# CORROSION OF LEAD IN DILUTE SULFURIC ACID

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CONTENTS


| | Page |
|---|---|
| Summary | 1 |
| Introduction and Literature Survey | 4 |
| Materials | 8 |
| Equipment | 9 |
| Procedure | 10 |
| Results | 12 |
| Discussion | 14 |
| Bibliography | 16 |
| Acknowledgment | 17 |
| Figure 1 -- Experimental Set-up | |
| Figure 2 -- Corrosion Samples | |
| Figure 3 -- Pure Lead and Tellurium Lead Samples | |
| Appendix A -- Observed Weight Changes | 18 |
| Appendix B -- Surface Area and Density of Samples | 20 |
| Appendix C -- Calculation of Results | 22 |

# CORROSION OF LEAD IN DILUTE SULFURIC ACID

## SUMMARY

Lead has long been used as a material of construction because of its cheapness and resistance to corrosion, in spite of its low tensile strength, softness, and tendency to creep. Its corrosion resistance was taken for granted - the only design data available being the fact that the manufacturer did or did not recommend his product for certain conditions.

When lead alloys were introduced with the view of improving the physical properties of pure lead, it was observed that the corrosion resistance of the alloy usually was not as great as that of pure lead. Though noble alloys - Lead-Silver, for example - tend to decrease the corrosion rate, others increase the rate tremendously. Perry cites the case of a Lead-Bismuth alloy of only 0.05% bismuth in which the corrosion rate increased over 1000 per cent under certain conditions. (1).

Since there is no uniform product of corrosion under all conditions, the corrosion rate must be determined experimentally; providing limitless subjects for corrosion tests. In the tests, which were made for this thesis, samples of pure lead, chemical lead (0.06% Cu), tellurium lead (0.05% Tl), and antimony lead (2% Sb) were subjected to the corroding

effects of a dilute sulfuric acid solution which had the composition of a viscose rayon spinning bath. Plant conditions were duplicated in every way possible.

After 532 hours in the solution, the samples had formed surface films of varying protective powers. The tellurium lead was most resistant, forming a highly protective film while permitting a penetration of $2.24 \times 10^{-5}$ inches in the 532 hours. The penetration for similar samples in $10^{\circ}$ Be sulfuric acid was $0.68 \times 10^{-5}$ inches while the film formed in 575 hours. No further corrosion was noted when the samples were checked after 785 and 879 hours in solution. The antimony alloy was next best in corrosion resistance. The film formed in the same time as did that of the tellurium alloy; the penetration, however, was greater in this case.

In the case of pure lead and chemical lead, the samples gained weight during the formation of brittle films. These films scaled off in spots, leaving the surface exposed to fresh attack. Though the corrosion losses were slight, even with the scaling, the formation of the non-adherent film would be undesirable.

From these results it may be concluded that tellurium lead and antimony lead of these compositions are most satisfactory for use in handling dilute sulfuric acid. It would be advisable to check different compositions of these alloys under actual plant conditions with more than two samples of

each alloy, although the duplicate samples used in the present work checked closely.

# CORROSION OF LEAD IN DILUTE SULFURIC ACID

## Introduction and Literature Survey

Although corrosion has been observed for thousands of years, it was not until the past century that definite ideas as to the cause of corrosion were presented. In general, it is considered to be a chemical reaction between a metal and the non-metalic constituents of its environment - the occurrence of corrosion depending more on the character of the environment than on the composition of the metal.

Nernst's work in electrochemistry was the basis for the idea that in corrosion, both chemical and electrical changes took place. He thought that corrosion was electrolysis in which the metal served as both cathode and anode - the dissolution of the metal taking place when ions left the surface of the metal. (6)

Many factors have been found to influence the corrosion of various metals. Some of these are:

The effect of the presence of water, which is illustrated in the action of chlorine gas on steel. If the gas is dry, it can be stored in steel tanks; the presence of water, however, causes intensive corrosion due to the formation of hypochlorous acid.

The effect of the presence of oxygen or some other depolarizing agent, as in the case of a dry cell battery. The corrosion of the zinc case, which causes the formation of a hydrogen envelope on the carbon core, and the generation of the e.m.f. will cease when this envelope completely covers the surface of the core, unless a depolarizing agent is present to remove the hydrogen.

The visible displacement of hydrogen by the corroding solution. An example is the case of zinc in sulfuric acid. This factor is so evident that corrosion of this type is seldom encountered.

Failure of the metal to form an insoluble film which will stifle the reaction. In the case of lead and lead alloys, their high corrosion resistance is due to the formation of protective surface films.

Though the formation of an insoluble film will preserve the metal indefinitely, there are many conditions which tend to counteract the protective action of films. For a film to be effective, it must be insoluble in the corroding solution, be deposited in the right form at the right place, and be adherent. If the film were not completely insoluble, it might even enhance corrosion due to breaks in the film, since the film would tend to create concentration cells on the surface of the metal which would accelerate the corrosion. On

the subject of the proper form of the film, Evans observed that in the case of lead in dilute and concentrated sulfuric acid, the dilute acid formed the best film since the small lead sulfate crystals were more compact than the crystals formed in the concentrated acid.[7] Even though an insoluble film is formed, if it tends to be non-adherent, the corrosion resistance of the surface is lowered due to the setting up of voltalic couples between the metal and the remaining film. Protective films are rendered non-adherent by various conditions of environment. Changes in temperature cause scaling since the coefficients of expansion of the metal and the protective film differ. Also, a film which is insoluble at a low temperature may dissolve readily at a higher temperature; for example, lead sulfate, which is highly insoluble in sulfuric acid at ordinary temperatures, becomes quite soluble in sulfuric acid at 220° C. When the film is alternately wet and dried, there is a tendency on the part of heavy films to flake off. There is also the danger of film removal by abrasion. Rapidly flowing corrosive liquids or liquids with suspended solids may wear off the film and allow corrosion to begin afresh. Also, the effect of vibration is noticed where the films are formed on metal which is in contact with moving parts of machinery.

When there is a lack of homogeneity in the metal, the film may be non-adherent due to the different products of

corrosion. In regard to the homogeneity of the metal, there are two types of alloys - the solid solution and the mechanical mixture type. Of these, the solid solution is more nearly homogeneous and should be the more corrosive resistant.

In a general statement, Fink reports that in the case of an alloy, the base metal is the one which ultimately goes into solution. As an example of this, lead alloys in which lead is the base metal - Lead-Thallium and Lead-Silver, for instance - are more resistant than pure lead itself.(8) Evans agrees with this in his statement that, "Noble impurities, which would be expected to accelerate corrosion of lead in sulfuric acid, may actually assist in building up the sulfate film." (2)

These noble metal alloys are too expensive for general use as construction materials. However, there are several lead alloys which are very resistant to corrosion by dilute sulfuric acid. The oldest of these, chemical lead, is very satisfactory for most purposes. Formerly it was made from remelted scrap and was thought to have added corrosion resisting powers. Tests revealed, however, that the remelted scrap corroded more rapidly due to the accidental inclusion of antimony scrap. (3). According to Hawkins and Turner, lead containing antimony is superior to pure lead at low temperatures and worse at high temperatures. (4). The newest of the lead alloys is Tellurium-Lead, and it is claimed to be superior to

pure lead in all physical properties. (5).

Since no quantitative results of corrosion data on lead in dilute sulfuric acid were available, it was the object of this work to find the corrosion resistance of pure lead and some of its alloys. However, the work was done on a limited scale and is only valuable as an indication of the corrosion trends of the samples under the conditions considered.

## MATERIALS

### Samples

| Name | Composition | Sp. Gr. | Source |
|---|---|---|---|
| Tellurium lead | 0.05% Tl | 11.31 | National Lead Company |
| Antimony lead | 2.00% Sb | 11.2 | Made in laboratory * |
| Pure lead | 99.994% Pb | 11.38 | Eagle-Picher Lead Co. |
| Chemical lead | 0.06% Cu | 11.35 | From laboratory stock |

* The antimony lead was made from pure lead and C.P. antimony.

### Solutions

The corroding solutions were made up with C.P. materials. The first solution was $10^{\circ}$ Be sulfuric acid. The second was a spin bath solution of the following composition:

| Component | % |
|---|---|
| $H_2SO_4$ | 9.0 |
| $ZnSO_4$ | 1.0 |
| $Na_2SO_4$ | 16.0 |
| $H_2O$ | 73.0 |

EQUIPMENT

The equipment in the order of its use can be divided into two groups; that for preparing the samples and that which was used in carrying out the corrosion tests.

Under the first heading are: Graphite crucible, graphite mold, furnace, rolls, shears, punch, and balances. The tellurium and chemical lead samples were cut from sheet lead and, therefore, the crucible and mold were not used in these cases.

The corroding equipment consisted of a constant temperature bath of water heated by Calrod heating units which were controlled by a mercury switch (Precision Model A, Precision Instrument Company). The bath was a 3'x5' stainless steel tank, insulated with cork and asbestos paper. ( Figure 1 )

The samples were supported by glass hooks in 600 cc beakers which rested on a platform in the center of the bath. Watch glasses covered the beakers to prevent contamination and to aid condensation of the vapors. A 60 watt light bulb was used to reproduce plant conditions, since at no time in a plant running 24 hours a day would the lead be subjected to marked light changes.

PROCEDURE

The accessories for the constant temperature bath were gathered and assembled in order to have the bath working properly by the time the samples were ready. The temperature control was regulated to hold a temperature of 45° C. by using acetone in the mercury switch. The bath was operated at this temperature since, in actual operation, the temperature of a spinning bath would be 45° C.

The samples from sheet were rolled to a smooth finish on the small hand rolls. The samples which were made from the lead pig were melted down in the graphite crucible and cast into small ingots. After being rolled, the samples were sheared, punched, marked for identification purposes, and examined for flaws.

The 10° Be $H_2SO_4$ solution was the first one used since it was the simplest to make up and maintain at a fairly constant concentration (by hydrometer). The glass hooks were prepared so as to hold two samples in each beaker in such a manner that they would not touch each other.

When the equipment was assembled and ready, the samples were washed with soap and water to remove any oil from the surface of the samples. Next they were pickled in dilute $HNO_3$ for a short time to equipotentialize the surface.

After the initial weights had been recorded two samples of chemical, tellurium, and pure lead were partially immersed

in 400 cc 10° Be $H_2SO_4$. The antimony samples were started 120 hours later. The weights were checked at the end of the first 24 hours. After that, the weights were taken at greater intervals due to the small change in the weights.

The technique of washing and drying the samples before weighing was developed previously on strips of lead similar to the samples. The strips were washed lightly with a soft hair brush for 10 strokes of the brush, under slowly running water. This assured the removal of the solution but did not disturb the formation of any permanent films. The samples were thoroughly dried between filter paper before they were weighed.

Since the boundary effect of partial immersion was being checked, the samples were measured after the first time interval at which the solution line could be seen. The solution in the beakers was held as nearly as possible at this line, though evaporation of the solution made this difficult.

The samples which were corroded in the spin bath solution were started two weeks after those in the 10° Be acid. This solution could not be checked accurately with the hydrometer due to the various materials in solution. Therefore, it was assumed that any evaporation loss would be mainly water, and distilled water was used to keep the specific gravity down to 1.15. This assumption was logical since the specific gravity rose decidedly if evaporation took place

without make-up water being added. Fresh solution, however, was made up three times during the run.

The water level in the constant temperature bath was held constant - the loss by evaporation being made up by addition of water through a siphon. It was necessary to keep the level near the top of the heating units to prevent their overheating.

RESULTS

Since the samples gained weight for a short interval upon being placed in the solutions, the first two corrosion periods in each case were not considered. This procedure is similar to that recommended for short corrosion tests in Perry's Handbook. The time periods which were used are indicated on the data sheets.

Tellurium lead

In the $10^{o}$ Be $H_2SO_4$, the film formed in 575 hours and no further corrosion had taken place when the samples were checked at 210 and 304 hours later. The penetration during this time of film formation was $0.68 \times 10^{-5}$ inches.

In the spin bath solution, the film was almost formed in 532 hours and the indication was that it would have formed in 600 hours, at most. The penetration during the 532 hours was $2.24 \times 10^{-5}$ inches.

Antimony lead

In the 10° Be $H_2SO_4$, the film formed in 759 hours. The penetration during this time was $3.85 \times 10^{-5}$ inches.

In the spin bath solution, after 532 hours, changes in weight were taking place in the fourth place only. The penetration was $3.46 \times 10^{-5}$ inches during this time.

Pure lead

In the 10° Be sulfuric acid, the samples gained weight until a film was formed. After 879 hours the weights were practically constant (small changes in fourth place). The gain in weight was found to be $3.4 \times 10^{-2}$ gm./sq.in. of exposed area.

In the spin bath solution, the samples gained weight so rapidly in forming the film that, after 150 hours, the film started scaling off. This loss of film caused increased corrosion - the loss over the period of the run (532 hours) occurring at the rate of $1.26 \times 10^{-2}$ inches per year.

Chemical lead

In 10° Be $H_2SO_4$, the film had not formed completely in 879 hours. The gain in weight during this time was $5.5 \times 10^{-3}$ grams per square inch.

In the spin bath solution, one sample had a rolling defect which caused very rapid corrosion. The other sample gained but did not reach a constant weight in 532 hours.

DISCUSSION

In Figure 2 the effects of the corrosion on all the samples are shown; and from the small losses observed in the tests, it may be concluded that any of these leads could be used in dilute sulfuric acid. The pure lead, however, would be objectionable because of its tendency to form a non-adherent film. This non-adherent film of the pure lead is contrasted with the protective film of the tellurium lead samples in Figure 3. The film on the pure lead had scaled off while the only indication of a film on the tellurium lead was the immersion line. The chemical lead formed the same type of film as did the pure lead; this film, however, formed more slowly and appeared to be more adherent.

In general, the type of film most desirable would be the dark gray film which formed on the antimony and tellurium alloys. This film formed by replacing some of the surface metal, while the film on the pure lead seemed to build up without becoming ingrained with the surface. When scaling occurred, the exposed surface appeared as clean and bright as it had been after pickling.

The tellurium alloy lost weight while the film was forming but the appearance of the surface did not change noticeably. The part of the sample exposed to the corroding

solution became darker as the film formed but no pitting or visible scale formation occurred. The surface of the antimony alloy samples showed the line of immersion and had no evidence of pitting. However, there was a trace of the white scale over the surface which had been in the spin bath solution.

From the literature, it was found that the presence of antimony was blamed for the corrosion of the old type of chemical lead. If that assumption were true, the antimony must have been present in greater than 2% of the composition. It is known that 10% antimony in lead does cause rapid corrosion. Therefore, it would be desirable to run corrosion tests on different alloys between the composition of 2% and 10% antimony to observe the changes in corrosion resistance. Also, it would be desirable to test alloys of lead in which both tellurium and antimony are present.

Though the tests which were made are of value as indications of corrosion resistance, actual plant tests would be most useful in this work and could be run on the spinning machine by using porous containers. This would also be better than the beakers for partial immersion tests, since the liquid level on the sample would remain constant.

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Figure 1 -- Experimental Set-up

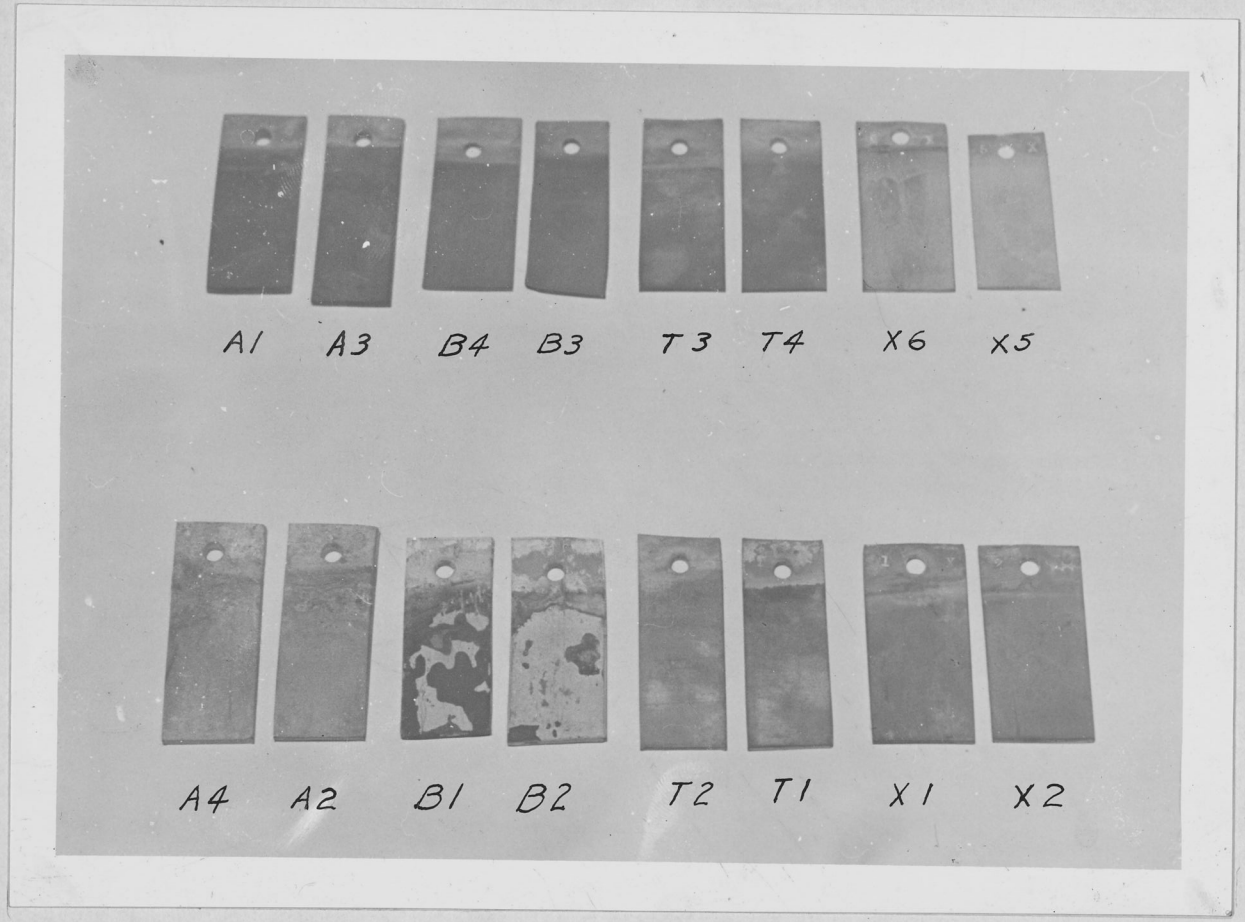



Figure 2 -- Corrosion Samples

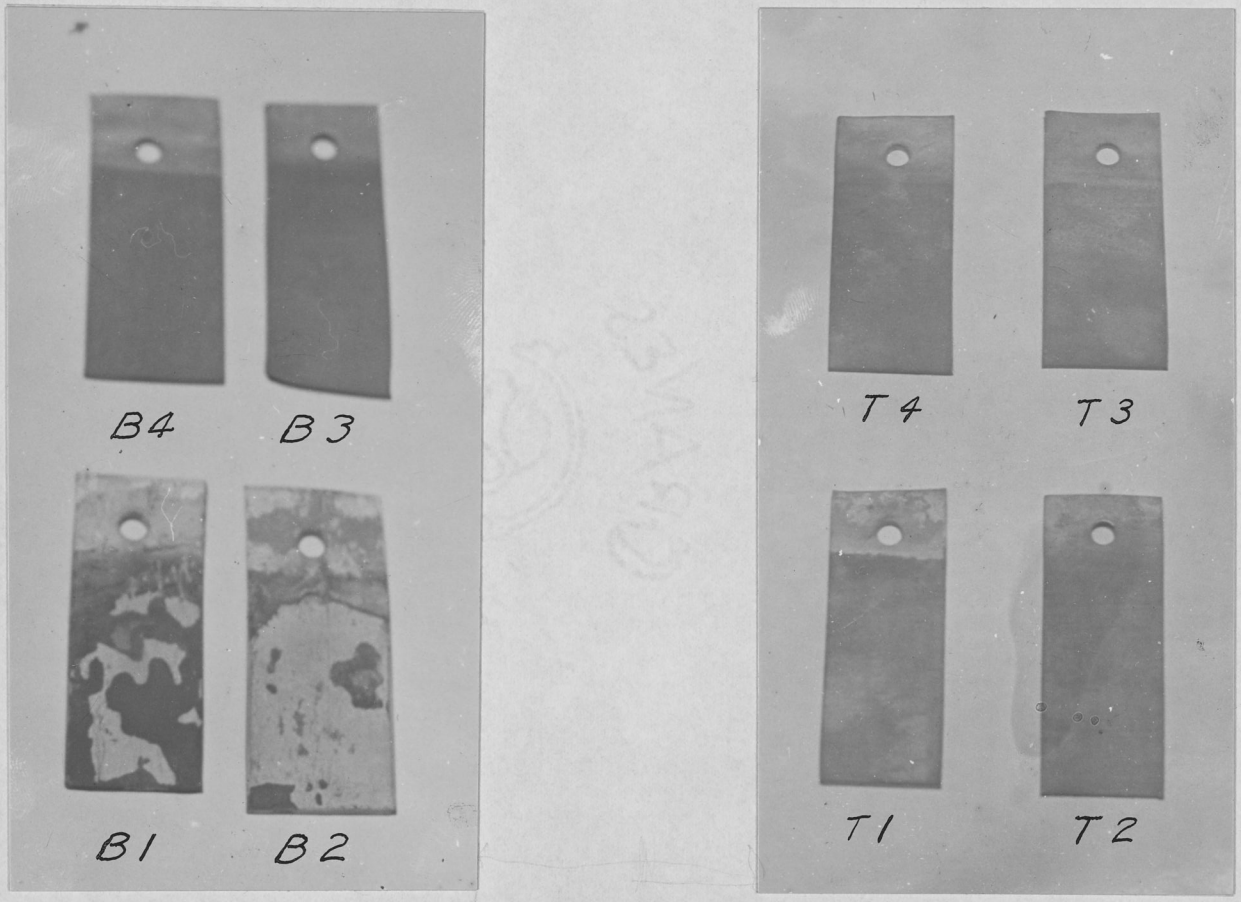



Figure 3 -- Pure Lead and Tellurium Lead Samples

# APPENDIX A

## Observed Weight Changes

Samples in 10°Be Sulfuric Acid — weight in grams

| Time hours | Tellurium lead T1 | T2 | Chemical lead A1 | A3 | Pure lead B1 | B2 | Antimony lead X5 | X6 |
|---|---|---|---|---|---|---|---|---|
| 0 | 38.7657 | 39.4228 | 90.0420 | 99.5900 | 57.9687 | 62.9857 | | |
| 24 | 38.7610 | 39.4200 | 90.0480 | 99.5920 | 57.9640 | 62.9926 | | |
| 72 | 38.7635 | 39.4259 | 90.0448 | 99.5918 | 57.9673 | 62.9843 | | |
| 120 | 38.7615 | 39.4230 | 90.0469 | 99.6000 | 57.9676 | 62.9897 | 29.4573 | 36.2101 |
| 192 | 38.7580 | 39.4217 | 90.0485 | 99.5910 | 57.9669 | 62.9900 | 29.4702 | 36.1978 |
| 264 | 38.7578 | 39.4216 | 90.0588 | 99.5950 | 57.9700 | 62.9950 | 29.4670 | 36.1890 |
| 384 | 38.7590 | 39.4200 | 90.0590 | 99.5960 | 57.9743 | 62.9990 | 29.4570 | 36.1767 |
| 521 | 38.7550 | 39.4180 | 90.0570 | 99.6030 | 57.9840 | 62.9950 | 29.4561 | 36.1733 |
| 551 | 38.7560 | 39.4180 | 90.0690 | 99.6020 | 57.9820 | 62.9950 | 29.4404 | 36.1578 |
| 647 | 38.7580 | 39.4190 | 90.0620 | 99.6040 | 57.9800 | 62.9960 | 29.4400 | 36.1503 |
| 857 | 38.7580 | 39.4190 | 90.0750 | 99.6100 | 57.9825 | 62.9970 | 29.4409 | 36.1500 |
| 951 | 38.7580 | 39.4190 | 90.0730 | 99.6084 | 57.9823 | 62.9962 | 29.4415 | 36.1500 |

The Antimony alloy samples were not prepared in time to be started with the other samples.

Samples in Viscose Rayon Spinning Bath Solution

weight in grams

| Time hours | Tellurium lead T3 | T4 | Chemical lead A2 | A4 | Pure lead B3 | B4 | Antimony lead X1 | X2 |
|---|---|---|---|---|---|---|---|---|
| 0 | 37.1767 | 39.3367 | 97.7192 | 99.3794 | 58.7115 | 64.1413 | 65.7366 | 67.4890 |
| 48 | 37.1900 | 39.3529 | 97.7100 | 99.3900 | 58.7309 | 64.1586 | 65.7229 | 67.4950 |
| 96 | 37.2223 | 39.3834 | 97.7100 | 99.4102 | 58.7517 | 64.1500 | 65.7211 | 67.4820 |
| 144 | 37.2515 | 39.3795 | 97.7352 | 99.4260 | 58.7519 | 64.1238 | 65.7177 | 67.4710 |
| 216 | 37.2518 | 39.3760 | 97.7370 | 99.3950 | 58.6250 | 64.0050 | 65.7140 | 67.4680 |
| 246 | 37.2270 | 39.3699 | 97.7500 | 99.3930 | 58.6030 | 64.0055 | 65.7160 | 67.4640 |
| 342 | 37.2220 | 39.3700 | 97.8000 | 99.4000 | 58.6700 | 64.0550 | 65.7154 | 67.4640 |
| 438 | 37.2150 | 39.3698 | 97.8100 | 99.3500 | 58.1500 | 63.6600 | 65.7160 | 67.4630 |
| 534 | 37.2000 | 39.3670 | 97.7570 | 99.3250 | 57.9772 | 63.6859 | 65.7160 | 67.4625 |
| 628 | 37.1998 | 39.3661 | 97.7679 | 99.3030 | 57.9747 | 63.6800 | 65.7160 | 67.4624 |

Loss in Weight

| $10^{\circ}$Be acid | Spin bath |
|---|---|
| T1 - 0.0055 gm. loss in 879 hrs. | T3 - 0.0223 gm. loss in 532 hrs. |
| T2 - 0.0069 gm. loss in 879 hrs. | T4 - 0.0164 gm. loss in 532 hrs. |
| A1 - 0.0301 gm. gain in 879 hrs. | A2 - 0.0470 gm. gain in 532 hrs. |
| A3 - 0.0182 gm. gain in 879 hrs. | A4 - 0.0650 gm. loss in 532 hrs. |
| B1 - 0.0152 gm. gain in 879 hrs. | B3 - 0.7745 gm. loss in 532 hrs. |
| B2 - 0.0127 gm. gain in 879 hrs. | B4 - 0.4727 gm. loss in 532 hrs. |
| X5 - 0.0261 gm. loss in 687 hrs. | X1 - 0.0170 gm. loss in 532 hrs. |
| X6 - 0.0390 gm. loss in 687 hrs. | X2 - 0.0320 gm. loss in 532 hrs. |

# APPENDIX B

## Surface Area of Samples Exposed

Dimensions in inches

| Sample | Width | Length | Thickness | Surface Area-$in^2$ |
|---|---|---|---|---|
| B4 | 1-3/16 | 2-1/8 | 3/32 | 5.5550 |
| B3 | 1-1/8 | 2-1/8 | 3/32 | 5.2730 |
| A2 | 1-1/8 | 2-3/8 | 5/32 | 6.2632 |
| A4 | 1-1/8 | 2-3/8 | 5/32 | 6.2632 |
| X5 | 1-1/8 | 2-1/4 | 1/16 | 5.4050 |
| X6 | 1-1/4 | 2-3/8 | 1/16 | 6.3220 |
| T4 | 1-3/32 | 2-3/8 | 3/64 | 5.4722 |
| T3 | 1-5/64 | 2-3/8 | 3/64 | 5.3822 |
| T1 | 1-9/64 | 2-1/4 | 4/64 | 5.0850 |
| T2 | 1-2/16 | 2-1/4 | 1/16 | 5.4050 |
| A1 | 1-1/16 | 2-1/4 | 5/32 | 5.6550 |
| A3 | 1-1/8 | 2-1/4 | 5/32 | 5.9250 |
| B1 | 1 | 2 | 3/32 | 4.0700 |
| B2 | 1-1/16 | 2 | 3/32 | 4.7250 |
| X1 | 1-1/8 | 2-1/8 | 3/32 | 5.2730 |
| X2 | 1-1/16 | 2-1/8 | 3/32 | 5.0100 |

## Density of the Samples

Density of water(25°C) - 0.997 gm/cc

Tellurium lead

| | | | |
|---|---|---|---|
| weight in air | 12.6838 | $\frac{12.6838 \times 0.997}{1.1158}$ = | 11.31 gm/cc |
| weight in water | 11.5680 | | |
| | 1.1158 gm | | |

Antimony lead

| | | | |
|---|---|---|---|
| weight in air | 13.7704 | $\frac{13.7704 \times 0.997}{1.2264}$ = | 11.2 gm/cc |
| weight in water | 12.5440 | | |
| | 1.2264 gm | | |

Chemical lead

| | | | |
|---|---|---|---|
| weight in air | 14.7930 | $\frac{14.7930 \times 0.997}{1.2994}$ = | 11.35 gm/cc |
| weight in water | 13.0936 | | |
| | 1.2994 gm | | |

Pure lead

| | | | |
|---|---|---|---|
| weight in air | 17.9630 | $\frac{17.9630 \times 0.997}{1.565}$ = | 11.38 gm/cc |
| weight in water | 16.3980 | | |
| | 1.5650 gm | | |

# APPENDIX C

## Calculation of Results

If W is the weight(in grams) of the test piece; A is the surface area of the test piece in square inches; S is the density of the metal in grams per cubic centimeter; and t is the time of exposure in hours: Then C is the rate of chemical corrosion expressed in inches of penetration per year:

$$C = \frac{W \times 24 \times 30 \times 12}{(2.54)^3 AST} \qquad \frac{(gm)(hr)/(yr)}{(2.54)^3(in)^2(gm)(hr)/(cc)}$$

This equation can be used only when loss in weight occurs. Therefore it can be applied only in the case of antimony and tellurium lead. In other cases, the results will be expressed in grams gained per square inch. Also, when a permanent film is formed, no futher corrosion takes place. The results in this case must be expressed in inches of penetration during the formation of the film.

Tellurium lead

in $10^{o}$Be acid $C = \frac{0.069}{(2.54)^3 \times 5.485 \times 11.31} = 0.68 \times 10^{-5}$ in.

in spin bath $C = \frac{0.0223}{16.45 \times 5.3822 \times 11.31} = 2.24 \times 10^{-5}$ in.

Antimony lead

in $10^{o}$Be acid $C = \frac{0.039}{16.45 \times 5.4722 \times 11.2} = 3.85 \times 10^{-5}$ in.

in spin bath $C = \frac{0.032}{16.45 \times 5.010 \times 11.2} = 3.46 \times 10^{-5}$ in.

Chemical lead

in 10°Be acid, gain in weight: $\frac{0.031}{5.650} = 5.5\times10^{-2}$ gm/sqin.

in spin bath, gain in weight: $\frac{0.047}{6.2632} = 7.5\times10^{-2}$ gm/sqin.

Pure lead

in 10°Be acid, gain in weight: $\frac{0.0152-}{4.470}$ $3.4\times10^{-2}$ gm/sqin.

in spin bath

$$C = \frac{0.7745 \times 24 \times 30 \times 12}{16.45 \times 5.273 \times 11.38 \times 532} = 1.26\times10^{-2} \text{in/year}$$

In future tests with antimony and tellurium lead, the area immersed could be controlled so as to give a resulting penetration one thousandth of the weight loss - as in the case of a sample of antimony lead: if A is 5.42 square inches,

$$C = \frac{4.0\times10^{-2}}{16.45\times5.42\times11.2} = 4.0\times10^{-5} \text{ in.}$$

This procedure would give the results at a glance.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarialy endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it was submitted.

Name David J. Mack

Title Asst Prof Chem Eng

Date May 30, 1940