# A STUDY
# OF A
# GRID FAILURE IN LEAD STORAGE BATTERIES

Thesis

by

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in Chemical Engineering

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The Purpose of this Research was to make a Study of a Grid Failure in Lead Storage Batteries.

## 1. HISTORY:

The metal used for casting grids for storage battery plates consists of an alloy of lead and antimony. Long practice has shown that the alloy which contains ninety-three per cent of lead and seven per cent antimony gives the best results. The impurities must be kept to a minimum. During the process of charge and discharge, the active material of the positive plate undergoes a large change of volume. This requires a grid of the greatest tensile strength possible. Due to the oxidizing action of the electric current on the positive plate, the grid must be resistant to corrosion.

The alloy in question gave good results when used in automobiles or stationary batteries where it was kept in a state of at least seventy per cent full charge. When placed in service where the plates received a slow complete discharge over a period of four weeks and then a recharge the results were not as good. After a period varying from one to three years the positive grid became badly corroded and the positive plate suffered fracture and later total disintegration. Due to the importance of this work it was considered advisable to investigate and determine the cause of the short life of the grids.

## 2. RELATED LITERATURE AND EXPERIENCE:

The storage battery industry is still in the secretive stage of development and relatively few books have been written which deal with the actual working conditions inside of a storage battery. The best and most modern of these is Vinal's "Storage Batteries." He devotes considerable space to "Troubles of Storage Batteries." The causes which he gives for corrosion on the grid of the positive plate consist in impurities in the electrolyte. The electrolyte used in the batteries under examination was very pure and had a minimum amount of impurities. Distilled water was used in replacing that lost by evaporation. Several other books, including those by Lyndon, Dolezalek, and Jantzen, were examined, but no specific data could be obtained.

## 3. MODE OF ATTACK:

An alloy was obtained which gave good service on this slow rate of discharge. It was decided to make some comparative tests on these two alloys. A chemical examination was made first. Several schemes of analysis were considered, but the one adopted by the American Society for Testing Materials was chosen as the best.

## 4. ANALYSIS OF PIG LEAD. PROCEEDINGS OF THE A. S. T. M. 1921 - Page 480:

### A. Determination of Silver:

Weigh 100 grams of the sample into a 3" scorifier and heat in a muffle furnace until the assay "covers." Pour into an iron mold and allow to cool. Free the resulting lead button from litharge, scorify again and pour as before. The button last obtained should not weigh over 20 grams and can be cupelled directly. Weigh the silver button obtained upon an assay balance.

### B. Determination of Bismuth:

Sodium Carbonate Solution - Dissolve 100 grams of $Na_2CO_3$ in a litre of distilled water.

Ammonium Carbonate Solution - Make a half saturated solution.

Alkaline Sulfide Wash Solution - Dissolve 200 grams of KOH in a litre of distilled water and mix one part of this solution with four parts of $H_2S$ water.

Dissolve 20 grams of the sample in a 400 c. c. beaker with 100 c. c. of $HNO_3$ (1:4), with the aid of heat. When solution is complete, add dilute $NH_4OH$ (1:2) with constant stirring, drop by drop from a burette, until a faint opalescence appears. If an actual precipitate is formed, redissolve by the addition of a small amount of $HNO_3$ (1:4) and repeat the addition of $NH_4OH$. Now add 5 c. c. of HCl (1:9), fill the beaker with hot water, bring to boiling, and allow to stand on a steam bath for two hours. (See Note below). The assay while standing must not reach the boiling temperature. Filter through a 7 cm. paper. Transfer the precipitate completely to the paper by means of a "policeman" and wash twice with hot water. Carefully examine the filtrate, washings, and any decanted liquid, and reject if clear. Dissolve the precipitate by dropping around the edges, from a 5 c. c. pipette, 5 c. c. of boiling HCl (1:9), receiving the solution in the original beaker. Wash the paper thoroughly with hot water, fill the beaker with water, bring to boiling, and allow to stand as before. Filter the Bismuth Oxy-Chloride upon a weighed Gooch crucible, wash thoroughly with water, once with alcohol, once with ether, and dry on a hot plate, cool and weigh.

Note: - If the precipitate is allowed to stand over night, it will settle and the clear supernatant solution can be decanted.

C. Determination of Arsenic:

Dissolve 111.11 grams of the sample in 550 c. c. of $HNO_3$ (1:4). When solution is complete wash into a graduated litre flask, add 75 c. c. of $H_2SO_4$ (1:1), cool and make up to the mark with water. Mix thoroughly, allow to settle, and filter off 900 c. c., equivalent to a 100 gram charge. Evaporate in a large porcelain dish until only enough $H_2SO_4$ is left to moisten the residue. When cool, wash into a small distilling flask with 60 c. c. of HCl (Sp. Gr. 1.20) and 20 c. c. of water, cleaning the dish carefully. Add 10 grams of $FeSO_4$ and distill, boiling to as small a volume as possible. When cool add 50 c. c. more HCl (Sp. Gr. 1.20) and redistill. Pass $H_2S$ through the cold distillate for 45 mins. Filter, and weigh the $As_2S_3$ on a Gooch crucible, washing with cold water, alcohol, and $CS_2$. After drying and weighing, redissolve with $(NH_4)_2 CO_3$ solution and reweigh the Gooch crucible, calculating the loss in weight to arsenic.

D. Determination of the Remaining Metals:

Tartaric Acid Solution - Dissolve 50 grams of tartaric acid in 250 c. c. of distilled water to which has been added 250 c. c. of HCl (Sp. Gr. 1.2).

Dissolve 222.23 grams of the sample in 1100 c. c. of $HNO_3$ (1:4) using a 1300 c. c. beaker. When solution is complete, examine for color and turbidity. If clear, wash the solution at once into a 2000 c. c. graduated flask. In case of a residue (Note 1.), however, dilute to 1100 c. c. and allow to stand until the supernatant liquid is clear. Decant as much as possible into the 2000 c. c. flask, filter the remainder and receive the filtrate in the same flask. Wash the precipitate well, and then place it together with the filter paper in a 100 c.c.

beaker and add 20 c. c. of the tartaric acid mixture. Heat to boiling and when the paper is well pulped, allow to digest warm for 30 minutes. Now add 50 c. c. of hot water, filter and wash. (Note 2.). Carefully dry the residue and ignite. If any appreciable residue remains, brush it into a small, silver dish containing 1 gram of molten KOH. Fuse for 5 minutes, and after cooling dissolve in as little hot water as possible and add to the above mentioned tartaric acid filtrate. Render this solution just alkaline with ammonia and then just acid with HCl, and saturate hot with $H_2S$ gas. After digesting for 30 minutes on the steam bath, pass $H_2S$ through the solution again for 15 minutes. Filter and wash with slightly acidified $H_2S$ water. Reject the filtrate. Wash the sulfides from the paper into the original beaker and add 5 c. c. of KOH solution (1:5) for every 25 c. c. of volume present. Digest hot for 5 minutes and filter through the original paper into a small flask graduated to 110 c. c. After washing with $H_2S$ water containing a little of the KOH solution, cool the filtrate and make up to the mark. Mix and reserve 100 c. c. as Alkaline Sulfide Solution No. 1. The precipitate may be discarded.

Add slowly to the main solution in the 2000 c. c. flask 150 c. c. of $H_2SO_4$ (1:1). After cooling and filling up to the mark, pour into a clean 3-litre flask provided with a rubber stopper. Rinse the flask out with 50 c. c. of water, which is equivalent to the volume of lead sulfate present, and is added to the portion. After mixing thoroughly by shaking, allow the precipitate to settle and filter off 1800 c. c. of the liquid. This is equivalent to a 200 gram charge. Place this in a No. 9 porcelain evaporating dish and evaporate, first over a free flame and later on the hot plate until only enough $H_2SO_4$

remains to moisten the residue. Add 50 c. c. of water and, after digesting warm for a short time, wash the solution into a 250 c. c. beaker, cleaning the dish carefully. Allow the solution to digest on the steam bath for 4 or 5 hours. (Note 3.). Then filter, wash and evaporate to 200-250 c. c. Place any residue (Note 4.) together with the filter paper in a 100 c. c. beaker and treat with 20 c. c. of tartaric acid mixture. Boil for 5 minutes, dilute with 50 c. c. of hot water and filter. Make the filtrate alkaline with ammonia and just acid with HCl and obtain the antimony, arsenic, and tin - as previously described - reserving the whole of the alkaline sulfide solution as Solution No. 2. Reject the sulfide residue.

To the filtrate from the lead sulfate, add ammonia until the neutral point is reached, and then for every 50 c. c. of the solution present, add 2 c. c. of HCl (Sp. Gr. 1.20). Pass $H_2S$ gas into the hot solution until saturated, digest for 30 minutes on the steam bath, and again pass $H_2S$ gas into the solution. Filter and wash with $H_2S$ water slightly acidified (Note 5.). Separate the antimony, arsenic, and tin in the precipitate with KOH solution as usual, obtaining an alkaline sulfide solution No. 3. (Note 6.).

To sum up: three alkaline sulfide solutions have been obtained, containing antimony, arsenic, and tin; a precipitate of metallic sulfides, containing copper, lead, etc., and a solution, containing iron, zinc, nickel, etc.

Notes:

1. A residue indicates the presence of antimony, tin, possibly arsenic, or sulfur as lead sulfate.

2. It has been found that even this treatment occasionally fails to dissolve stannic acid completely.

3. If it is preferred, allow the solution to stand over night to insure complete solution of all soluble salts.

4. Any residue of lead sulfate may contain some antimony, tin, or possibly arsenic.

5. The filtrate will contain any iron, zinc, nickel, cobalt, and manganese; while in the precipitate will be found any copper, cadmium, lead, silver, bismuth, tin, antimony, and arsenic.

6. When separating the sulfides of arsenic, antimony, and tin from the sulfides of copper, lead, etc., it is necessary to wash all the sulfide back into the beaker in which they were precipitated. These sulfides sometimes cling so tenaciously to the paper that in dislodging them more water than the 25 c. c. specified is required. In this case, allow the sulfides to settle and decant the clear supernatant liquor through the filter until the volume is reduced to 25 c. c. Before rejecting the decanted fluid always test with $H_2S$ water.

In washing sulfide precipitates with water, much trouble is experienced from the tendency of the precipitate to pass through the filter in colloidal form. This is particularly true in washing sulfides that have been digested with KOH. Time and trouble will be saved by washing all the sulfides precipitated from mineral acid solutions with $H_2S$ water, containing a little of the acid in which they were precipitated. The same is true of sulfides precipitated in or filtered from alkaline solutions.

When working with alkaline solutions in which tin is to be determined, avoid the use of Jena or other glass that contains zinc. The zinc content of the glass may influence the result.

## 1. Determination of Antimony and Tin:

Solutions:

KI - Dissolve 100 grams in a litre of distilled water.

$Na_2S_2O_3$ - Dissolve 24.8 grams of $Na_2S_2O_3 \cdot 5\,H_2O$ in 1000 c. c. of distilled water and allow to stand for 24 hours. Standardize against C. P. antimony metal, using same quantity of reagents and same procedure as under method. Each c. c. of solution is equivalent to approximately 0.006 grams of antimony.

Wash the alkaline sulfide solutions Nos. 1, 2, and 3 into a 600 c. c. beaker, and acidify with 5 c. c. of $HNO_3$ (1.42) and 20 c. c. of HCl (1.20). Evaporate the solution to dryness on the steam bath. Dissolve the residue in 200 c. c. of water, add 10 grams of oxalic acid and 10 grams of ammonium oxalate, and heat the solution until it is clear. Then pass $H_2S$ gas through the boiling solution for 45 minutes. Filter off the precipitate - consisting of $As_2S_3$ and $Sb_2S_3$ - and wash with hot water. Determine the tin electrolytically in the filtrate, continuing the electrolysis until all of the oxalic acid is decomposed and the solution is alkaline. Dissolve the deposit on the cathode with a small amount of HCl and examine qualitatively for tin.

Dissolve the sulfides of antimony and arsenic in KOH as usual, collecting the filtrate in a 500 c. c. Erlenmeyer flask. Add 50 c. c. of HCl (1.20) and boil the solution until about 30 c. c. are left. Expel the arsenic as chloride. Now oxidize the solution with a pinch of $KClO_3$ and boil until no more chlorine remains. Cool and add 5 c. c. of KI solution. Titrate the liberated $I_2$ with N/10 $Na_2S_2O_3$ solution, using $CS_2$ as an indicator.

2. Determination of Copper and Cadmium:

Solutions:

NaCl Sol. No. 1 - Dissolve 1 gram in 100 grams $H_2O$.

NaCl Sol. No. 2 - Dissolve 10 grams in 100 grams $H_2O$.

KCN - Dissolve 2 grams of KCN in a litre of distilled water and standardize against a known amount of copper as treated in the analysis.

$Na_2CO_3$ Sol. No. 1 - Dissolve 50 grams of $Na_2CO_3$ in 1 litre of distilled $H_2O$.

$Na_2CO_3$ Sol. No. 2 - Dissolve $Na_2CO_3$ in distilled water to saturation.

Method:

(a) Where copper exceeds 0.0025%.

Place the filter containing the sulfides in a 100 c. c. beaker and add 20 c. c. of $HNO_3$ (1:4). Heat with occasional stirring until paper is thoroughly pulped and the sulfides are completely dissolved. Filter into a 250 c. c. beaker. Dry the residue, which generally contains a small amount of copper; ignite in a porcelain crucible; boil with 5 c. c. of $HNO_3$ (1:1), and wash into the main portion, keeping volume below 100 c. c. Render it strongly alkaline with $NH_3$, and add 5 grams of KCN, then saturate it in the cold with $H_2S$ gas. (Note 1). Filter the solution and evaporate to a volume of 20 to 30 c. c. in a 4" casserole. Boil until solution is complete. Add 20 c. c. of $H_2SO_4$ (1:1) and evaporate the solution under a hood until dense fumes of $H_2SO_4$ escape. Cool, dilute and warm until all the $CuSO_4$ is dissolved.

Now filter, if necessary, into a 200 c. c. beaker, render it just alkaline with $NH_3$, make acid by the addition of 3 c. c. of $HNO_3$ per 100 c. c. solution, and electrolyze for copper.

Dissolve the precipitate of sulfide in the usual manner with 20 c. c. of $HNO_3$ (1:4). Add 1 c. c. of NaCl solution No. 1 to the solution, still containing the pulped filter, and digest for 1/2 hour. Filter off the AgCl, wash and reject. Make the filtrate - not exceeding 100 c. c. - alkaline with a slight excess of $Na_2CO_3$ and add 5 grams of KCN. Digest for 1 hour. Filter and wash with $Na_2CO_3$ No. 1. Reject the precipitate of bismuth. Now add a few c. c. of ammonium sulfide solution to the filtrate to precipitate the cadmium as yellow CdS. Filter on a weighed Gooch crucible and weigh as CdS (Note 2.).

Note 1: Cu remains in the solution, while Pb, Ag, Bi, and Cd are precipitated.

Note 2: If any appreciable amount of CdS is found, it should be converted to, and weighed as $CdSO_4$, according to method for Cd under Standard Methods of Chemical Analysis of Spelter (B 38) of A. S. T. M.

### 3. Determination of Iron:

Method:

Evaporate the filtrate containing the iron, zinc, etc. to 100 c. c. and oxidize with a few drops of $HNO_3$. Separate the iron with $NH_3$ as usual, making two separations and receive the filtrate in a 500 c. c. Erlenmeyer flask. Redissolve the Fe with hot HCl (1:1) or dilute $H_2SO_4$ and determine the Fe volumetrically by any of the standard methods.

## 4. Determination of Zinc:

Method:

Add to the filtrate from the $Fe(OH)_3$ 1 c. c. of cochineal indicator, and render just neutral with HCl. Then add 15 drops of 2 Normal HCl for each 100 c. c. of solution. Saturate cold with $H_2S$ gas and allow the flask, loosely stoppered, to stand over night. Filter, and wash with $H_2S$ water acidified in the same manner as described above. Dry the precipitate of ZnS, carefully ignite in a porcelain crucible, and weigh as ZnO.

## 5. Determination of Nickel and Cobalt:

$H_2S$ wash water - To each 100 c. c. of $H_2S$ water, add 20 c. c. of neutral $NH_4Ac$.

Method:

Render the filtrate alkaline with $NH_3$ and saturate cold with $H_2S$. Heat to boiling and then make just acid with HAc, add 20 c. c. of neutral ammonium acetate solution, and boil until the sulfides of Ni and Co separate out. Filter and wash with warm $H_2S$ wash water. Dry the precipitate and paper in a porcelain crucible and carefully ignite. If there is an appreciable amount of residue after ignition, dissolve by boiling with 10 c. c. of aqua-regia, wash into a 250 c. c. beaker, add 10 c. c. of $H_2SO_4$ (1:1), evaporate until fumes appear, cool, dilute to 200 c. c., make alkaline with $NH_3$, and add 15 c. c. of concentrated $NH_3$. Then electrolyze the solution and weigh the Ni and Co as such.

Notes:

If the amount of Ni and Co is small, it can be weighed as oxide. If the filtrate from the NiS and CoS shows a brown color, it indicates that the precipitation has not been complete. In this case make ammoniacal and repeat.

### 6. Determination of Manganese:

Solutions:

Standard $KMnO_4$ - Mix 10 c. c. of N/10 $KMnO_4$ and 100 c. c. of distilled water. Each c. c. is equivalent to approximately 0.00011 grams of Mn.

Dilute $H_2SO_4$ - Add 25 c. c. of conc. $H_2SO_4$ to 1000 c. c. of distilled water.

Nitric Acid Wash - Add 300 c. c. of $HNO_3$ to 1000 c. c. of distilled water.

Method:

Evaporate the filtrate, which should now contain only Mn, to dryness in a porcelain dish and heat carefully over an Argand Burner until all the $NH_3$ salts have been driven off. (Note 1.). After cooling moisten the residue with a little HCl and warm until dissolved. Add 1 c. c. of $H_2SO_4$ (1:1) and evaporate the solution until fumes appear, continuing the fuming until nearly all the $H_2SO_4$ has been driven off. Cool, and add 50 c. c. of $HNO_3$ (1:3) and 0.5 grams of sodium bismuthate (Note 2.). Boil the solution until the pink color is destroyed. If any Mn is precipitated, dissolve by the addition of a few cubic centimeters of dilute $Na_2S_2O_3$ solution. In this case the solution must again be boiled until free from all fumes. After cooling add an excess of sodium bismuthate, stir a few minutes and filter through ignited asbestos into a 100 c. c. Nessler tube. Wash with dilute $HNO_3$ and make filtrate up to the mark. Into another similar tube put 100 c. c. of dilute $H_2SO_4$ which has been made very faintly pink with $KMnO_4$ solution. Now add standard solution of $KMnO_4$ from a burette until the color of the sample is exactly matched.

Note 1: It is best to bake here over a Bunsen flame until all the organic matter has been destroyed.

Note 2: The $HNO_3$ must be freed from nitrous fumes, by passing a current of air through the acid for 1/2 hour.

The Sample gave the following analysis: Column (a) gives the Company specifications for lead antimony alloy; Column (b) gives the analysis of sample by the methods given above; Column (c) gives the analysis by Industrial Testing Laboratories, L. A. -

| | (a) | (b) | (c) |
|---|---|---|---|
| Cadmium | 0.050% | absent | 0.00004% |
| Silver | None | 0.003% | 0.004 |
| Arsenic | 0.050 | 0.0009% | 0.0009 |
| Tin | 0.050 | ------ | 0.0001 |
| Bismuth | 0.100 | ------ | 0.048 |
| Copper | 0.050 | 0.042% | absent |
| Iron | 0.050 | less 0.001% | trace |
| Zinc | 0.100 | " 0.003% | 0.024 |
| Cobalt ......)<br>Nickel ......) | 0.005 | " 0.002% | trace |
| Manganese | 0.005 | " 0.001% | absent |
| Antimony | 7.00 | 4.8% | 2.46 |

The results of the analyses showed that apparently the sample complied with the requirements except in the antimony content.

Several determinations were run on the sample to obtain the correct value of the antimony content. A comparative check was also run on a sample of an alloy which gave satisfactory results. In some cases where possible the above method was shortened. The standard solutions were run against pure antimony using the same proceedure as in the case of the sample.

<u>Antimony Per cent</u>:

| | Sample | Good Alloy |
|---|---|---|
| | 4.8 | 4.9 |
| | 4.8 | 7.5 |
| | 5.10 | 6.0 |
| | 6.8 | 5.0 |
| | 4.3 | 5.4 |
| | 4.3 | |
| Ave. | 5.02 | 5.8 |

The antimony content was also determined by the freezing

point

<u>Method</u>:

The temperature of the freezing points of lead antimony alloys between 0% and 13% antimony when plotted against the per cent of antimony gives a straight line curve. This method gives quite accurate results when used with a calibrated thermometer. The results of this test showed the sample to have an antimony content of 7.2%

Due to the wide variation between these two sets of results and between the various chemical results themselves, it was decided to determine the antimony chemically by a different method.

The following proceedure, which is the standard used by several battery manufacturers, was used:

Method:

To 1/2 gram of the sample in a 200 c. c. Erlenmeyer flask add 4 grams of fused $KHSO_4$ and 10 c. c. of Conc. $H_2SO_4$. Grasp the flask with a pair of crucible tongs and heat with a rotary motion over a free flame until copious fumes of $SO_3$ are evolved and no sulfur is left on the neck of the flask. Cool, add 30 c. c. of $H_2O$ and 5-10 c. c. of HCl. Boil 1 minute to expel $SO_2$ and As. Cool, titrate with 1/10 N. $KMnO_4$.

Several determinations were made and checked against pure antimony. The results gave 7.1% which checked the results found by the freezing point method. The sample of good alloy had a content of 7.25% as determined by this method.

## CONCLUSIONS:

Although separate determinations of Sb were made, using the method of the A. S. T. M., the results were evidently not very valuable. The loss was due either to the number of precipitations necessary or else to incomplete oxidation by $KClO_3$.

The analysis shows the sample to conform in all respects to the requirements laid down for lead-antimony alloy to be used for storage battery grids.

It is known that lead suboxide is somewhat soluble in molten lead. It may be that in the smelting of this lead that some of this oxide may have been dissolved in the metal due to over-heating. Lead suboxide when dissolved in lead-antimony alloy produces a brittle alloy which has a lower tensile strength than an alloy free from suboxide. Lead suboxide also makes the alloy more susceptible to corrosion under the oxidizing action of the electric current. As this would give a grid metal of much shorter life,great effort is made by manufacturers to obtain either virgin lead or one free from suboxide.

Further research along this line to discover a method for determining and eliminating lead suboxide would be very valuable to the storage battery industry.

The writer wishes to thank Dr. William N. Lacey under whose direction this work was done.

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