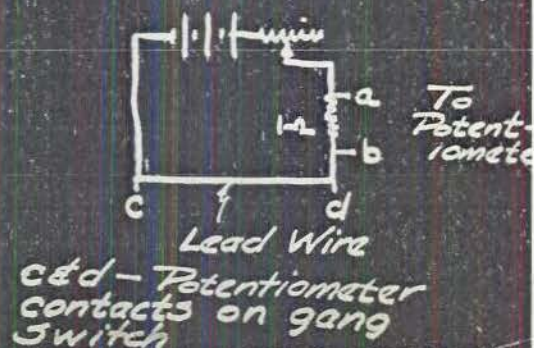
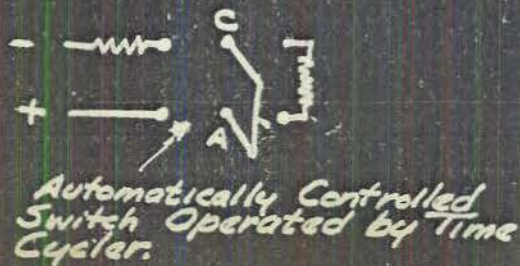


RESISTANCE METHOD FOR MEASURING CORROSION

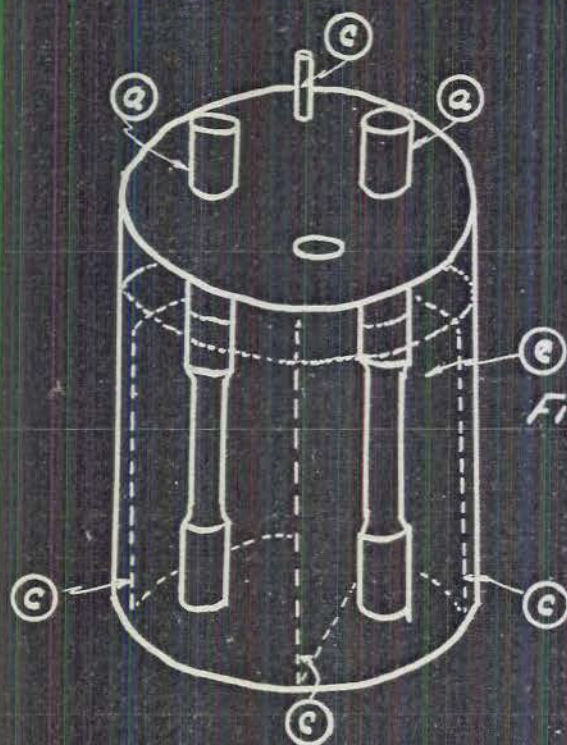


Hook-Up for Resistance Measurements

Cycling Hook-Up



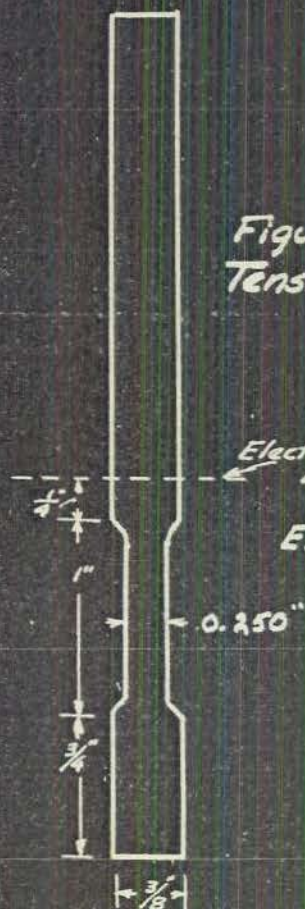
ANODIC CORROSION ASSEMBLY



a - anodes
(Tensile Specimens)
c - Pure Lead Cathode
e - Electrolyte

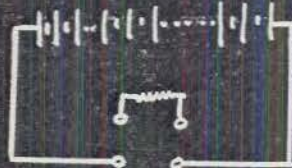
Figure A

Figure B
Tensile Specimen



Exposed Area = 13.4 sq. cm.

Figure C
Cycling Hook-Up



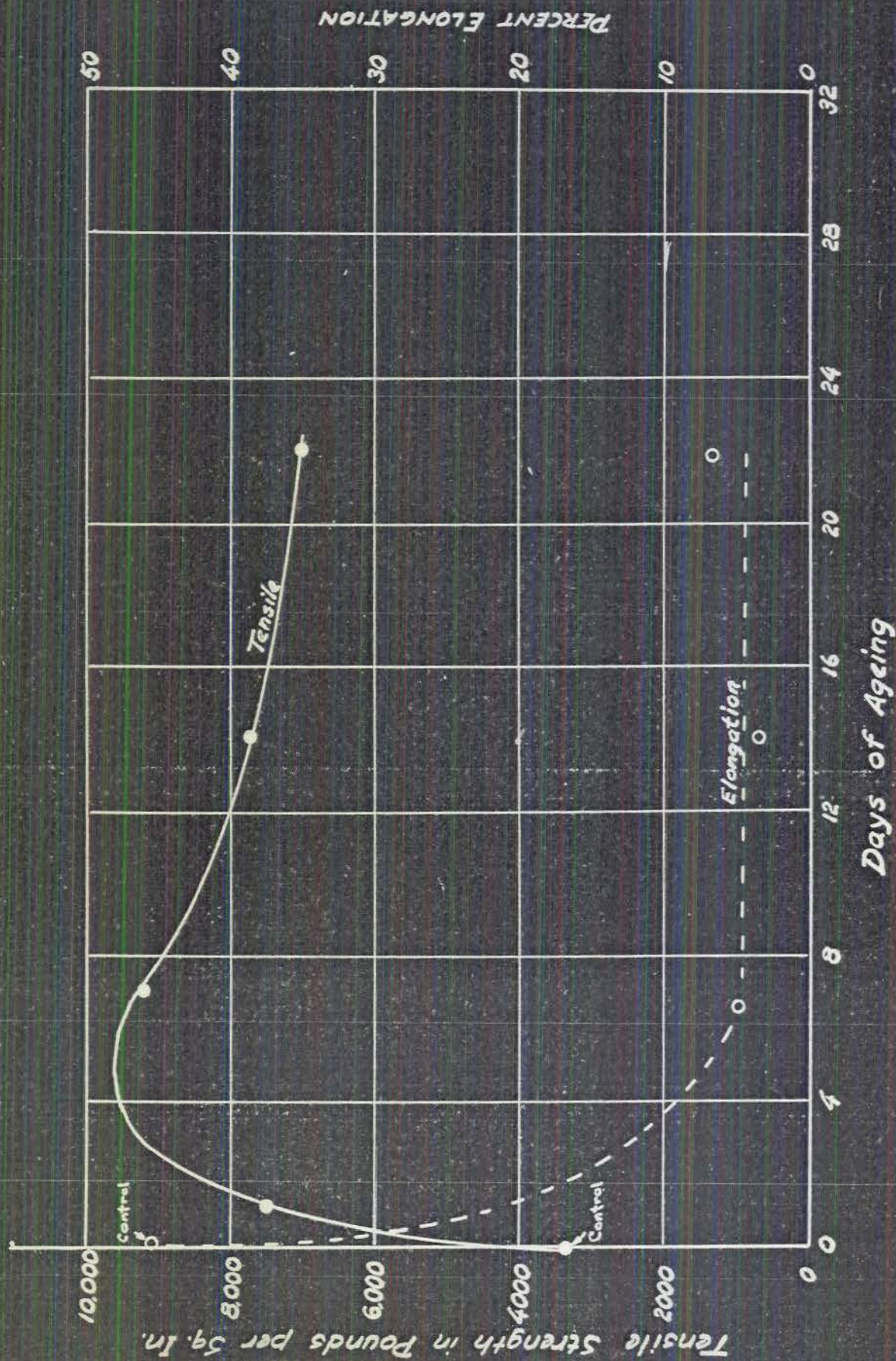
Automatic Switch
for
Charge and Discharge

110 D.C.

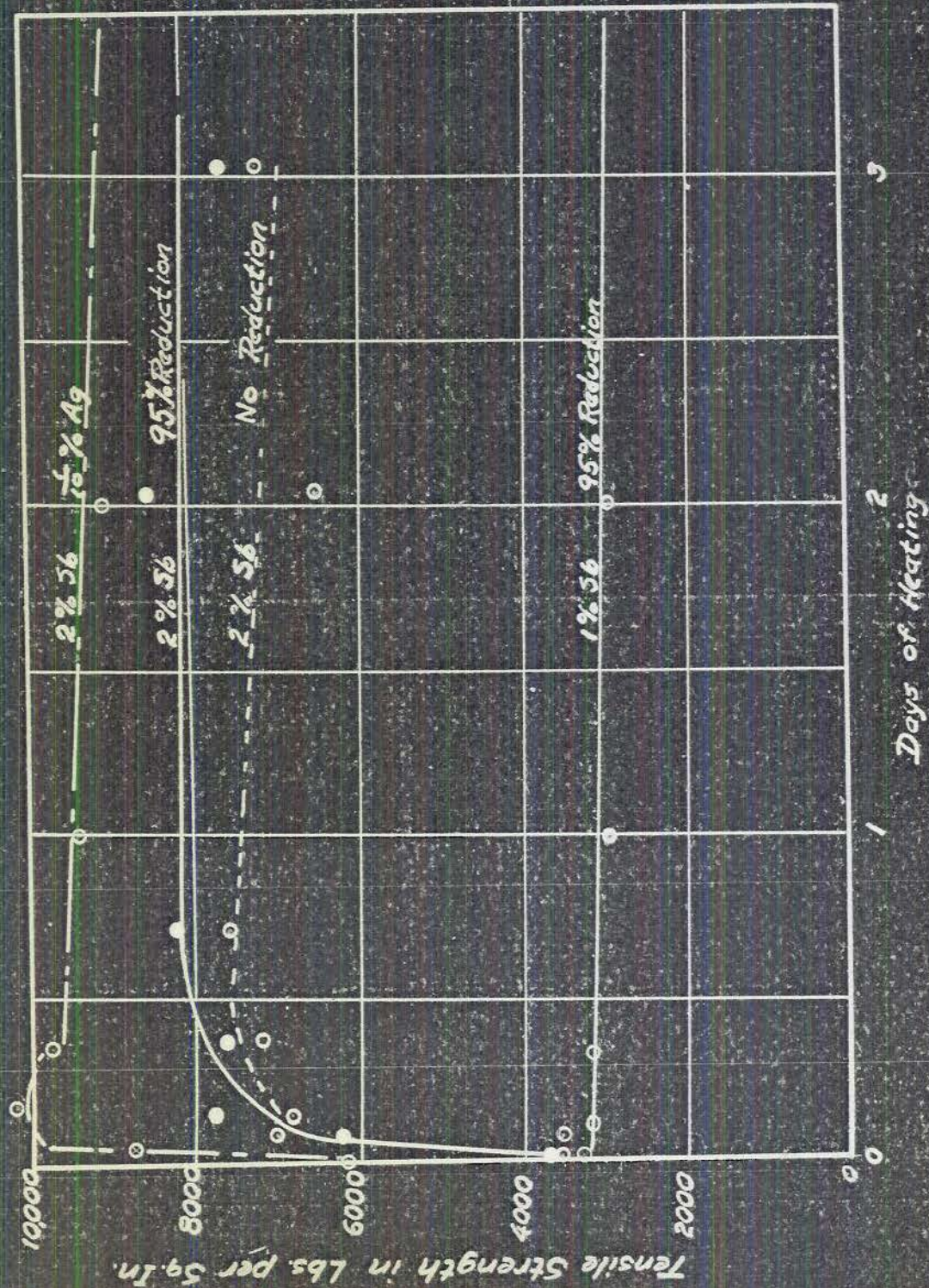


Figure D
Cathodes of
Pure Lead
Sheet

EFFECT OF AGEING ON TENSILE STRENGTH AND ELONGATION
OF 2% Sb-Pb ALLOYS, 95% REDUCED, HEATED 92 HOURS AT 240°C.



EFFECT OF HEAT TREATMENT ON TENSILE
OF 2% Sb-Pb ALLOYS
AND
1% Sb-Pb ALLOYS



CYCLERS FOR THE EVALUATION OF CORROSION CURRENTS

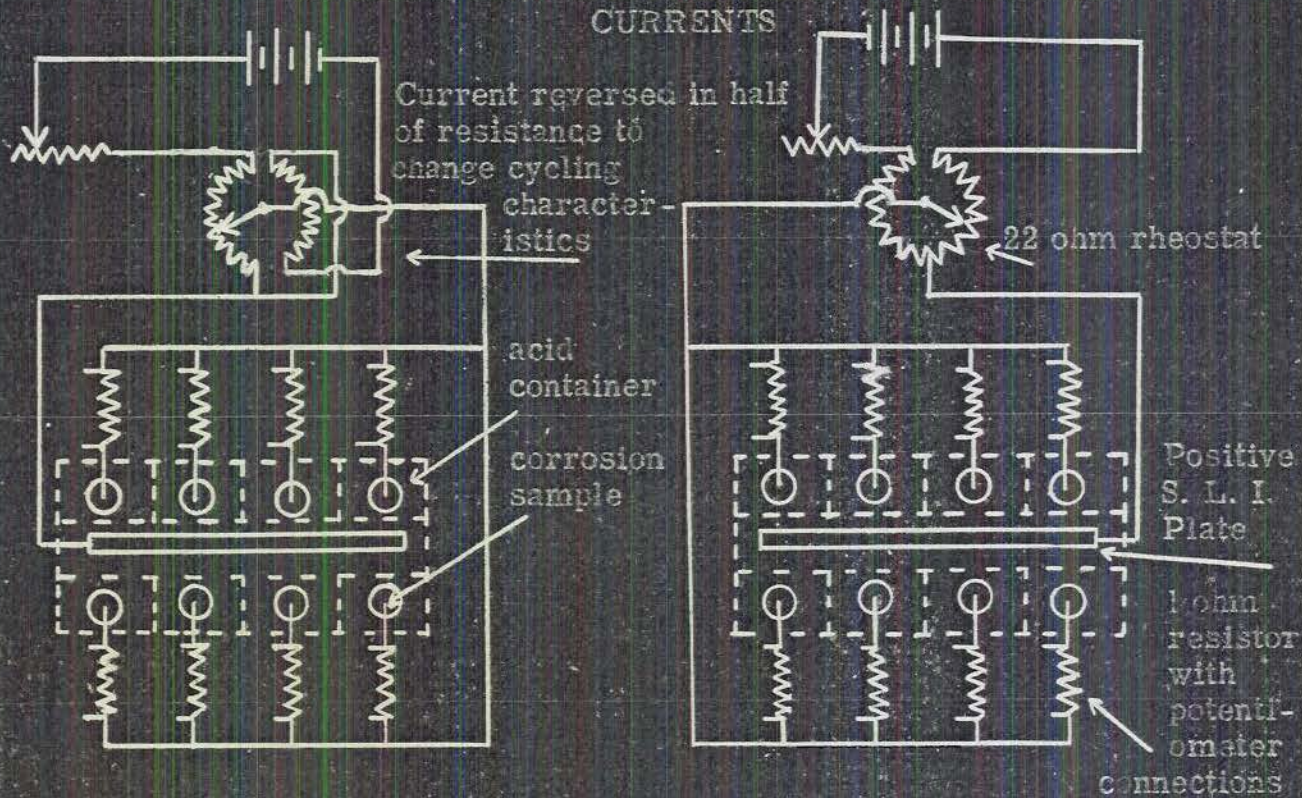
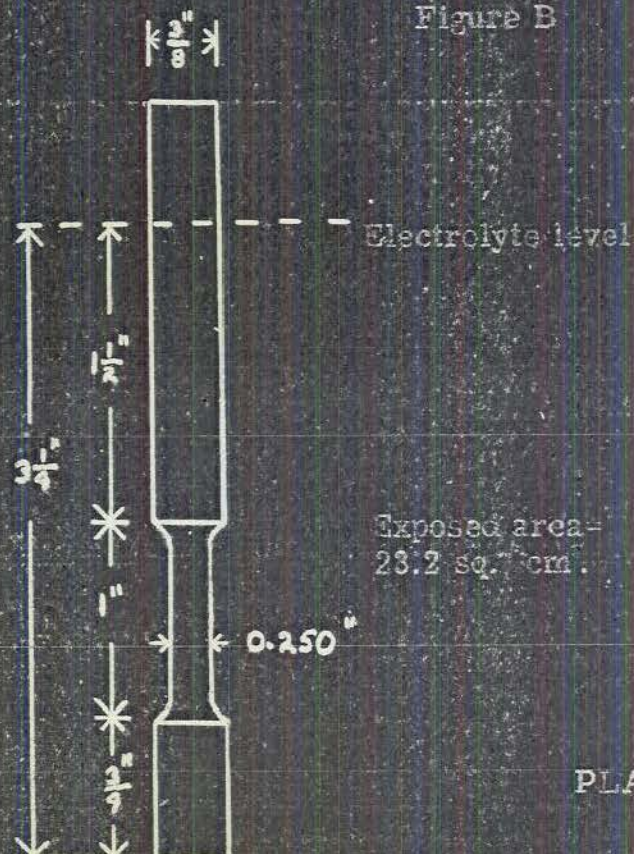


Figure A

Figure B

Figure C
Tensile Specimen



CAPACITY OF DIOXIDE FILMS

Figure 1

— Pure Lead
 --- Pure Lead with 1/16 % Silver



Figure 2

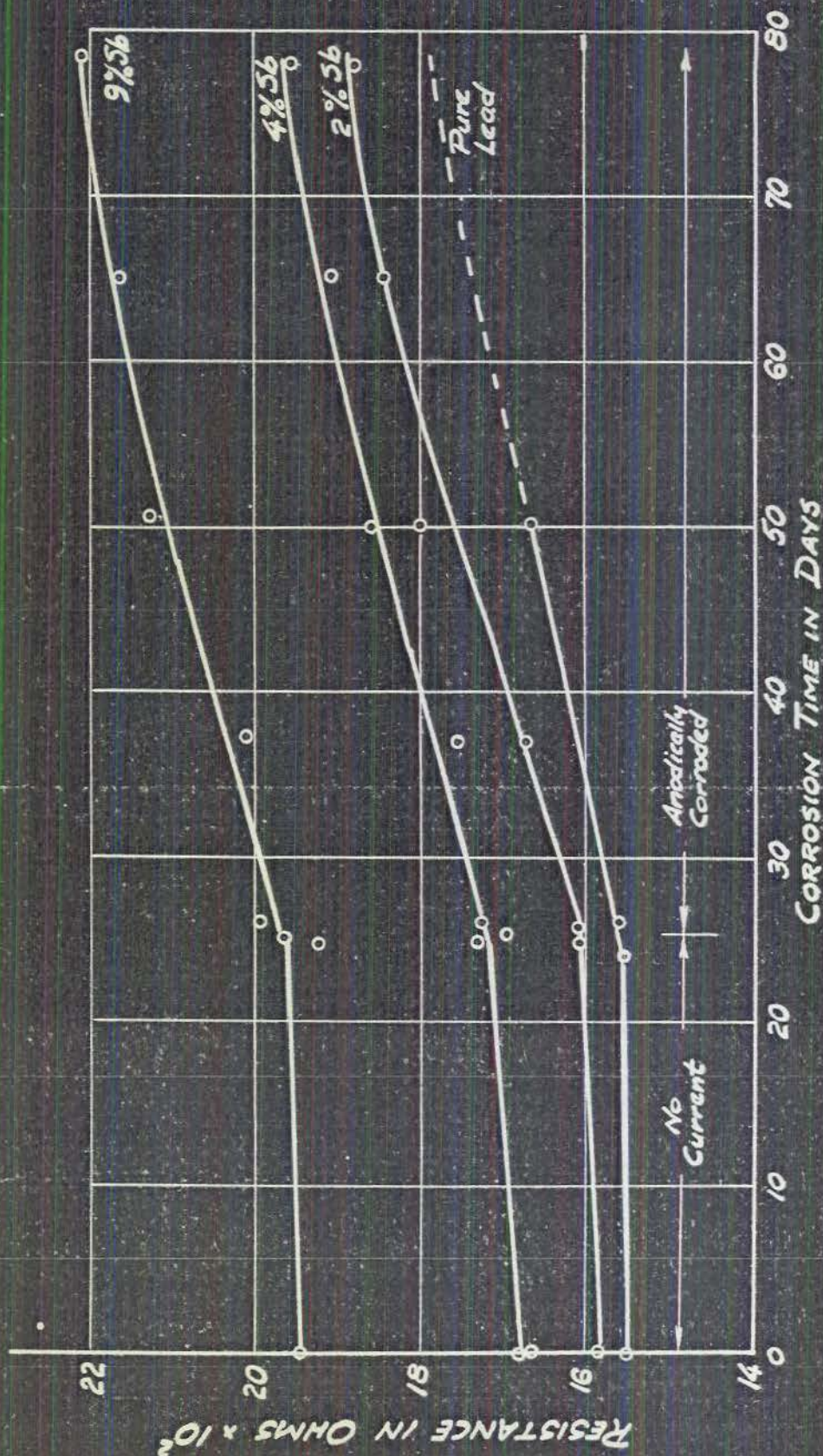


1 sq. in. = 3.56×10^{-2} amp. min.

MINUTES

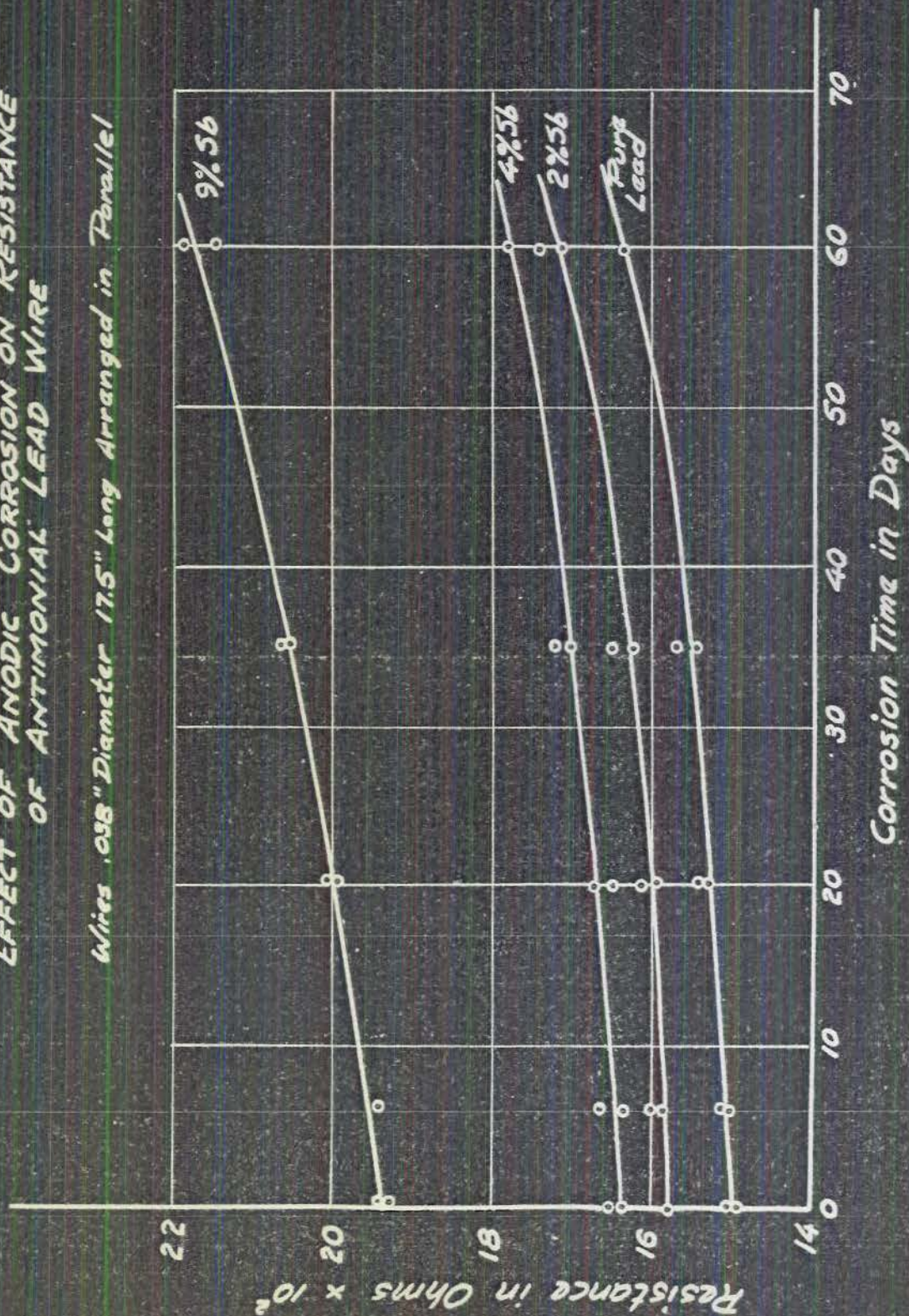
EFFECT OF ANODIC CORROSION ON RESISTANCE OF ANTIMONIAL LEAD WIRE

Wires 0.038" Diameter x 18.5" Long Arranged in Series

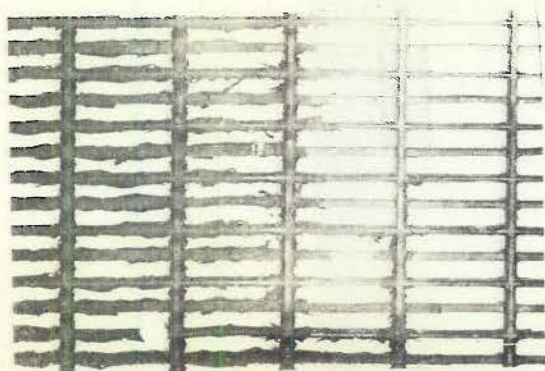


EFFECT OF ANODIC CORROSION ON RESISTANCE OF ANTIMONIAL LEAD WIRE

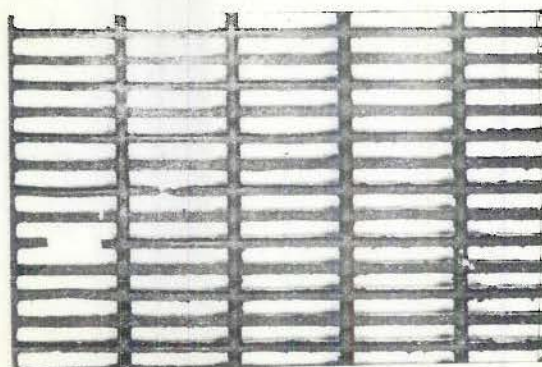
Wires .038" Diameter 17.5" Long Arranged in Parallel



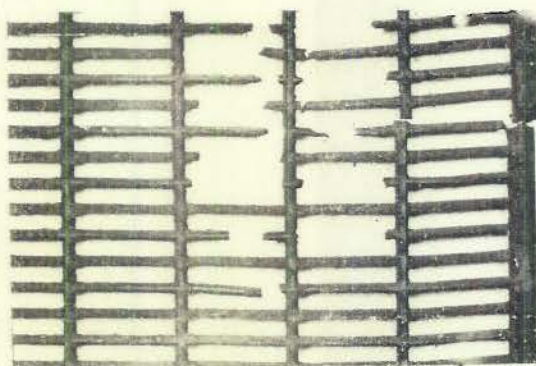
EFFECT OF HEAT TREATING UPON CORROSION RESISTANCE
OF 2% ANTIMONIAL LEAD



0% Sb

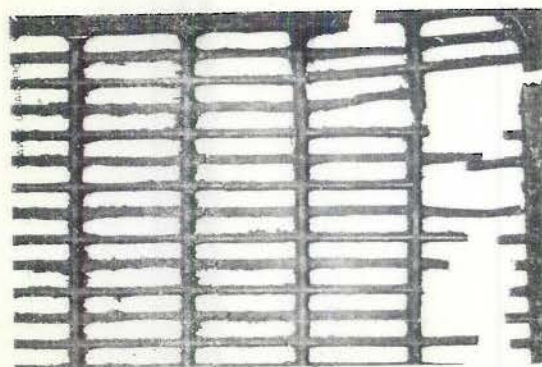


2% Sb



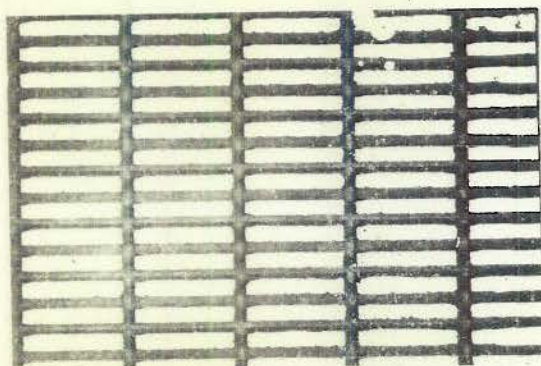
2% Sb

1 HR. HEAT TREATMENT AT 240° C.

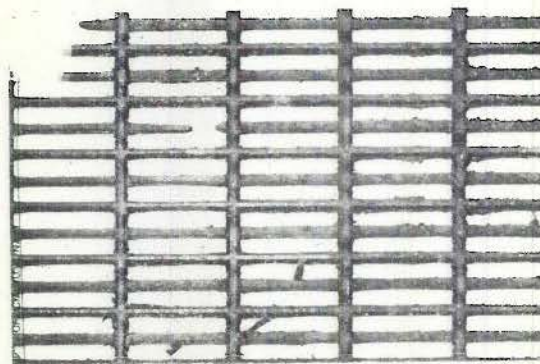


2% Sb

14 DAYS HEAT TREATMENT AT 240° C.



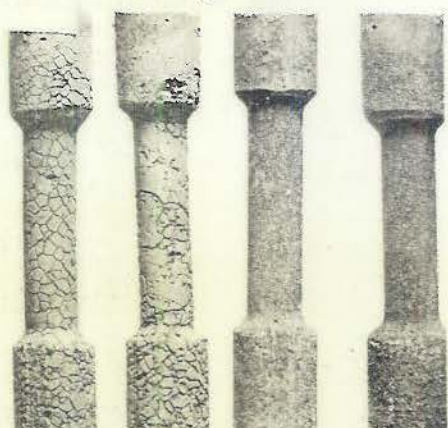
4% Sb



9% Sb

ANODIC CORROSION OF LEAD ALLOYS
33 DAYS. IN 1.300 H_2SO_4 AT 1.4 AMPERES PER SQ. DM.

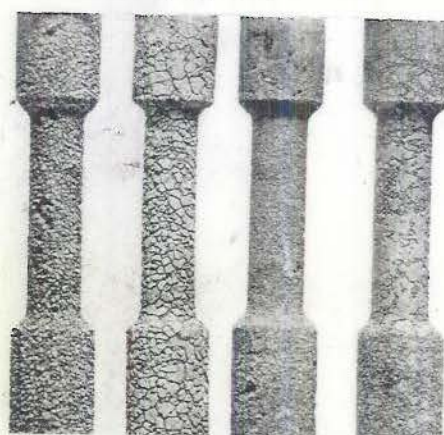
0% Sb



A B C D

FIGURE 1

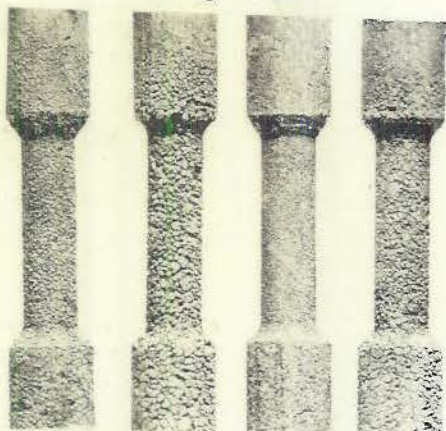
1% Sb



A B C D

FIGURE 2

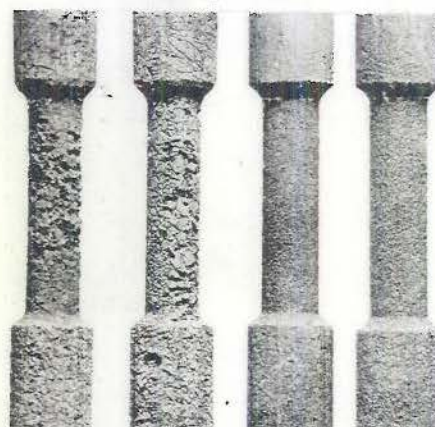
2% Sb



A B C D

FIGURE 3

3% Sb



A B C D

FIGURE 4

CODE

- A- NOT HEAT TREATED
- B- HEAT TREATED
- C- 0.1% SILVER, NOT HEAT TREATED
- D- 0.1% SILVER, HEAT TREATED

ANODIC CORROSION OF LEAD ALLOYS
33 DAYS IN 1.300 H_2SO_4 AT 1.4 AMPERES PER SQ. DM.

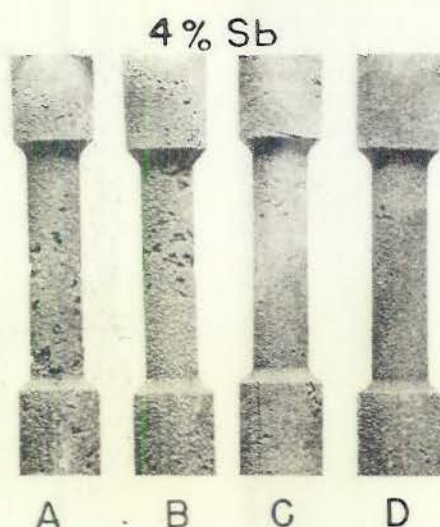


FIGURE 1

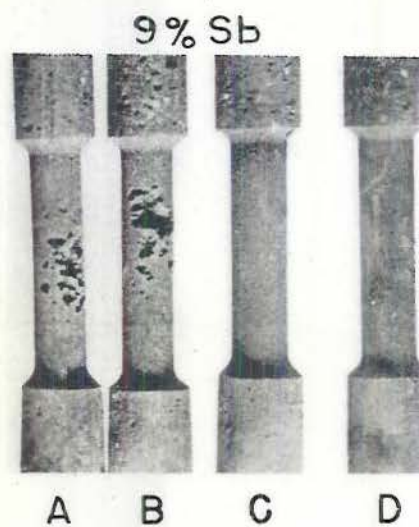


FIGURE 2

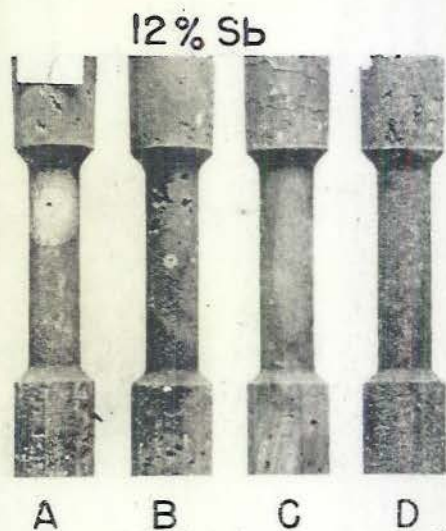


FIGURE 3

CODE

A-NOT HEATTREATED

B-HEAT TREATED

C-0.1% SILVER, NOT HEAT TREATED

D-0.1% SILVER, HEAT TREATED

ANODIC CORROSION OF LEAD ALLOYS
33 DAYS IN 1.300 H_2SO_4 AT 1.4 AMPERES PER SQ. DM.
MAGNIFICATION 25X



0% Ag



0.1% Ag



0% Ag
HEAT TREATED



0.1% Ag
HEAT TREATED

ANODIC CORROSION OF LEAD ALLOYS
33 DAYS IN 1.300 H_2SO_4 AT 1.4 AMPERES PER SQ. DM.
MAGNIFICATION 25X



2 % Sb



2 % Sb - 0.1 % Ag

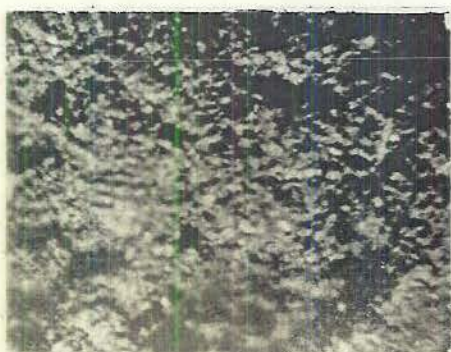


2 % Sb
HEAT TREATED



2 % Sb - 0.1 % Ag
HEAT TREATED

ANODIC CORROSION OF LEAD ALLOYS
33 DAYS IN 1.300 H_2SO_4 AT 1.4 AMPERES PER SQ. DM.
MAGNIFICATION 25X



3% Sb



3% Sb-0.1% Ag

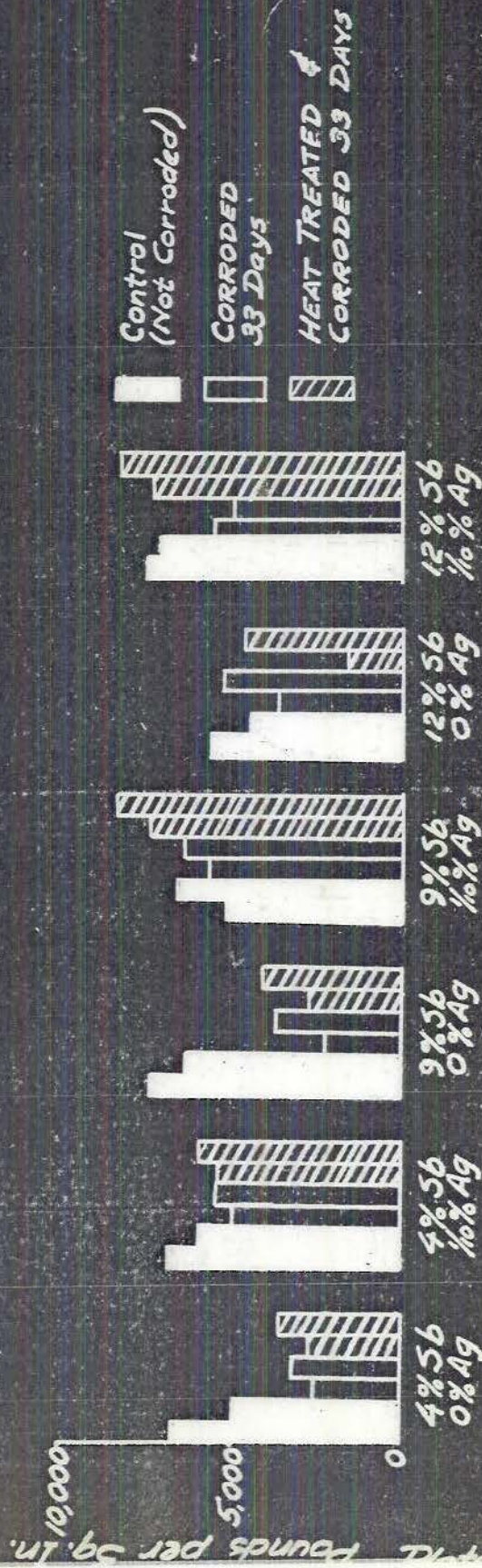
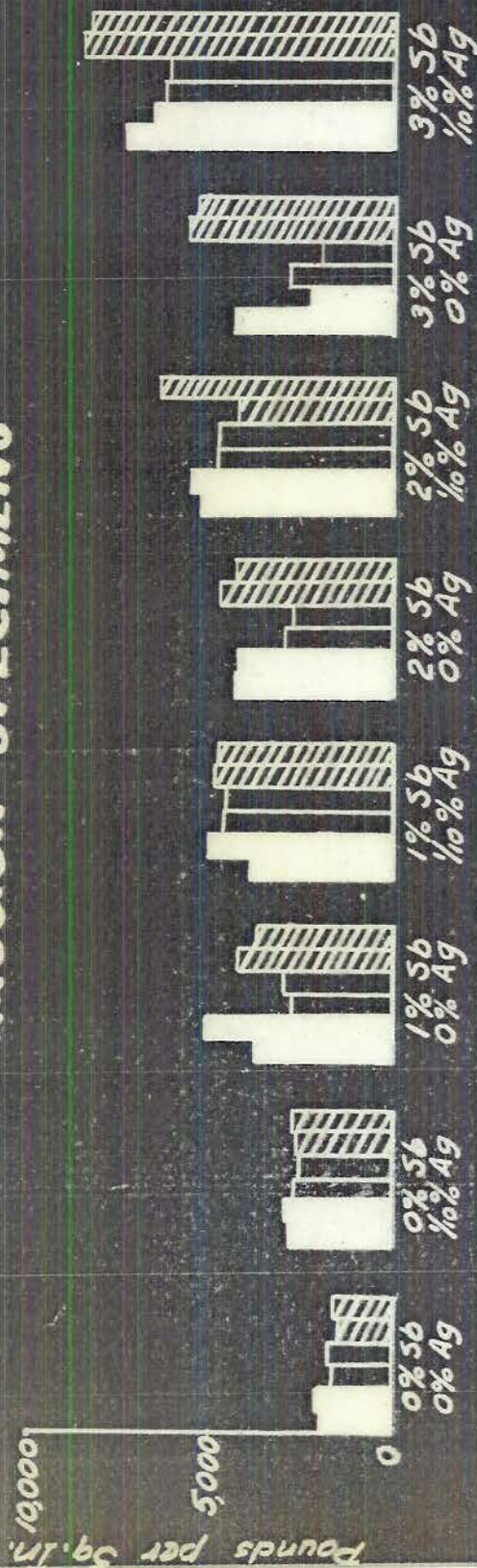


3% Sb
HEAT TREATED

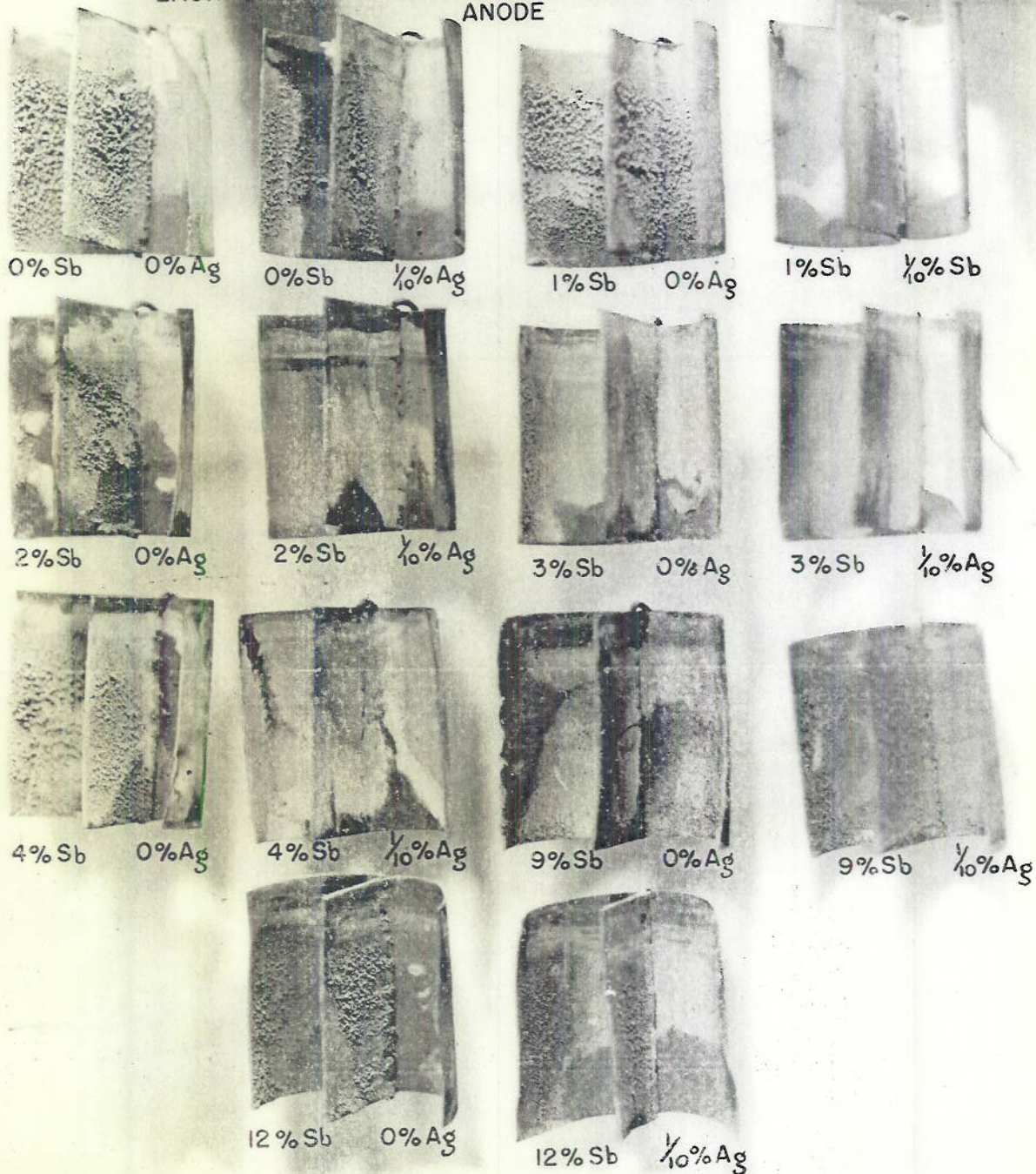


3% Sb-0.1% Ag
HEAT TREATED

TENSILE STRENGTHS OF CORROSION SPECIMENS



CATHODES OF CORROSION SPECIMENS
 ANODES NOT HEAT TREATED
 EACH CATHODE LABELED WITH COMPOSITION OF CORRESPONDING
 ANODE



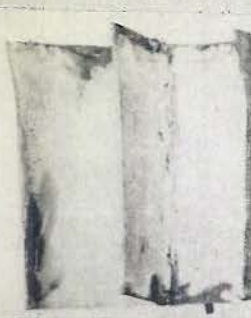
CATHODES OF CORROSION SPECIMENS
ANODES HEAT TREATED
EACH CATHODE LABELED WITH COMPOSITION OF
CORRESPONDING ANODE



0% Sb



0% Sb $\frac{1}{10}\%$ Ag



1% Sb



1% Sb $\frac{1}{10}\%$ A



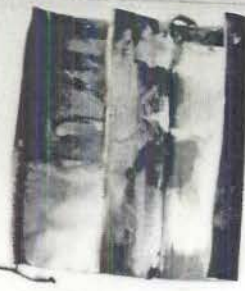
2% Sb



2% Sb $\frac{1}{10}\%$ Ag



3% Sb



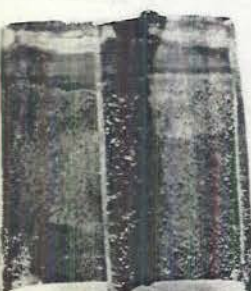
3% Sb $\frac{1}{10}\%$ Ag



4% Sb



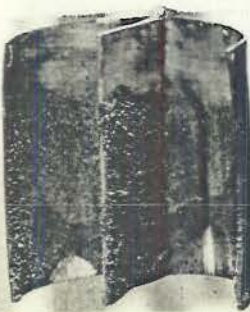
4% Sb $\frac{1}{10}\%$ Ag



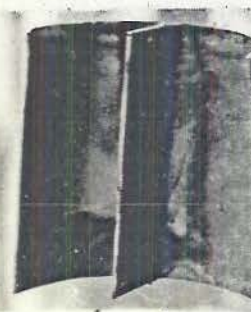
9% Sb



9% Sb $\frac{1}{10}\%$ Ag

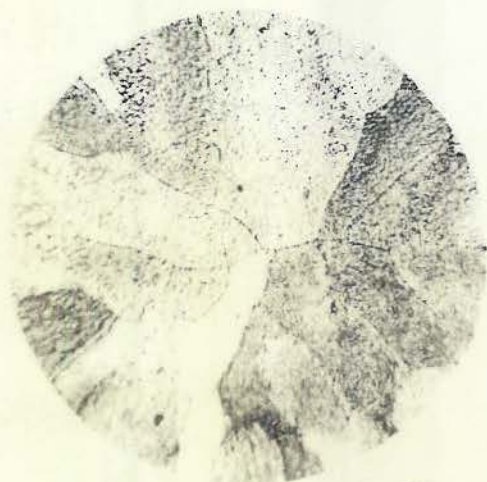


12% Sb



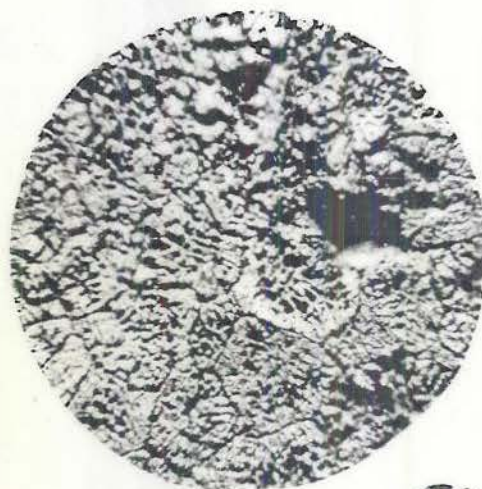
12% Sb $\frac{1}{10}\%$ Ag

ANTIMONY-LEAD SPECIMENS
48 HOURS ANODIC CORROSION



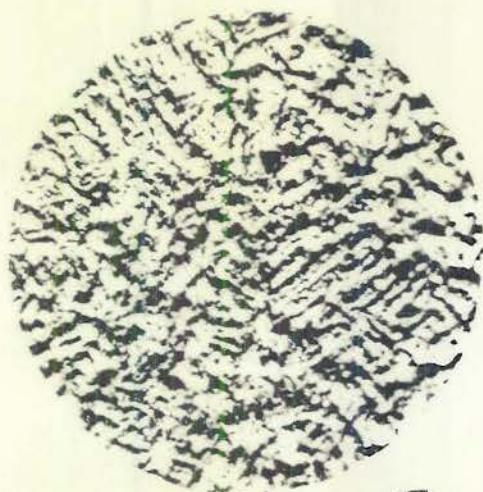
20x

PURE LEAD *Fig. A*



50x

2% Sb *Fig. B*



50x

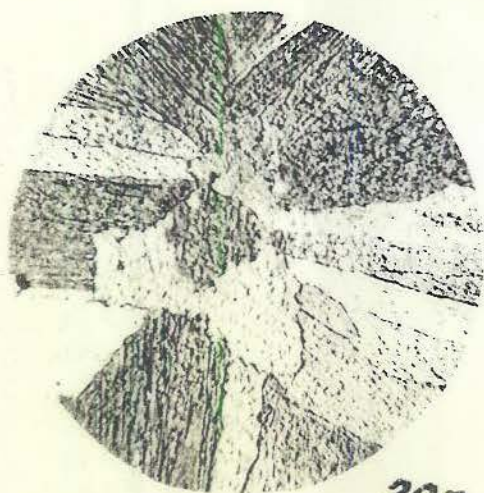
4% Sb *Fig. C*



50x

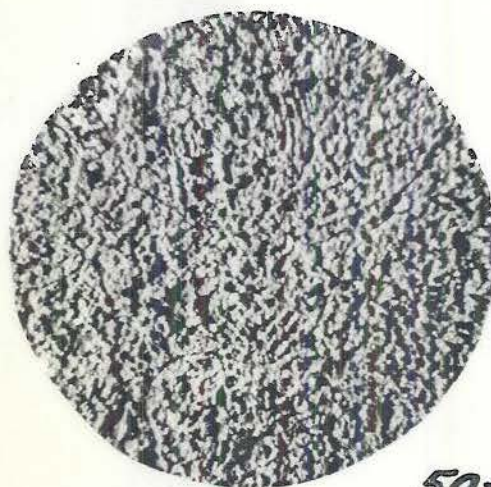
9% Sb *Fig. D*

ANTIMONY-SILVER-LEAD SPECIMENS **48 HOURS ANODIC CORROSION**



20x

0% Sb 10% Ag
 Fig. A



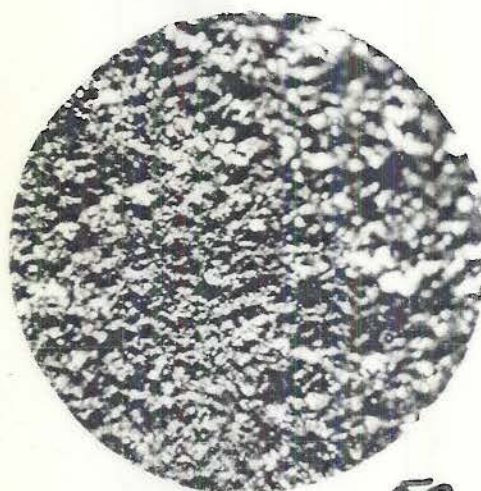
50x

2% Sb 10% Ag
 Fig. B



50x

4% Sb 10% Ag
 Fig. C

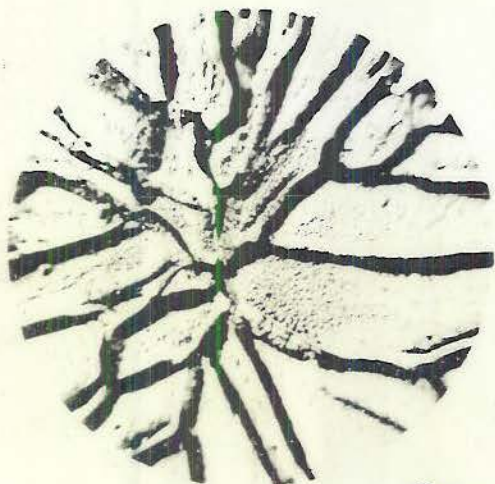


50x

9% Sb 10% Ag
 Fig. D

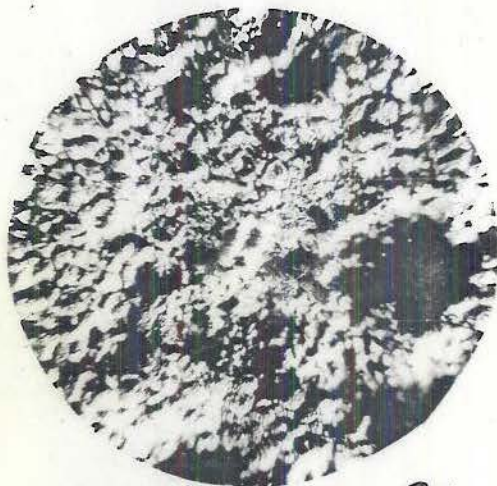
ANTIMONY-LEAD SPECIMENS

60 DAYS ANODIC CORROSION



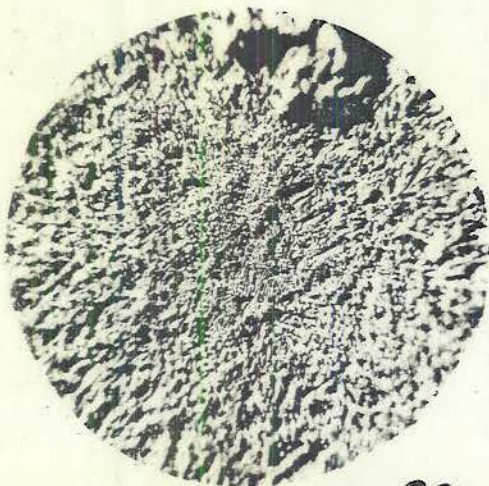
20x

PURE LEAD Fig. A



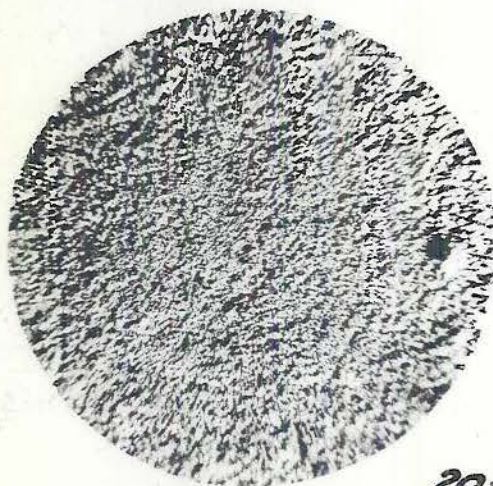
20x

2% Sb Fig. B



20x

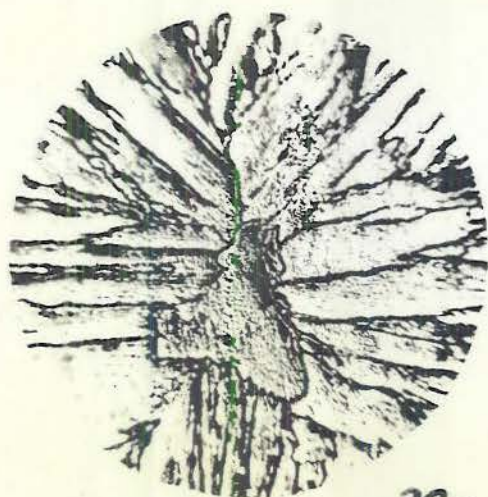
4% Sb Fig. C



20x

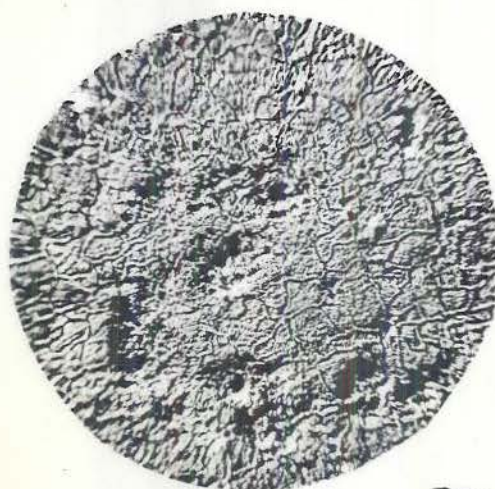
9% Sb Fig. D

ANTIMONY-SILVER-LEAD SPECIMENS **60 DAYS ANODIC CORROSION**



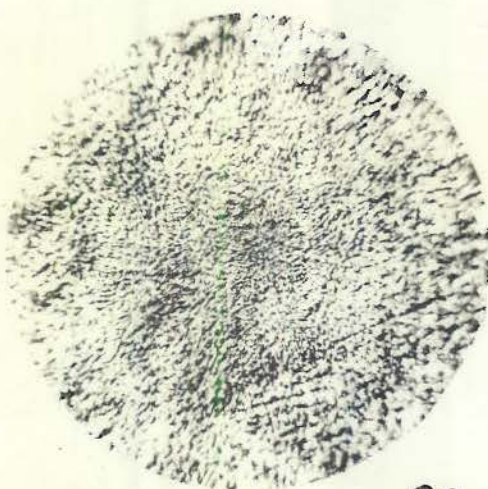
20x

0% Sb 10% Ag Fig. A



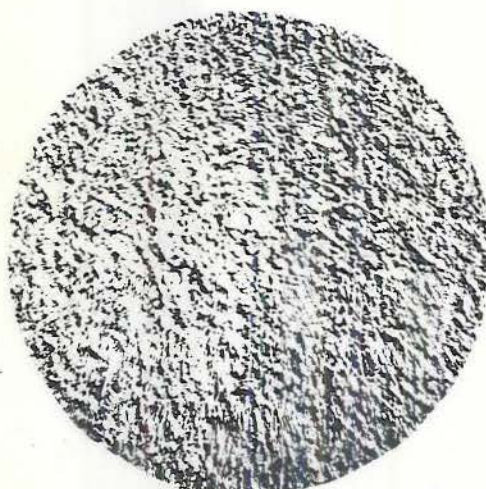
20x

2% Sb 10% Ag Fig. B



20x

4% Sb 10% Ag Fig. C



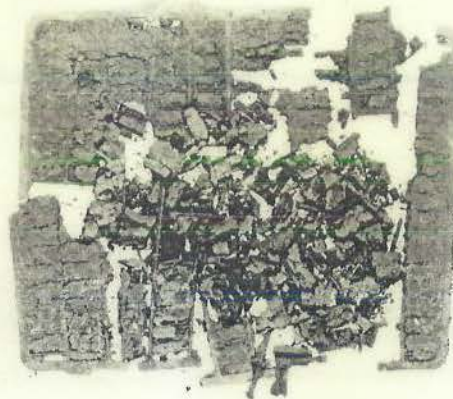
20x

9% Sb 10% Ag Fig. D



PURE LEAD

1



Ag 0.090 %

2

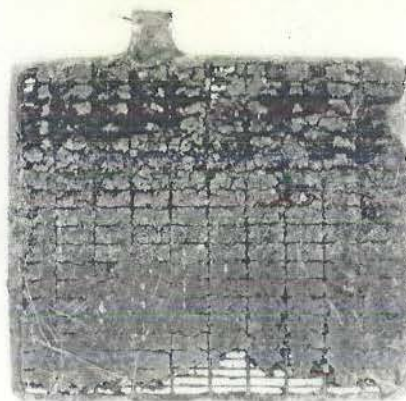
Sb 2.18 %



Ag 0.073 %

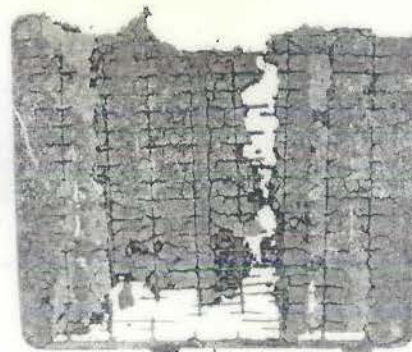
3

Sb 4.55 %



Sb 9.0 %

4

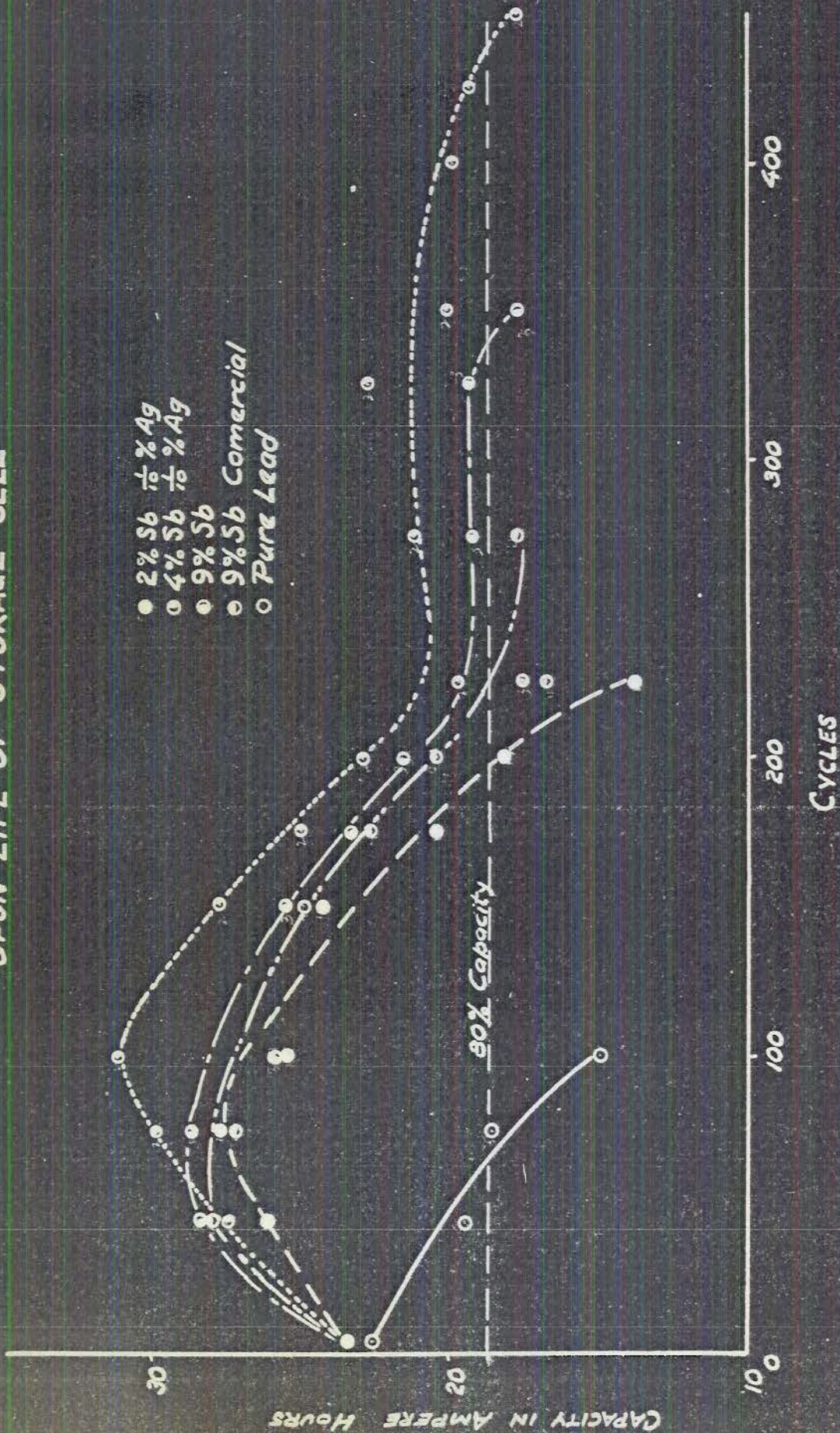


Sb 10. %

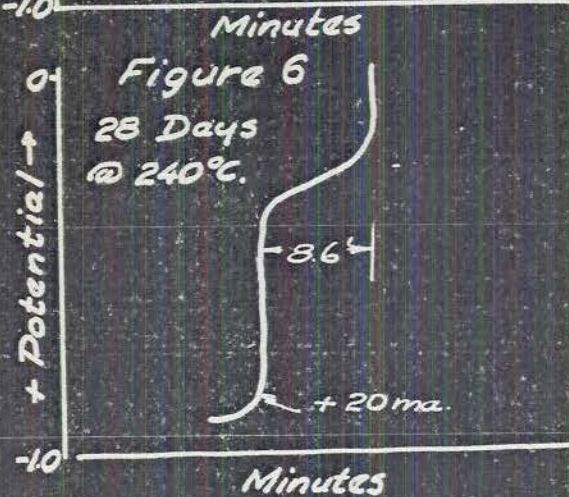
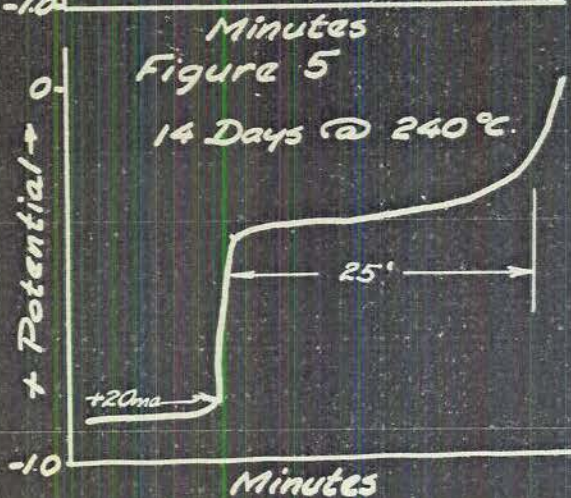
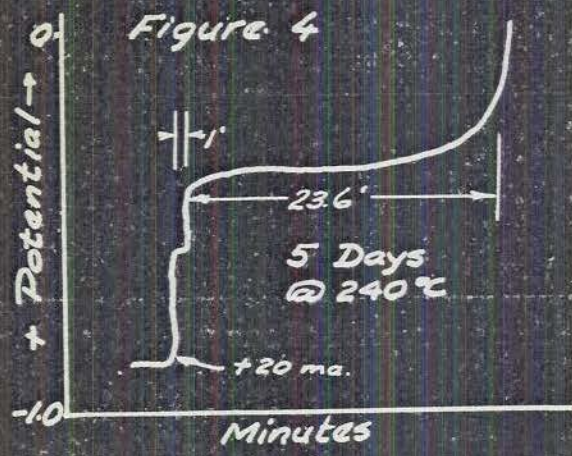
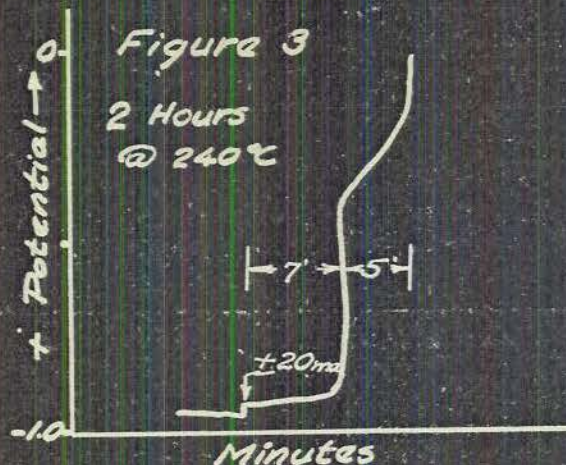
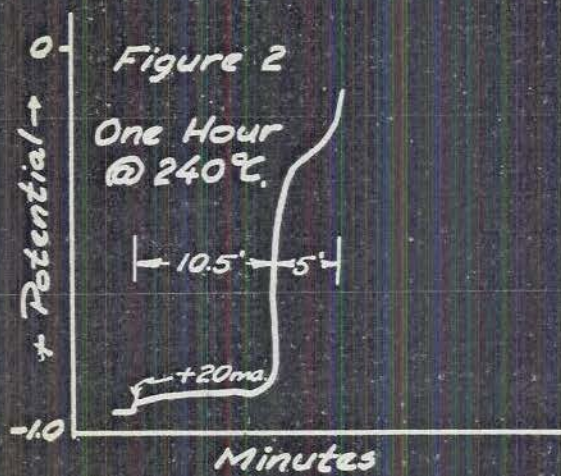
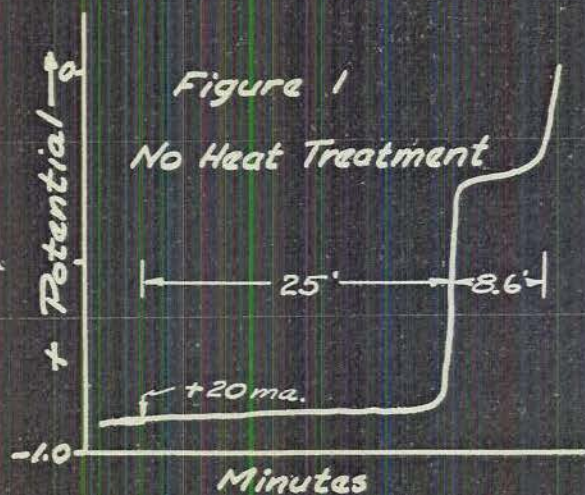
5

POSITIVE GRIDS AFTER LIFE TEST

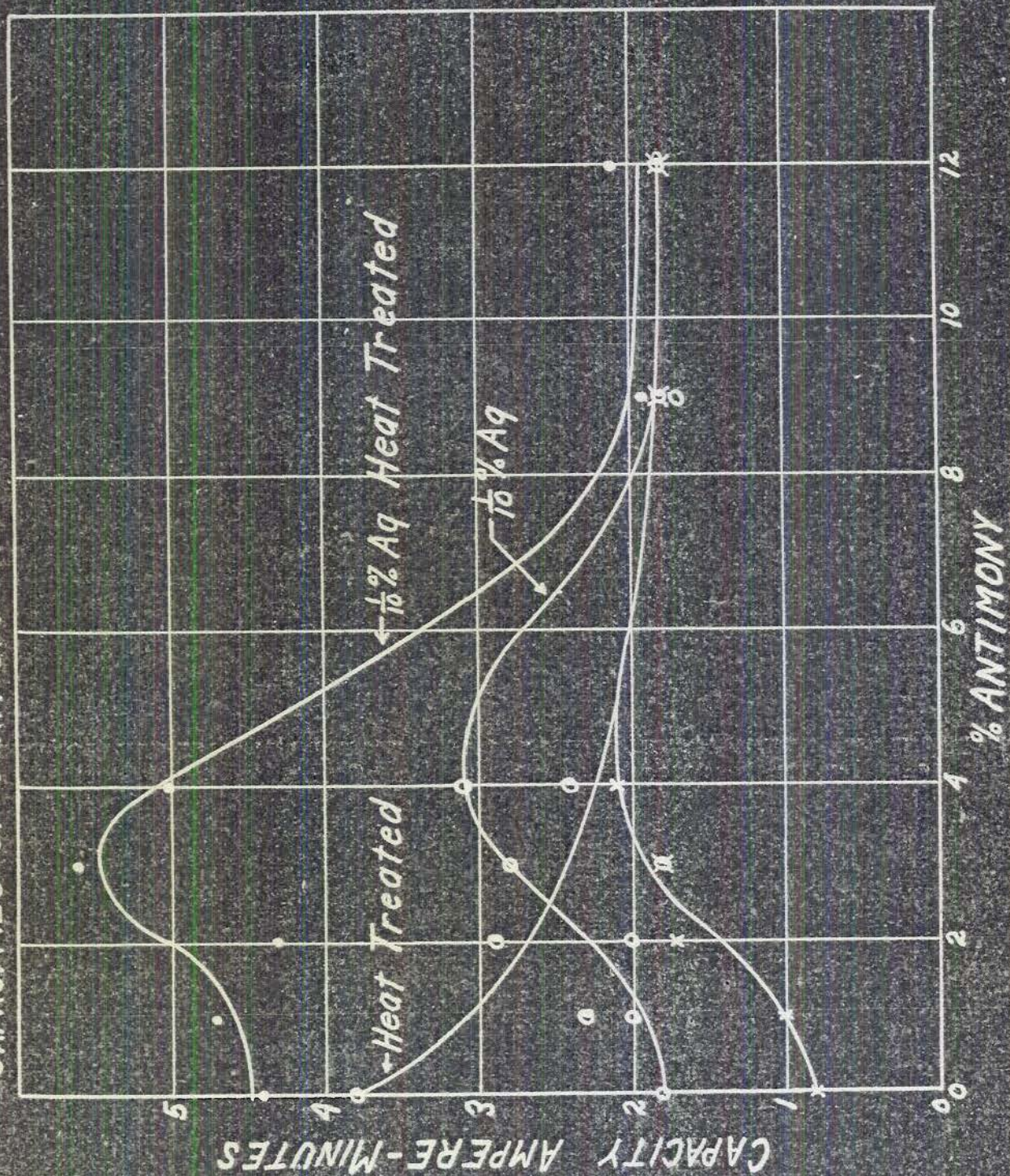
EFFECT OF POSITIVE GRID COMPOSITION UPON LIFE OF STORAGE CELL

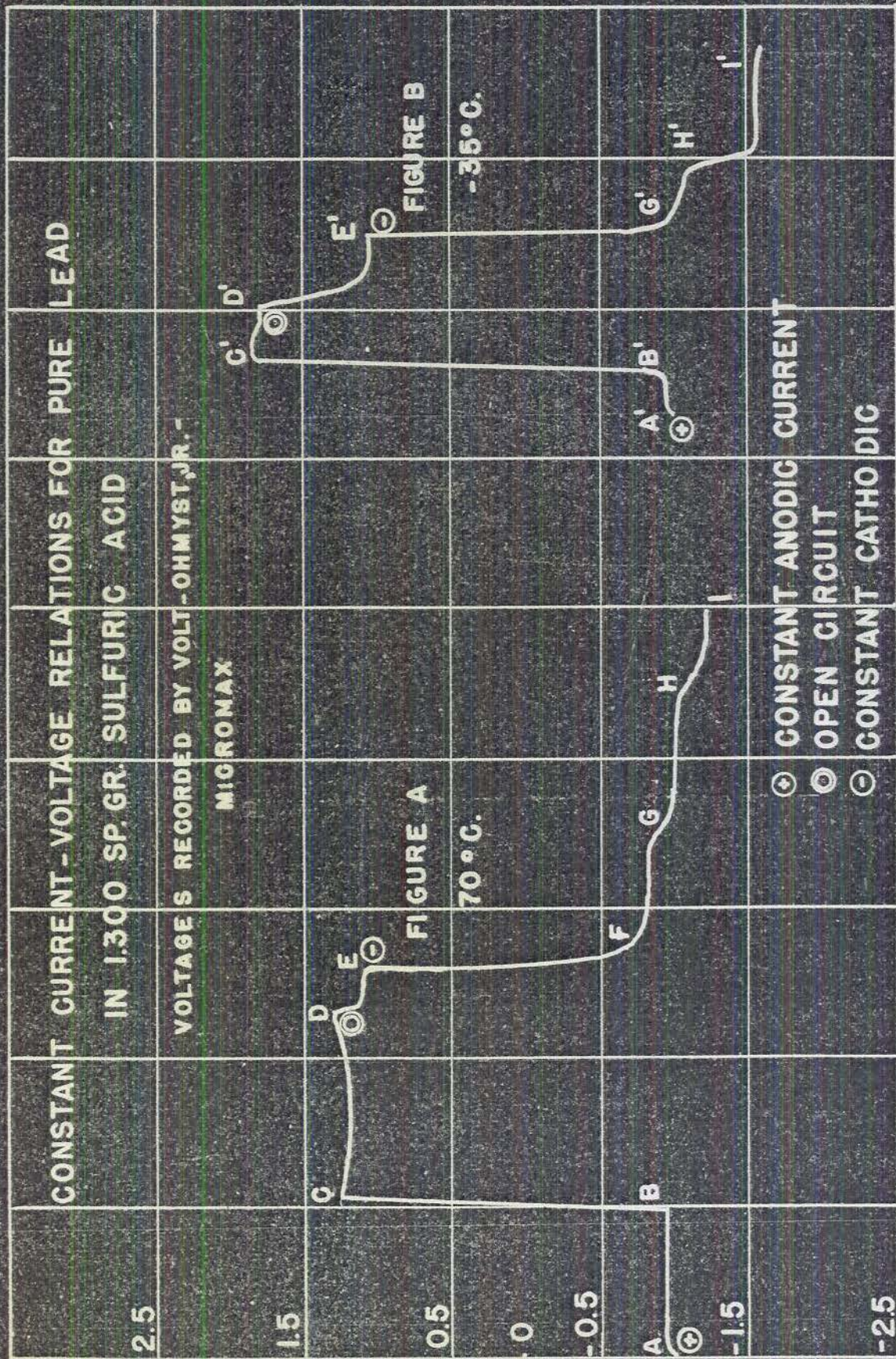


POTENTIAL-TIME RECORDS OF HEAT TREATED GRIDS CONTAINING 2% ANTIMONY



CAPACITIES OF CORRODED SPECIMENS AS CATHODES





TIME: ONE INCH = 10 MINUTES

DISTRIBUTION

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BuAer (5)

BuOrd (2)

ONR (2)

ONR, Technical Information Section (4)

JBAC (12)