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RESEARCH ON TREATED MAGNESIUM SURFACES

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FOREWORD

This report was prepared by Bjorksten Research Laboratories under USAF Contract No. AF 33(616)-2032. The contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73120, "Electrodeposition and Electrochemical Treatments", formerly RDO No. 611-11, "Electrodeposition and Electrochemical Treatments", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. O. O. Srp as initial project engineer, later succeeded by Mr. B. Cohen.

The work was performed at Bjorksten Research Laboratories, Madison, Wisconsin, with Mr. S. E. Rohowetz as project leader. Contributing staff member was Mr. W. Stabenau. The report was edited by Miss B. A. Harker.

This report covers work conducted from March 1953 to October 1954.

ABSTRACT

Research for the development of an accelerated performance test for treated magnesium alloys included the following corrosion resistance tests:

(1) pH increase in 1.0N KCl.
(2) Open circuit potential comparisons.
(3) Short circuit current comparisons.
(4) Hydrogen evolution rates in 1.0N KCl (gasometric method).

The following tests of adhesion of zinc chromate primer (MIL-P-6889A) to the treated surfaces were also included:

(1) Adhesion in shear (wrought alloy specimens).
(2) Adhesion in tension (cast alloy specimens).
(3) Impact, ultrasonic vibratory, and pressure-sensitive tape tests (qualitative).

The gasometric method was the most promising test for evaluation of corrosion resistance. It was critical in its evaluation of unprimed treated magnesium alloys within five hours and of primed specimens in seven days.

The Dow #7 acid chromate treatment gave lower hydrogen evolution rates than the Dow #12 alkaline anodic treatment on all alloys tested.

In the shear and tension adhesion tests, the Dow #7 gave higher adhesion to the primer than the Dow #12.

Corrosion rates for unprimed treated specimens obtained from several weathering tests did not correlate with the rates from accelerated laboratory tests. The corrosion rate of the Dow #7 was nonlinear and increased after a given time due to depletion of the protective chrominum ions. Painted specimen rates, however, were in agreement with the accelerated test rates and showed the superiority of the Dow #7 over the Dow #12.

The corrosion resistance of primed-lacquered specimens far exceeded the difference in resistance afforded by the various treatments.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

The purpose of the research described in this report was to develop practical test methods for evaluating the quality of chemical and electrochemical surface treatments of magnesium alloys with respect to:

(1) The corrosion resistance afforded by the treatments to the base metal.

(2) The adherence between paint type coatings and the base metal afforded by the surface treatments.

Test methods of these types are needed to determine the acceptability of treated magnesium alloys submitted to the Military Services. The methods must be suitable as inspection tests for incorporation in a revision of Military Specification MIL-M-3171A (Magnesium Alloys, Processes for Corrosion Protection of) into a performance type specification.

Any test method developed must also meet the following requirements:

(1) The test must be satisfactorily reproducible.
(2) It must be applicable to commercially available magnesium alloys in both sheet and cast forms.
(3) It must be a laboratory test which can be performed with standard laboratory equipment or easily constructed equipment.
(4) The test specimens must be easily prepared.
(5) The test duration must not exceed 14 days.
(6) The test must be capable of differentiating the relative protective ability of the treatments used on the magnesium alloys.
(7) The adhesion test must be capable of differentiating the relative paint adhesion qualities of the treatments.

The magnesium alloys specified for investigation included sheet alloy AZ-31 (Federal Specification QQ-M-44) and sand casting alloys AZ-63 and AZ-92 (Federal Specification QQ-M-56). These are commonly known as FS-1 sheet alloy and "C" and "H" cast alloys.

The specified treatments consisted of Dow #7 and Dow #12 as outlined in Military Specification MIL-M-3171A. The Dow #7 is an acid dichromate treatment, and the Dow #12 is an alkaline anodic treatment applied to the metal as the anode. Some work was also done with Dow #17, another anodic treatment, and with Iridite #15. The Dow #7, #12, and #17 are products of the Dow Chemical Co. Iridite #15 is produced by Allied Research Products Co.

The paint system for adhesion tests was the zinc chromate primer of Military Specification MIL-P-6889A and the top-coat aluminized lacquer of Military Specification MIL-L-7178.

A literature search on corrosion and adhesion measurements was made before the laboratory investigation. A discussion of the pertinent information from this search and a bibliography are presented in the Appendix.

Based on the literature search, the following methods were selected for evaluation of corrosion resistance:

(1) Electrochemical measurements with specimens immersed in electrolytes.

  (a) Open circuit potential comparisons.
  (b) Short circuit current comparisons.
  (c) Polarographic analysis of corrosion products.

(2) Measurements of change in hydrogen ion concentration of an electrolyte caused by corrosion of a specimen.
(3) Determination of the rate of hydrogen evolution when a specimen is immersed in an electrolyte.

For evaluation of the adhesion of the paint system, the following methods were selected:

(1) Standardized pressure-sensitive tape tests.
(2) Impact tests.
(3) Shear and tension adhesion tests.
(4) Ultrasonic vibratory tests.

Weathering tests were also included in the test program for correlation with performance in accelerated laboratory tests.

I. PREPARATION AND TREATMENT OF TEST SPECIMENS

The methods used for preparation of test specimens from the various alloys and for application of the various treatments, zinc chromate primer, and aluminized lacquer are described in this section. Some of the problems presented in removal of corrosion products from specimens exposed to accelerated and weathering tests are also discussed.

A. Preparation of Specimens

Sand casting and sheet magnesium alloys were obtained from the Dow Chemical Co. The sheet alloy was wrought alloy FS-1-H24 and the casting alloys were Dowmetal "C" and "H". These will be referred to throughout this report as FS-1 (wrought) alloy and "C" and "H" cast alloys.

1. FS-1 Wrought Alloy

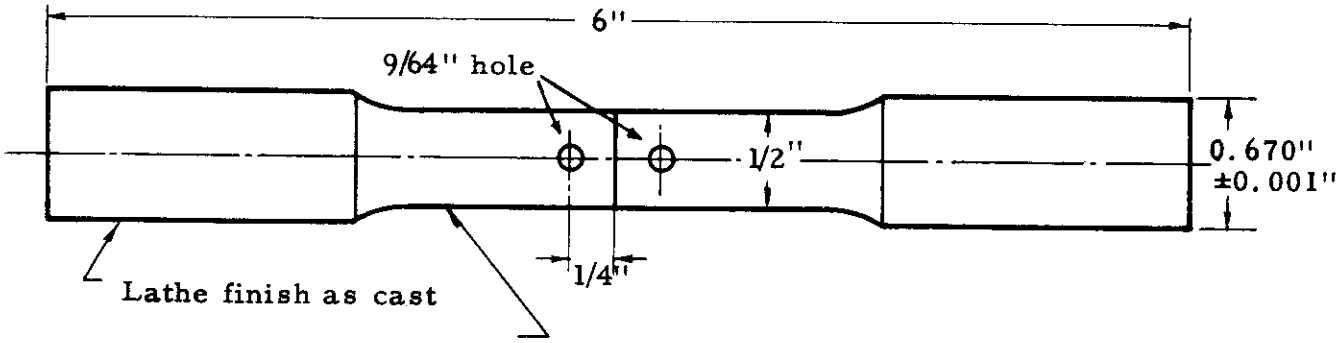
Alloy sheet 6' x 4' x 0.040" was hand picked from stock by the Technical Service and Development Department, Magnesium Division of the Dow Chemical Co. This stock was acetic-nitrate "pickled" and interleaved with paper for shipment. Specimens 1-1/2" x 3" (lower drawing, Figure 1) and 4" x 6" were cut from this sheet with a metal shear. The edges were deburred and polished with an alumina polishing belt. A 9/64 inch hole was drilled in one end to permit suspension of the samples in the various treatments. The specimens were numbered in one corner with a Vibra tool and given a light acetic-nitrate "pickle."

2. "C" and "H" Cast Alloys

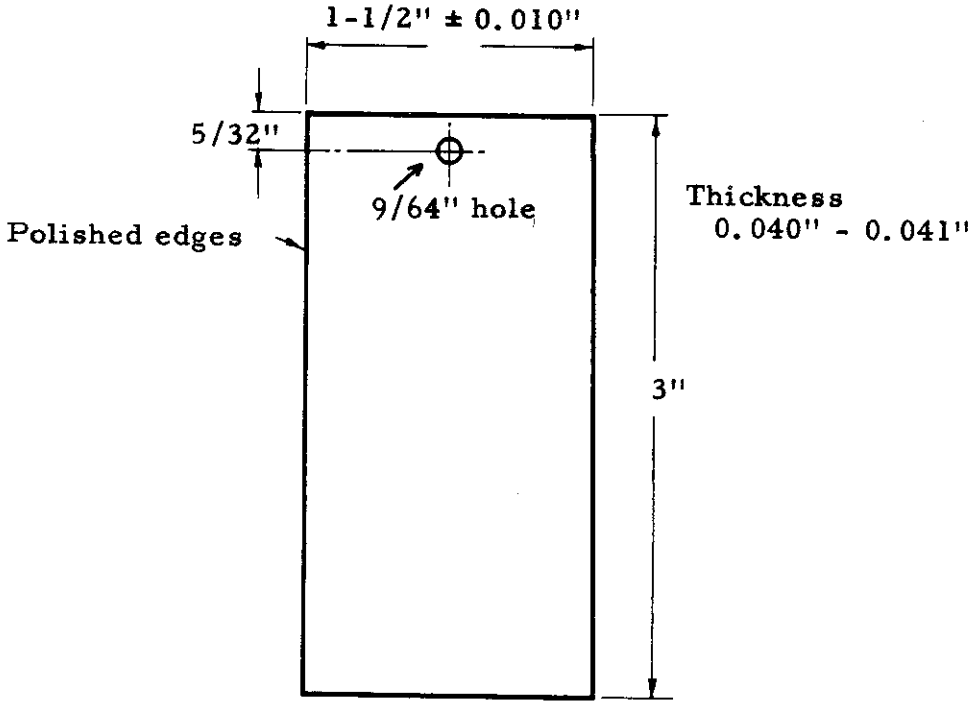
The cast alloys were available for test specimens as tensile test bars. These molded bars were given the T-4 heat treatment at the Dow plant. This treatment is shown below:

"C" Alloy	-	670° - 770°F in 2 hours. 770° for 6 hours. Cool to 665° - hold 2 hours. Heat to 770° for 10 hours.
"H" Alloy	-	670° - 730°F in 2 hours. 730° for 12 hours.

The surface of the tensile test bars was rough and unsuited to adhesion tests, current measurements, etc. Therefore, the ends of the bars were turned to a 0.67 inch diameter and given a smooth finish on the lathe (upper drawing, Figure 1). The bars were cut in two and holes drilled in the shank to permit suspension in the treating tanks. The specimens were then given a sulfuric-nitrate or an acetic-nitrate "pickle."



Specimen Type for Sand Castings "C" and "H"



Specimen FS-1 H-24
Magnesium Sheet

Figure 1. Magnesium Alloy Test Specimens.

The tensile test bars were unsuited for weathering and adhesion tests which require flat surfaces. Therefore, for the weathering tests, disc specimens, 3" x 0.2", were cut from cast bar stock and the flat facial surfaces machined smooth. These specimens were also in the T-4 temper condition.

"C" and "H" cast alloys were also obtained with the dimensions 3/8" x 3" x 8". These rectangles were cut into specimens 3/8" x 1-1/2" x 3" for the adhesion tests. The specimens had rough "as cast" surfaces.

B. Dow #7 Treatment

Specification Dow #7 treatment was applied according to MIL-M-3171A using potassium acid fluoride as the pretreatment dip. Initially, a number of specimens were treated using hydrofluoric acid. The potassium acid fluoride was more convenient to work with, however, and no appreciable difference was noted between the two types.

The specimens were mounted on a 1/16 inch magnesium rod for immersion in the treating tanks. Polyethylene tubing served as spacers between the specimens. pH control determinations were made before and after each series of specimens was treated. The initial pH was adjusted at 4.2 and was not allowed to go above 5.2 - 5.3. With proper control of all variables, good uniform dark coatings were obtained. Specimens were dried and interleaved with tissue until needed.

Specimens with a light Dow #7 treatment were obtained by reducing the time in the dichromate bath from the usual 30 minutes to 20 minutes and allowing the pH to go above 5.2.

Very heavy Dow #7 treatment was applied by 30 minute treatment in dichromate at a pH of 3.5 - 4.0. The specimens were touching the stainless steel tank during this treatment.

Specimens designated only as "Dow #7" received the specification treatment.

C. Dow #12 Treatment

For application of the Dow #12 treatment specimens were returned to the Dow Chemical Co. Both wrought and cast specimens received the specification 20-25 minute anodic treatment with a current of 15 amperes per square foot (A.S.F.).

A number of FS-1 specimens also were given light and heavy Dow #12 treatments as follows:

Light Dow #12 - 5 minute anodic treatment at 15 A. S. F.

Heavy Dow #12 - 35 minute anodic treatment at 15 A. S. F.

Specimens designated only as "Dow #12" received the specification treatment.

All Dow #12 specimens were neutralized after treatment as prescribed in Specification MIL-M-3171A.

D. Dow #17 Treatment

The anodic Dow #17 treatment has become increasingly popular and to some extent has replaced the Dow #12 treatment. For this reason, it was included in the test program in the latter stages.

Only FS-1 specimens received the Dow #17 treatment, which was applied at the Dow Chemical Co. Both light and heavy treatments were applied. The light treatment resulted from a 60 volt anodization and the heavy treatment from a 90 volt anodization.

E. Iridite #15 Treatment (Allied Research Products Co.)

This treatment was included for comparison with the Dow #7 treatment. It was applied to FS-1 specimens according to the manufacturer's recommendations.

F. Application of Zinc Chromate Primer

Specification MIL-P-6889A (Type 1) zinc chromate was applied to cast and wrought specimens by both dip and spray techniques.

1. Spray Method

In the spray method, the primer was diluted with two volumes of toluene and applied with a Model 19 Bink's Spray Gun using 45 pounds air pressure.

FS-1 specimens were hung on a board by hooks through their 9/64 inch holes and sprayed first on one side and then on the other.

"C" and "H" cast bar specimens were held by a short rubber tube attached to an electric motor. These specimens were rotated slowly as the primer was applied. The larger circular and rectangular cast specimens were hung on the spray board for application of the primer.

Two coats of primer were applied, with a 12 hour drying period between applications. The thickness of each coat was measured with a micrometer. A total thickness of 0.5 to 0.7 mil of primer was applied.

The best results by the spray method were obtained when the spray wet the surface evenly and a smooth coating was formed. In early efforts rough or granulated coatings were produced as a result of holding the spray gun too far from the specimens.

2. Dip Method

A dip method was investigated in which a variable speed drive mechanism was used to withdraw the specimens from the primer at rates between 3 and 8 inches per minute. A withdrawal rate of 3 inches per minute from a primer diluted with one-half part of toluene gave smooth applications. Two dips in primer of this dilution, however, deposited a film of greater thickness than the specified 0.5 to 0.7 mil. Another difficulty was the nonuniform coverage of edge areas, especially on the FS-1 specimens. The dip method was therefore abandoned in favor of spray application.

G. Application of Aluminized Lacquer

The aluminized lacquer (Specification MIL-L-7178) was also applied by spraying. The lacquer was diluted with one volume of specification lacquer thinner. Four or five coats were required for a final dry film thickness of 1.0 - 1.5 mils. Each coat was allowed to dry 40 minutes before the next coat was applied. The final coat was dried at least 12 hours before testing. Film thicknesses were measured with a micrometer.

H. Corrosion Product Removal

The removal of corrosion products from specimens exposed to accelerated and weathering tests was complicated by the alkaline nature of the Dow #12 treatment. This treatment is composed mainly of MgO which dissolves in acidic regents generally used to remove hydroxide corrosion products. The Dow #7 treatment is essentially an acid treatment and resists solubilization.

All of the organic and inorganic acids or acid salts tried removed the Dow #12 treatment (Table No. 1).

Immersion in ammonium chromate (10%) for 12 hours was used to remove corrosion products from unprimed specimens in initial tests. An alternate procedure was immersion in boiling chromic acid (10%) for 3-5 minutes. A small amount of silver chromate was included in the bath to precipitate chlorides.

TABLE NO. 1

CORROSION PRODUCT REMOVAL

Reagent	Corroded Dow #7 Specimen	Corroded Dow #12 Specimen
0.1N Acetic acid	45-55 min. immersion - Dow #7 resistant, corrosion products removed.	20 min. immersion - Dow #12 was dissolved.
5% Citric acid	25 min. immersion required for scale removal. Dow #7 resistant for this period.	Dow #12 completely removed in 10 min.
10% $(NH_4)_2CrO_4$ pH = 8.0 (unstirred)	20 hr. immersion - no attack on the Dow #7, corrosion products removed.	Dow #12 appeared resistant.
10% Tartaric acid	2 min. immersion - poor removal of corrosion products; too reactive.	Dow #12 reacted.
5% Boric acid	85 min. immersion required to remove corrosion products. Dow #7 resisted attack.	Dow #12 reacted.
5% $NaHCO_3$	55 min. immersion required to remove corrosion products; very reactive.	Dow #12 reacted.

Since these procedures removed the Dow #12 coating as well as the corrosion products, the following blank values were established for the weight losses of uncorroded treated specimens after immersion in 10% ammonium chromate or 10% chromic acid:

Dow #12 FS-1	(3 sq. in. surface) = 0.0427 gram
Dow #7 FS-1	(3 sq. in. surface) = 0.0021 gram
Dow #12 "C" alloy	(2.46 sq. in. surface) = 0.0246 gram
Dow #12 "H" alloy	(2.46 sq. in. surface) = 0.0341 gram
Dow #7 "C" alloy	(2.46 sq. in. surface) = 0.002 gram
Dow #7 "H" alloy	(2.46 sq. in. surface) = 0.001 gram

These blanks were subtracted from the observed weight losses for corroded specimens. Some variation in weight loss from specimen to specimen was noted with the Dow #12.

Corrosion products on primed or lacquered specimens were conveniently removed by immersion in cold 0.1N acetic acid or 10% chromic acid for 3-5 minutes.

After treatment for corrosion product removal, all specimens were rinsed in distilled water and dried one hour at 37°C.

II. CORROSION RESISTANCE TESTS

The methods investigated for measurement of corrosion resistance included hydrogen ion concentration change, open circuit potential comparisons, short circuit current comparisons, polarographic analysis of corrosion products, and hydrogen evolution rate comparisons (gasometric method).

For the evaluation of these corrosion resistance test methods, the following methods were used for specimen preparation:

(1) Dow #7 or #12 treatment.
(2) Dow #7 or #12 treatment plus the application of zinc chromate primer.
(3) Dow #7 or #12 treatment plus the application of zinc chromate primer and aluminized lacquer.

To simplify and clarify discussion of variously treated specimens, the above will be referred to as treated, primed, and lacquered specimens, respectively. Specimens referred to as untreated were cleaned with acetic-nitrate "pickle" but received no other treatment.

A. Hydrogen Ion Concentration Change

Several investigators have noted that the corrosion of metal specimens in an electrolyte solution such as an alkali metal chloride is generally accompanied by a change in the hydrogen ion concentration of the solution. Measurement of this pH change will indicate the rate of corrosion of the metal.

The pH changes caused in a corrosion medium by magnesium alloy specimens were measured in various electrolytes. The specimens were immersed in the electrolyte at room temperature, and the pH of the electrolyte was measured at intervals with a Beckman Model H2 pH meter equipped with a glass electrode and a constant voltage transformer.

FS-1 sheet specimens were completely immersed in the electrolyte. They were placed in glass containers so that the specimens rested on the bottom of the jar at an angle of about 15° from the vertical. The volume of electrolyte necessary to completely immerse these samples was about 150 milliliters. Screw caps were placed on the containers, but were not tightly closed. Complete immersion of cast

specimens was not feasible due to the irregularities of the unmachined shanks of the bars and the lack of protective coatings at the upper end of the shanks where the specimens were held during priming-lacquering operations. Therefore, only the machined ends of known diameter were immersed in the electrolyte. The specimens were held to a depth of one inch (total surface area exposed = 2.46 square inches) in the electrolyte by a rubber stopper through which the upper end of the shank could protrude. The volume of electrolyte used for the one inch immersion was 60 milliliters.

Initial tests were made in 3% sodium chloride, 0.1N zinc chloride, saturated potassium sulfate, and 1.0N potassium chloride solutions. The 1.0N potassium chloride was selected as the electrolyte for testing the complete series of specimens.

1. pH Change in NaCl and K_2SO_4

Preliminary pH change investigations were made by complete immersion of Dow #7 and Iridite #15 treated FS-1 specimens in neutral 3% NaCl and saturated K_2SO_4 solutions. The pH change was followed by taking readings every 15 minutes for about four hours. The electrolytes were unstirred during the course of the experiments.

The change in hydrogen ion concentration did not follow a steady rate in these experiments. Variation was noted with both the Dow #7 and the Iridite #15 specimens, but a faster initial rate increase was common for the Iridite specimens (Tables 2 and 3, Figure 2). The pH irregularities usually noted between a pH of 9.0-10.0 may have been due to the buffering action of the amphoteric corrosion products.

2. pH Change in KCl and $ZnCl_2$

One series of tests measured the progress of corrosion in 1.0N KCl of "C" and "H" alloy specimens prepared as described in Table No. 4. The effects of the different types of specimen preparation procedures on corrosion resistance are shown in Figures 3 and 4. The rapid rise to a high pH with treated specimens shows the more rapid corrosion of these specimens. Primed specimens did not corrode so rapidly, and lacquered specimens were obviously the most corrosion resistant over the 200 hour test period.

TABLE NO. 2

pH CHANGE OF 3% NaCl

BY DOW #7 FS-1 SAMPLES

Time (min.)	Sample No. 0065 Heavy Dow #7 Area = 4.542 in.^{2}	Sample No. 0102 Light Dow #7 Area = 4.597 in.^{2}	Sample No. 0052 Specification Dow #7 Area = 4.594 in.^{2}	Sample No. 0111 Iridite #15 Area = 4.620 in.^{2}
	pH	pH	pH	pH
0	6.10	6.09	6.09	6.08
15	6.19	6.12	6.11	6.21
30	6.19	6.11	6.08	6.49
45	6.41	6.49	6.22	7.49
60	6.62	6.61	6.31	8.58
75	6.72	7.41	6.49	9.18
90	6.74	7.92	6.92	9.32
105	6.89	8.02	7.11	9.42
120	7.09	8.57	7.81	9.39
135	7.14	8.47	7.96	9.49
150	7.19	8.61	8.51	9.71
165	7.41	8.89	8.89	9.68
180	7.99	8.96	9.10	9.68
195	8.50	9.08	9.20	9.68
210	9.02	9.09	9.42	10.04
225	8.52	9.30	9.42	9.81
240	9.39	9.88	10.09	10.46

TABLE NO. 3

pH CHANGE OF NEUTRAL SATURATED K_2SO_4

BY DOW #7 FS-1 SAMPLES

Time (min.)	Sample No. 0049 Spec. Dow #7 Area = 4.576 in.^{2} pH	Sample No. 0063 Spec. Dow #7 Area = 4.596 in.^{2} pH	Sample No. 56 Iridite #15 Area = 4.350 in.^{2} pH
0	6.95	6.96	7.16
15	6.95	7.02	7.31
30	6.98	7.04	7.52
45	7.21	7.22	8.21
60	7.28	7.31	8.90
75	7.48	7.36	9.31
90	7.66	7.70	9.44
105	7.90	7.56	9.49
120	7.96	7.89	9.61
135	8.02	8.04	9.62
150	8.10	8.12	9.68
165	8.28	8.05	9.73
180	8.50	8.00	9.95
195	8.60	8.52	9.95
210	8.58	-	9.80
225	8.59	8.31	10.02
240	8.90	8.31	10.12
255	8.60	8.12	9.82
270	8.89	8.41	10.00
285	8.81	8.41	10.11

TABLE NO. 4

DETAILS OF PREPARATION OF DOW #7 CAST ALLOY SAMPLES FOR CORROSION IN 1.0N KCl SOLUTION

Sample No.	H0601	H0520	H0549	C0621	C0525	C0537
pH of Dow #7 treating bath	4.3 - 4.6	4.3 - 4.6	4.3 - 4.6	4.3 - 4.6	4.3 - 4.6	4.3 - 4.6
Thickness of zinc chromate primer coat (mils)	None	0.60	0.50	None	0.75	0.75
Thickness of aluminized lacquer coat (mils)	None	None	1.0	None	None	1.2
Total coating thickness (mils)	None	0.60	1.5	None	0.75	1.9
Total weight loss after corrosion for 235 hours (grams)	0.0481	0.0119	0.0002	0.1430	0.0048	0.0005

NOTES: All samples were cast alloy - alkaline cleaned and acetic-nitrate "pickled" before application of undercoating. They were corroded at room temperature without agitation of the electrolyte.

"H" and "C" prefixes on identification numbers indicate "H" and "C" alloys, respectively.

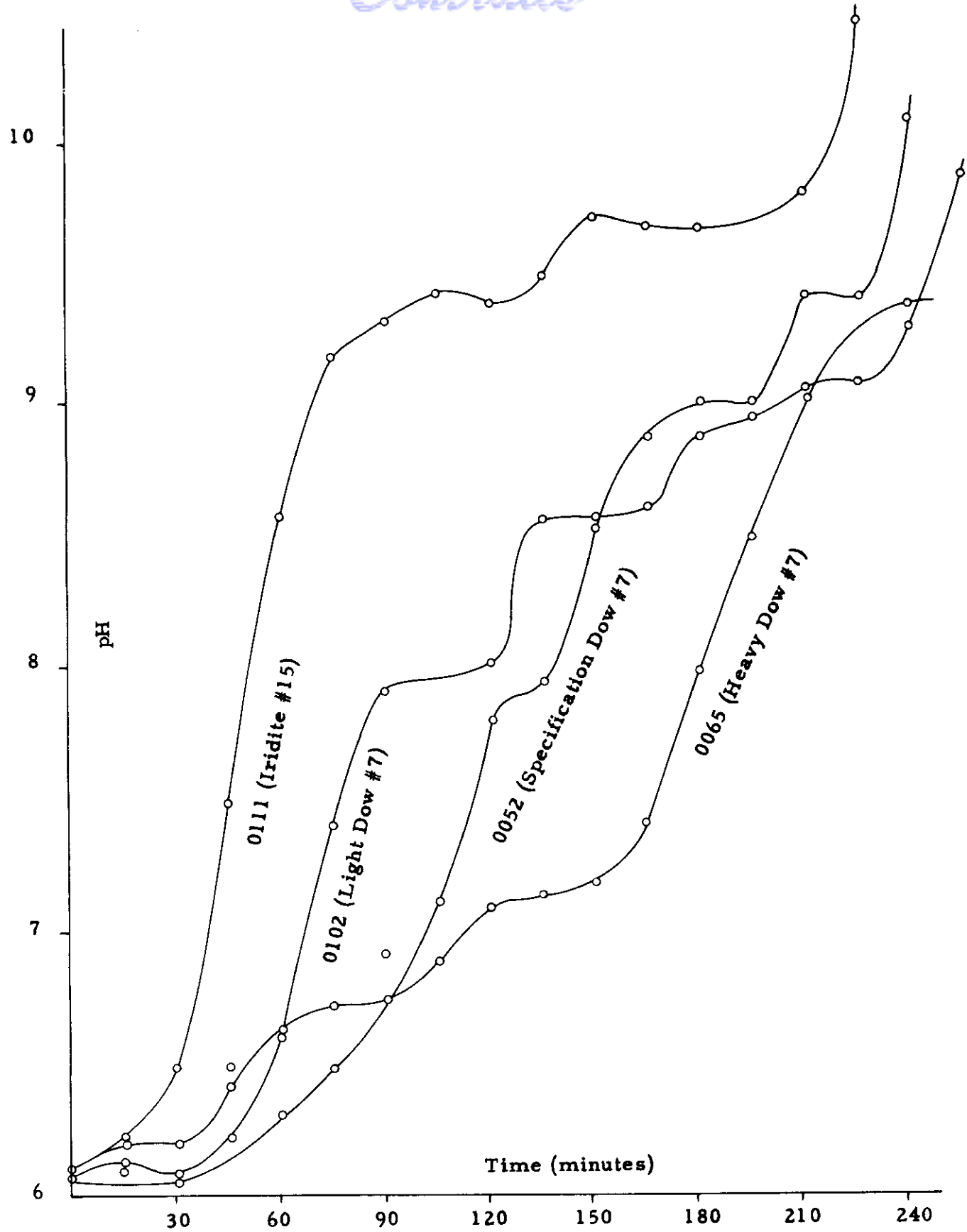


Figure 2. pH vs. Time: Dow #7 and Iridite #15 FS-1 Specimens in 3% NaCl.

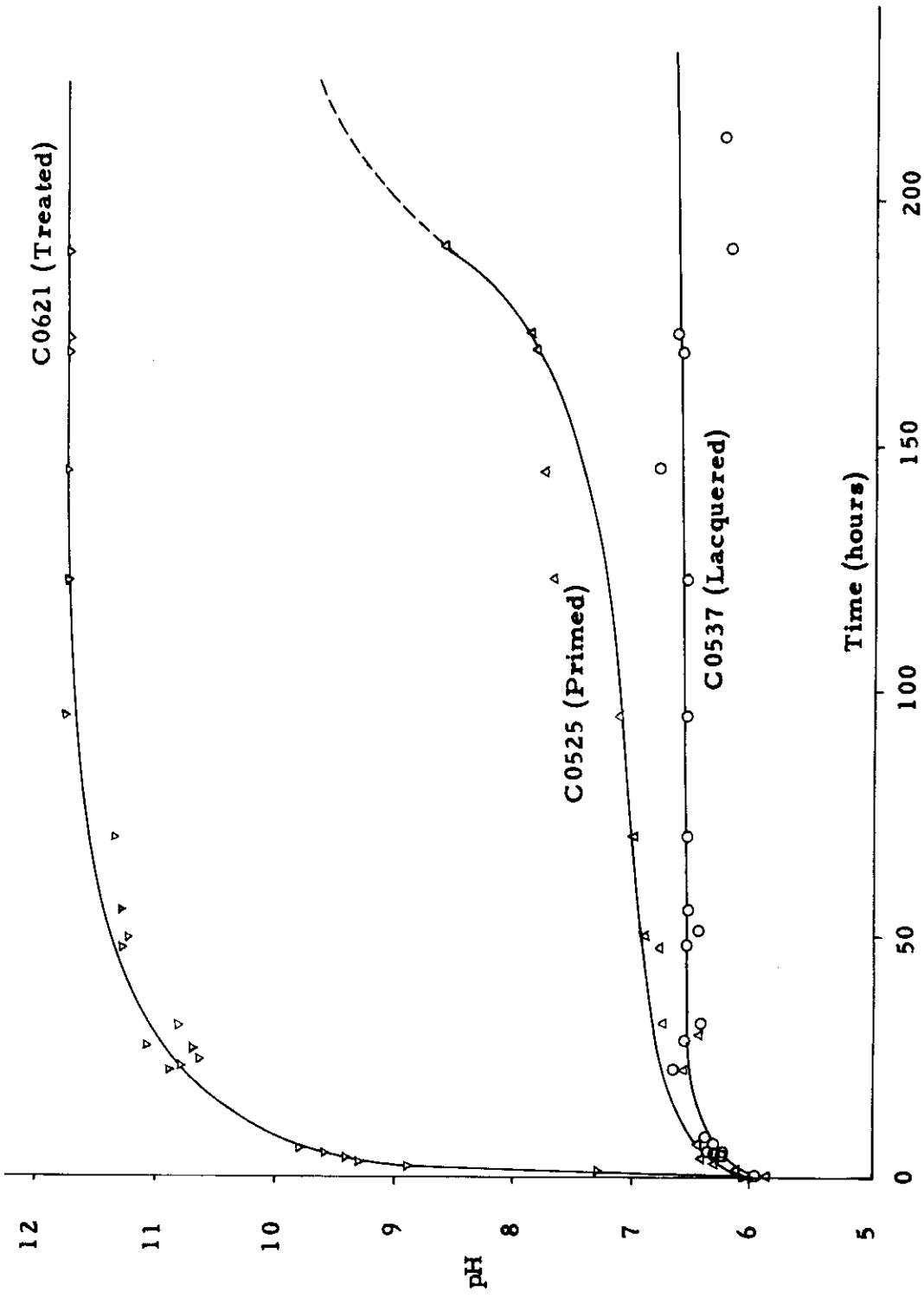


Figure 3. pH vs. Time: Dow #7 "C" Alloy in 1.0N KCl.

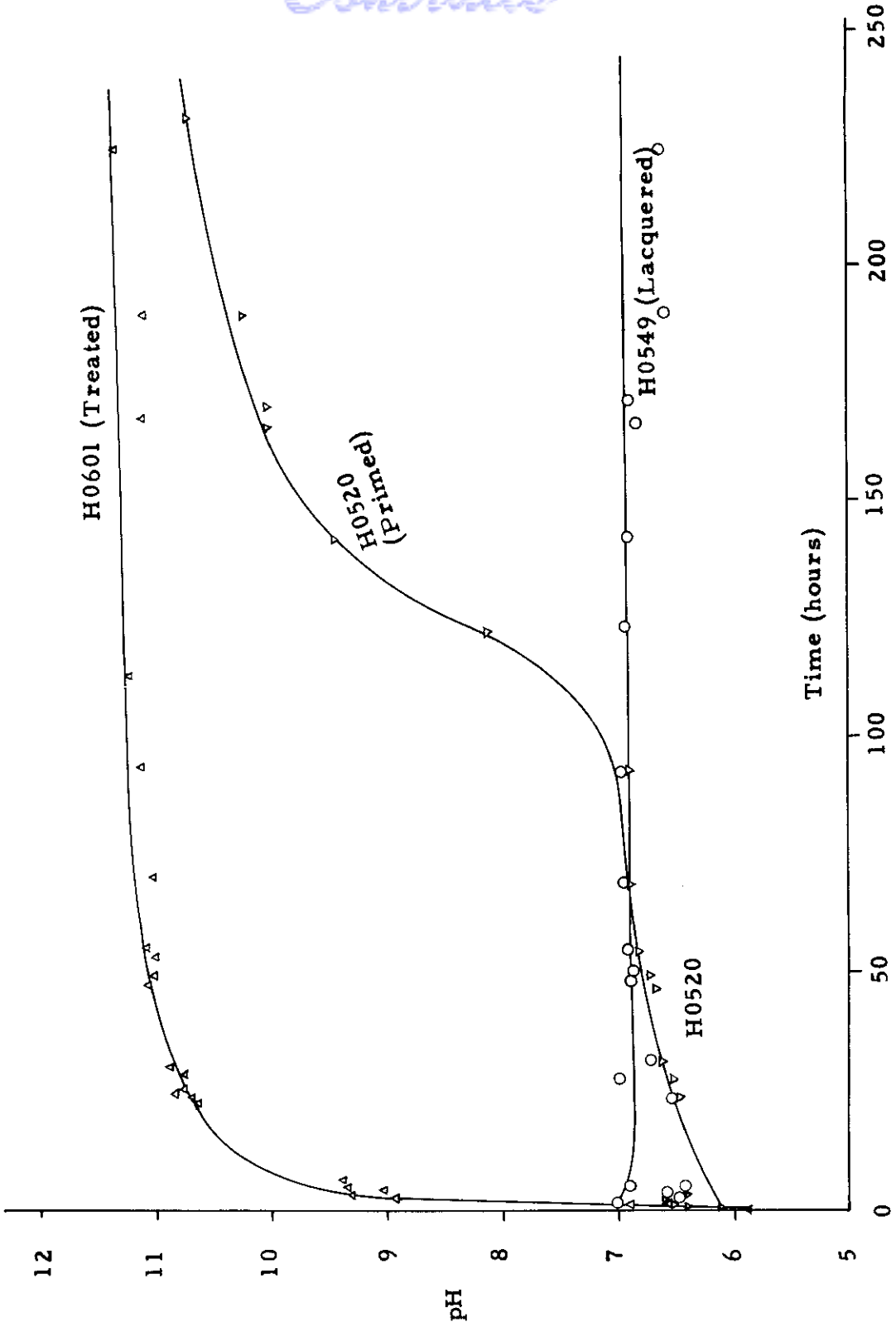


Figure 4. pH vs. Time: Dow #7 "H" Alloy in 1.0N KCl.

FS-1 specimens prepared as described in Table No. 5 were tested by total immersion in 0.1N $ZnCl_2$ solution containing sufficient HCl to keep the zinc in a soluble form (pH = 2.67). The $ZnCl_2$ was employed in an effort to accelerate the breakdown of the protective paint coatings. It gave a gradation in rate of corrosion (Figure 5) similar to that with KCl but required a shorter time to corrode primed specimens.

The losses in weight of the Dow #7 FS-1, "C", and "H" alloy specimens are listed in Tables 4 and 5. These weight loss data are characteristic of the protection afforded by each preparation procedure (i.e., treated, primed, lacquered) and confirm the corrosive effects shown by the pH changes in Figures 3, 4, and 5.

The "induction period," or time interval from specimen immersion to rapid or consistent pH rise, indicates the time of corrosion initiation. In addition, the slope of the curve during the pH increase is an indication of the extent or rate of breakdown and consequent lack of protection. The Dow #7 treatment had a very short induction period in both $ZnCl_2$ and KCl solutions.

Additional pH change data obtained with untreated and Dow #7 and #12 treated FS-1 specimens in 0.1N $ZnCl_2$ are shown in Figures 6, 7, and 8. Average values of several specimens were plotted. The Dow #7 specimens in the three stages of completion produced a higher initial pH increase rate than the Dow #12 specimens. The Dow #12 treated specimens had longer induction periods.

The zinc chloride immersion was too corrosive to show differences in treated specimens since the protective quality of the treatments was ineffective in this solution. Corrosion rates observed on primed or lacquered specimens were influenced mainly by the number of flaws in the paint system. Tests with zinc chloride were therefore discontinued.

3. pH Change with Cast and Wrought Alloys in 1.0N KCl

Further pH increase investigations were made with both cast and wrought specimens using neutral 1.0N KCl as the electrolyte. Average pH values are shown graphically in Figures 9, 10, and 11. pH changes were slower in the 1.0N KCl than in the acidic zinc chloride, and characteristic rate changes were obtained for each treatment.

TABLE NO. 5

DETAILS OF PREPARATION OF DOW #7 FS-1 SAMPLES FOR CORROSION IN 0.1N $ZnCl_2$ SOLUTION

Sample No.	0439	0440	0269	0263	0485	0484
pH of Dow #7 treating bath	4.2 - 4.8	4.2 - 4.8	4.8 - 5.3	4.8 - 5.3	4.3 - 4.6	4.3 - 4.6
Thickness of zinc chromate primer coat (mils)	None	None	No data ca. 0.5	No data ca. 0.5	0.60	0.70
Thickness of aluminized lacquer coat (mils)	None	None	None	None	0.85	1.0
Total coating thickness (mils)	None	None	None	None	1.45	1.7
Total weight loss after corrosion for 90 hours (grams)	0.9411	0.9858	0.3060	0.3016	0.1875	0.1816

NOTES: All samples were FS-1 alloy - alkaline cleaned and acetic-nitrate "pickled" before application of undercoating. None of them had any special edge protection. They were corroded without agitation at room temperature.

Samples 0485 and 0484 had similar coatings, but sample 0484 with the thicker coating had the smaller weight loss during corrosion.

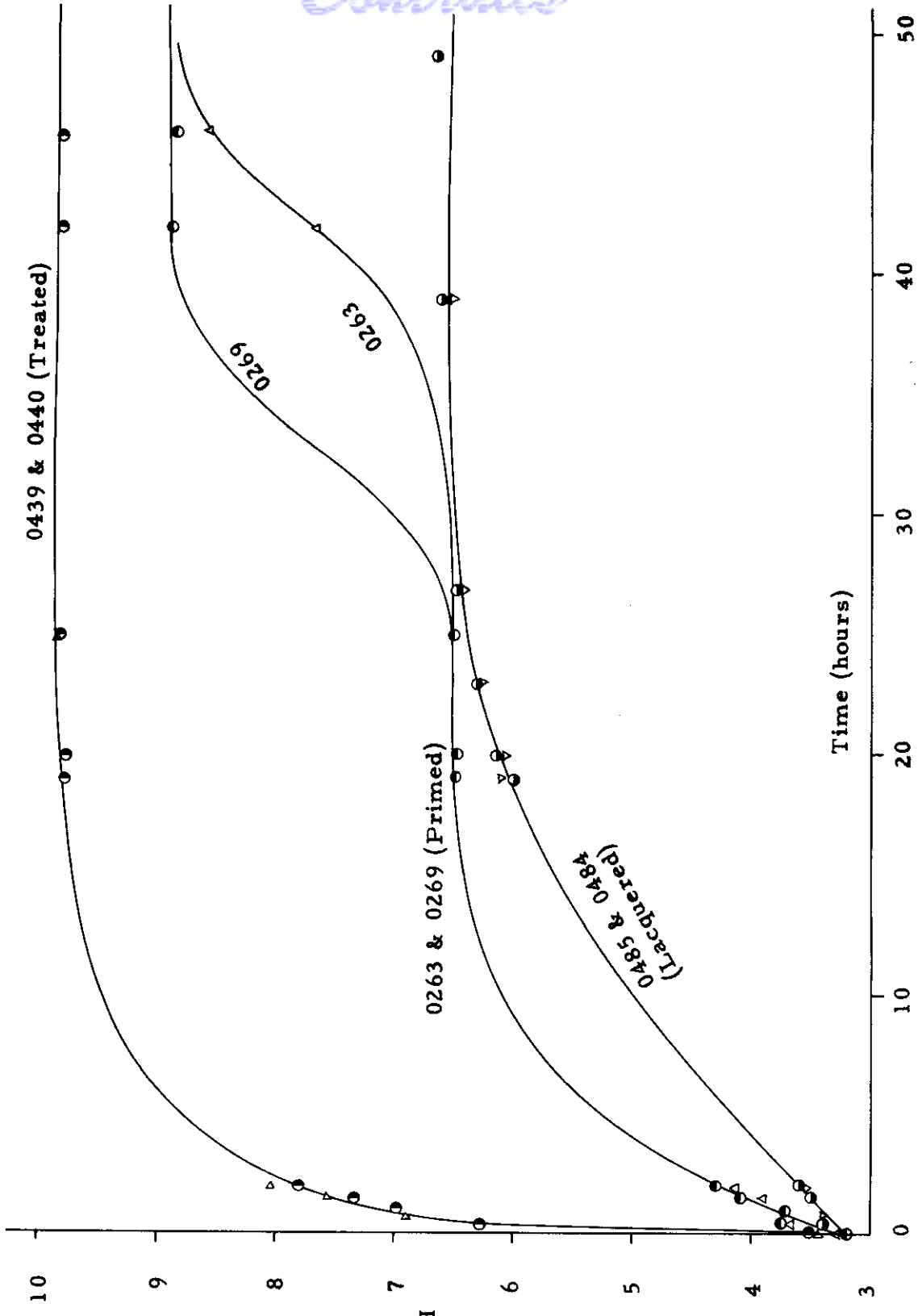


Figure 5. pH vs. Time: Dow #7 FS-1 Alloy in 0.1N $ZnCl_2$.

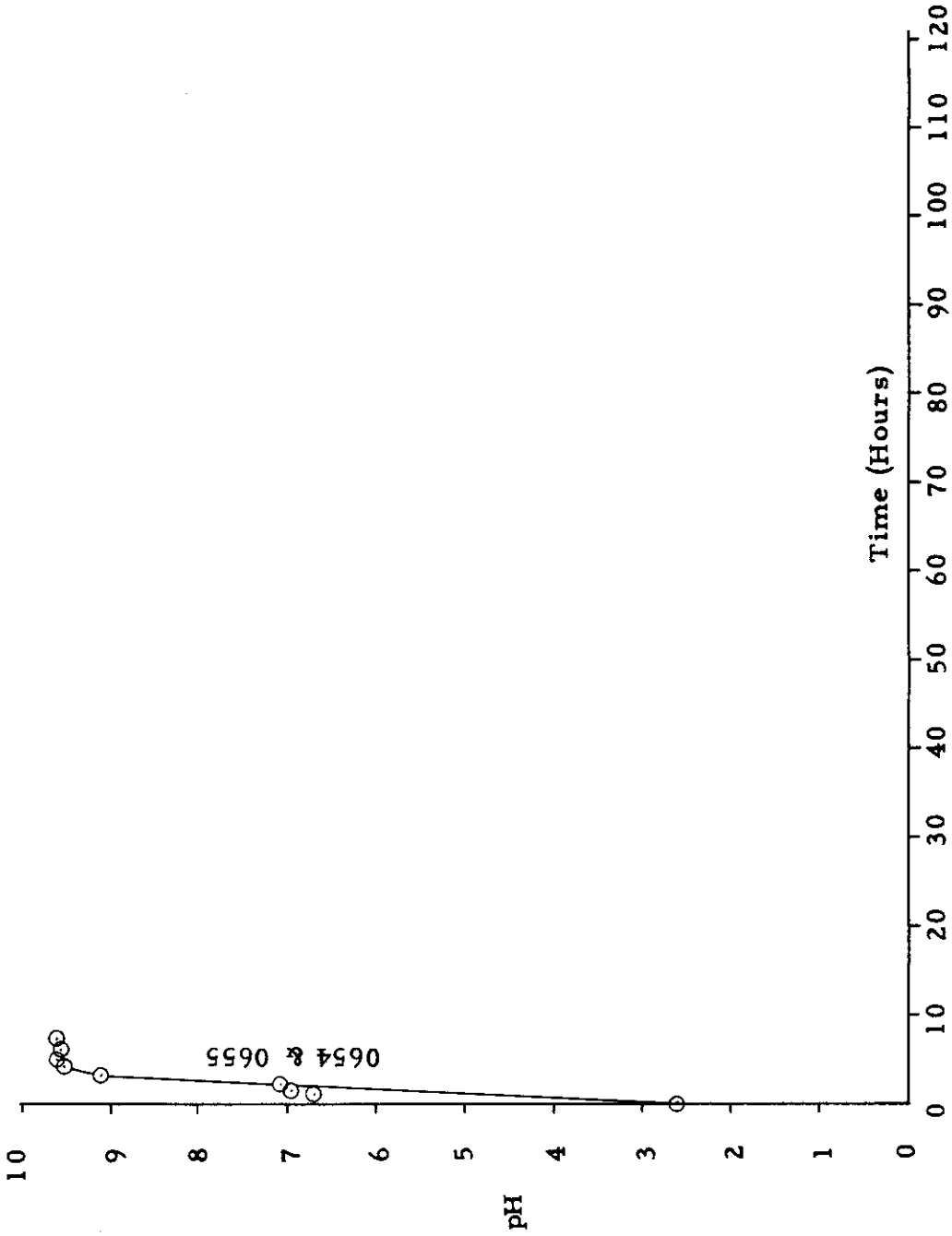


Figure 6. pH vs. Time: Untreated FS-1 Alloy in 0.1N $ZnCl_2$.

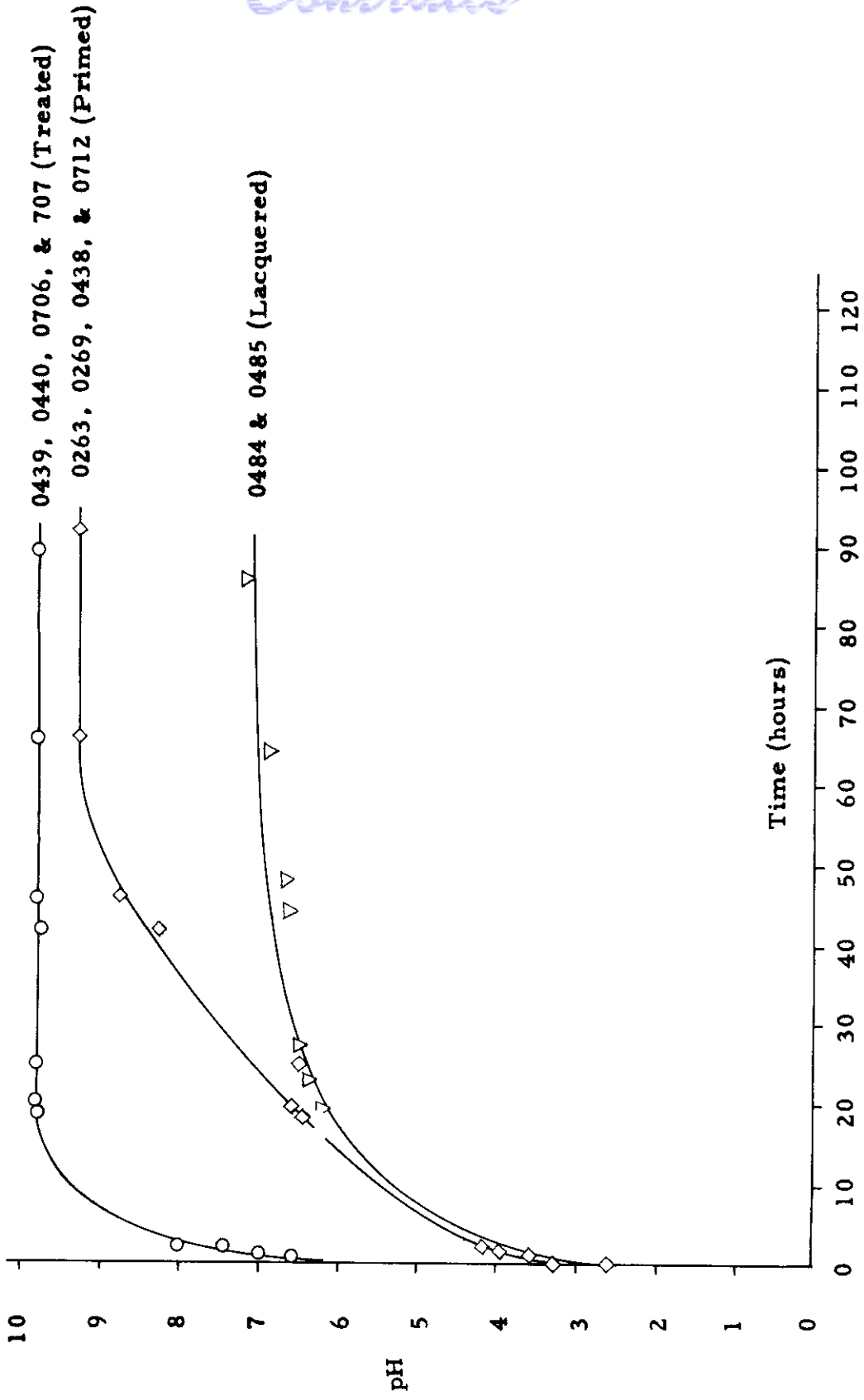


Figure 7. pH vs. Time: Dow #7 FS-1 Alloy in 0.1N $ZnCl_2$.

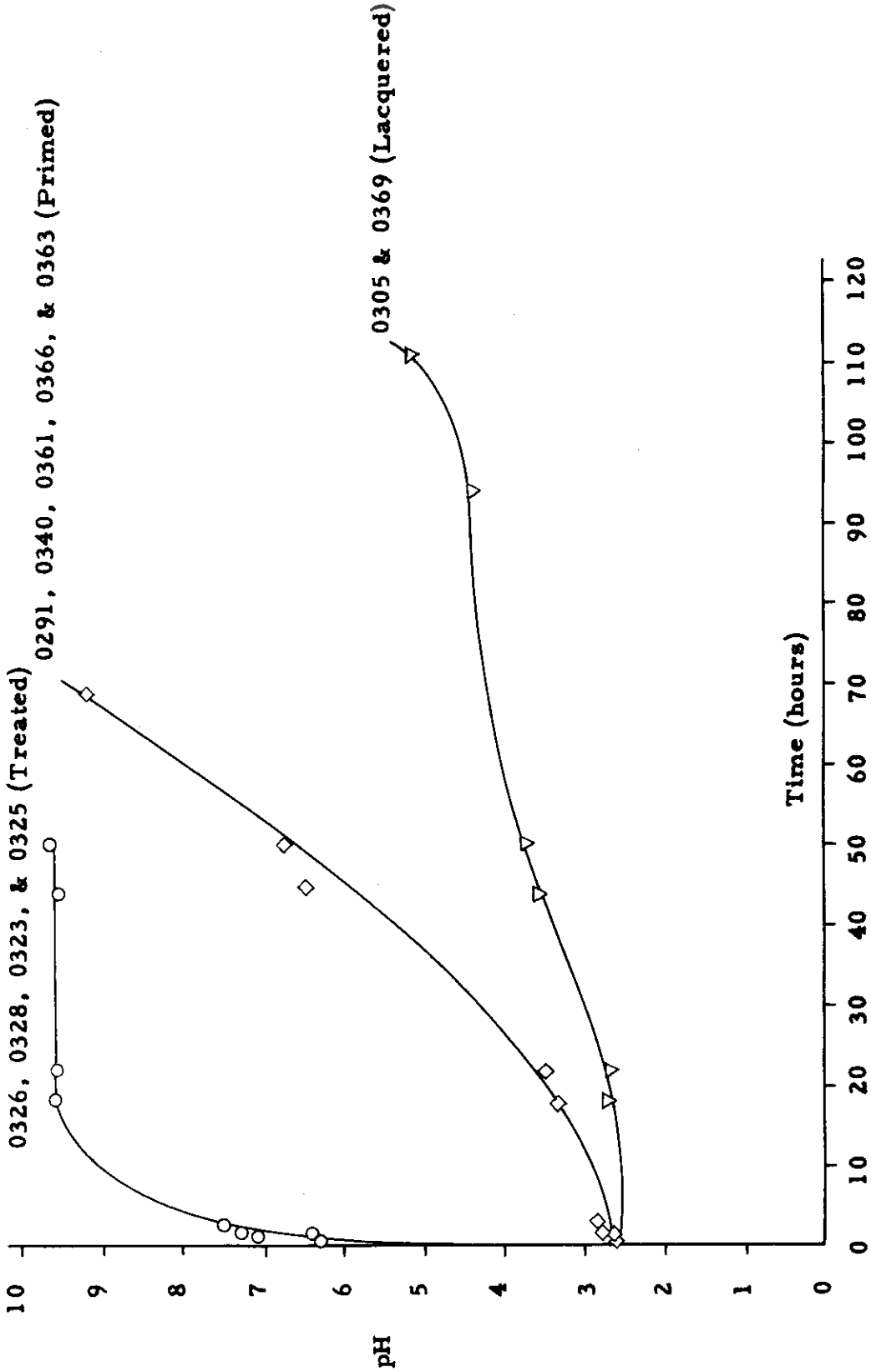


Figure 8. pH vs. Time: Dow #12 FS-1 Alloy in 0.1N $ZnCl_2$.

In this series no special edge protection was applied to the FS-1 specimens. However, each specimen was examined microscopically for uniformity of treatment or primer coating.

Figure 9 shows the average pH changes for untreated and treated FS-1 specimens. There was a deviation of ± 5% from the average for Dow #7 and #12 specimens.

The following values represent the average change in pH per square inch of exposed specimen and were calculated at the time of maximum change of pH:

Dow #12 FS-1	$\triangle$ pH = 0.255/hr./sq. in. between 1 - 2 hours
Dow #7 FS-1	$\triangle$ pH = 0.163/hr./sq. in. between 1 - 2 hours
Untreated FS-1	$\triangle$ pH = 0.520/hr./sq. in. between 0 - 1 hour.

Thus, on FS-1 specimens, the Dow #12 produced a higher $\triangle$pH value than the Dow #7 between 1 and 2 hours immersion time.

Figure 10 shows the comparative values for the "C" and "H" cast alloys in 1.0N KCl. The "C" alloy gave consistently higher $\triangle$pH values than the "H" alloy. As on the wrought alloy, the Dow #7 treatment resisted rapid pH increase on the cast alloys, particularly on the "H" alloy.

The following average $\triangle$pH values were calculated at the time of maximum change:

H Dow #12	$\triangle$pH = 0.737/hr./sq. in. between 0 - 2 hours
C Dow #12	$\triangle$pH = 0.798/hr./sq. in. between 0 - 2 hours
H Dow #7	$\triangle$pH = 0.448/hr./sq. in. between 3 - 4 hours
C Dow #7	$\triangle$pH = 0.734/hr./sq. in. between 2 - 3 hours
H - untreated	$\triangle$pH = 1.44/hr./sq. in. between 0 - 1 hour
C - untreated	$\triangle$pH = 1.61/hr./sq. in. between 0 - 1 hour.

Figure 11 shows the average pH changes for primed wrought and cast specimens. The deviation from the average values was 10 - 12% for primed specimens.

The average $\triangle$pH values at the time of maximum change were as follows:

Dow #12P FS-1	$\triangle$pH = 6.17×10^{-3}/hr./sq. in. between 30 - 54 hours
Dow #7P FS-1	$\triangle$pH = 1.68×10^{-3}/hr./sq. in. between 127 - 173 hours

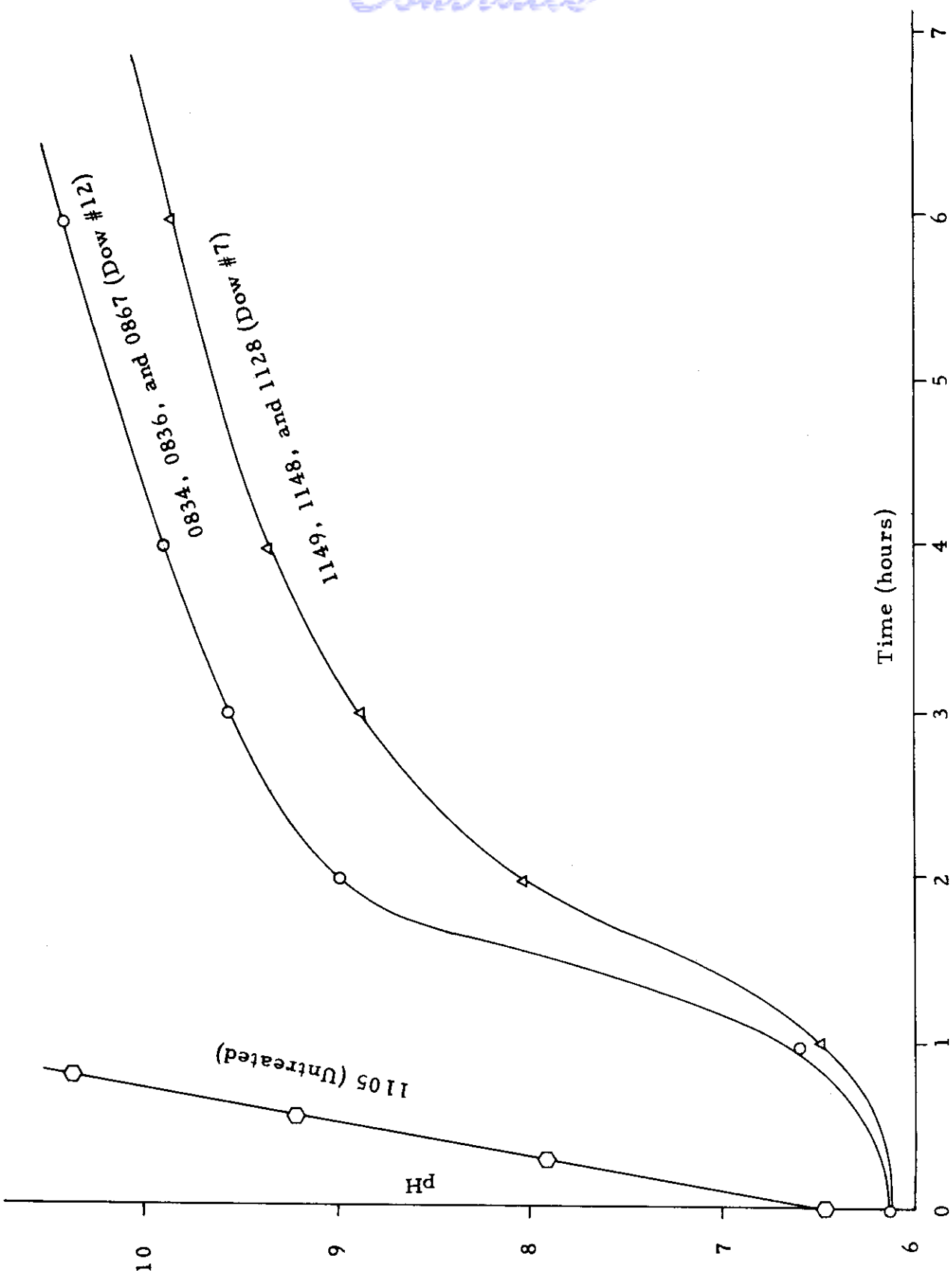


Figure 9. pH vs. Time: FS-1 Alloy in 1.0N KCl.

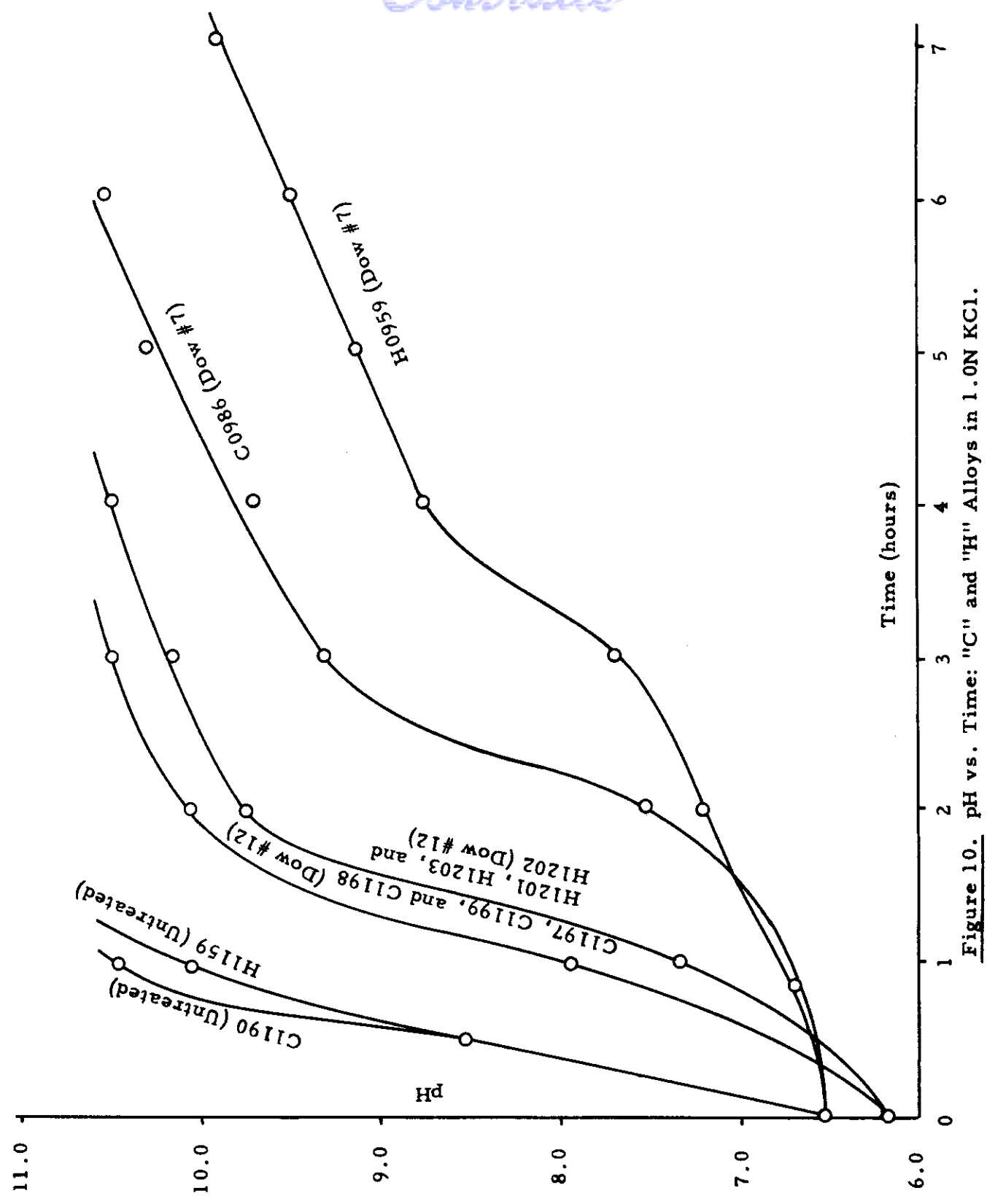


Figure 10. pH vs. Time: "C" and "H" Alloys in 1.0N KCl.

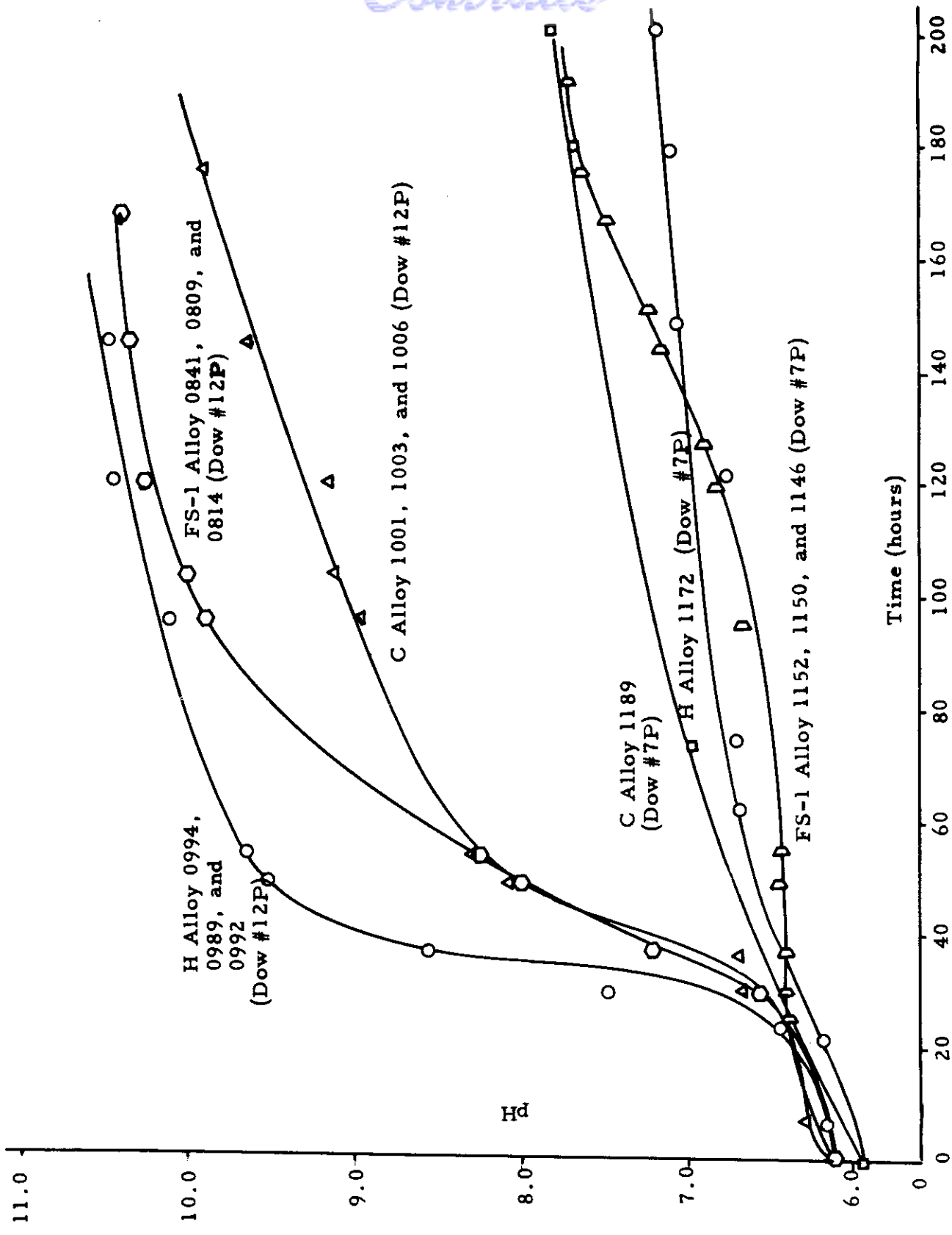


Figure 11. pH vs. Time: Primed Specimens in 1.0N KCl.

Dow #12P "H" alloy	Δ pH = 6.37×10^{-2}/hr./sq. in. between 30 - 37 hours
Dow #12P "C" alloy	Δ pH = 3.08×10^{-2}/hr./sq. in. between 37 - 54 hours
Dow # 7P "H" alloy	Δ pH = 2.49×10^{-3}/hr./sq. in. between 0 - 212 hours
Dow # 7P "C" alloy	Δ pH = 3.64×10^{-3}/hr./sq. in. between 0 - 212 hours.

The primed Dow #7 treated alloys were significantly superior in corrosion resistance. On prolonged immersion, the primer loosened markedly on the Dow #12 specimens and large bubbles appeared under the primer.

No pH change was noted in 1.0N KCl after immersion of lacquered specimens for 14 days.

The larger pH increases obtained with the Dow #12 treatment than with the Dow #7 treatment when specimens were immersed in 1.0N KCl were attributed in part to the solubility of this alkaline coating. The solubility of both the Dow #12 and #7 treatments on FS-1 alloy was determined by complete immersion of treated FS-1 specimens in distilled water for 24 hours. The pH was measured periodically, and the weight loss of each specimen was determined at the end of the test.

The following weight losses were observed:

Dow #12	0.007 gm./sq. in./24 hr.
Dow #7	0.005 gm./sq. in./24 hr.

The Δ pH values for the period of maximum change (between 1 and 2 hours) were:

Dow #7	Δ pH = 0.022/hr./sq. in.
Dow #12	Δ pH = 0.041/hr./sq. in.
Untreated FS-1	Δ pH = 0.149/hr./sq. in.

If no metallic corrosion on the treated specimens is assumed during this period, the ΔpH values for treated FS-1 specimens should be corrected as follows:

Dow #7	ΔpH = 0.163 - 0.022 = 0.141
Dow #12	Δ pH = 0.255 - 0.041 = 0.214

Since the corrections for the solubility of the Dow #12 and Dow #7 treatments on FS-1 alloy were very small and did not affect the relative ratings of the treatments, corrections were not determined for the treatments on "C" and "H" cast alloys.

B. Open Circuit Potentials

The electrochemical nature of the treated magnesium alloy surfaces was studied by recording the open circuit potentials of corroding specimens over a period of time. The open circuit potential method permits determination of whether the treated alloy is active or passive towards corrosion and how the protective film functions, i.e., whether it is anodic or cathodic. Film failures can also be detected by this method.

Unless otherwise noted, the following set-up was used in all open circuit potential determinations:

> A Lucite vessel was constructed such that the reference and specimen electrodes were held vertically and one inch apart. The electrodes were immersed to a depth of one inch in the electrolyte. The vessel was leveled and recordings were made without agitation of the solution. The electrodes were attached to a photoelectric recording potentiometer with a 10 - 5000 millivolt range, and recordings were made of the potentials.

1. Initial Open Circuit Potential Studies

Initial studies of open circuit potentials were made with FS-1 specimens versus a nickel reference electrode in saturated K_2SO_4. Representative data are presented in Table No. 6.

Specimens 0031-33, 53, 74, 84, 41, 54, and 85 indicate that treated and untreated specimens with nickel as a reference electrode all reached a fairly stable voltage of 1.20 - 1.25 volts in saturated K_2SO_4. The heavier Dow #7 coatings reached this maximum potential in less time than untreated specimens.

In another series in saturated K_2SO_4, untreated acetic-nitrate "pickled" FS-1 specimens of the same size as the treated specimens were used as reference electrodes. Representative data for this series are also given in Table No. 6 and characteristic potential - time curves in Figure 12.

Specimens 86, 55, 75, 0082, and 0089 show that the potential differences of coated specimens were dependent on the thickness of the treatment. Dow #7 treatments applied at a pH of 4.1 produced a much higher potential difference than when applied at pH = 5.4.

TABLE NO. 6

OPEN CIRCUIT POTENTIAL MEASUREMENTS

FS-1 SPECIMENS

Specimen No.	Specimen Treatment	Reference Electrode	Electrolyte	E_o * (volts)	E_5 ** (volts)	t_o *** (min.)
0031	Clean FS-1	Nickel	Sat. K_2SO_4	0.9	1.0	-
0032	Clean FS-1	Nickel	Sat. K_2SO_4	1.0	1.25	-
0033	Clean FS-1	Nickel	Sat. K_2SO_4	1.0	1.25	-
53	Iridite #15	Nickel	Sat. K_2SO_4	0.9	1.20	-
74	Dow #7 pH-5.3	Nickel	Sat. K_2SO_4	0.8	1.20	-
84	Dow #7 pH-4.1	Nickel	Sat. K_2SO_4	1.15	1.28	-
41	Dow #7 pH-4.8	Nickel	Sat. K_2SO_4	1.0	1.25	-
54	Iridite #15	Nickel	Sat. K_2SO_4	0.9	1.20	-
85	Dow #7 pH-4.1	Nickel	Sat. K_2SO_4	1.2	1.25	-
86	Dow #7 pH-4.1	Nickel	Sat. K_2SO_4	0.35	0.14	-
55	Iridite #15	Clean FS-1	Sat. K_2SO_4	0.125	0.090	-
75	Dow #7 pH-5.3	Clean FS-1	Sat. K_2SO_4	0.062	0.020	-
0082	Dow #7 pH-5.4	Clean FS-1	Sat. K_2SO_4	0.080	0.051	-

NOTES: Specimens immersed to depth of one inch in 115 milliliters of electrolyte and positioned one inch apart.

* E_o = Initial open circuit potential.

** E_5 = Voltage after 5 minute immersion.

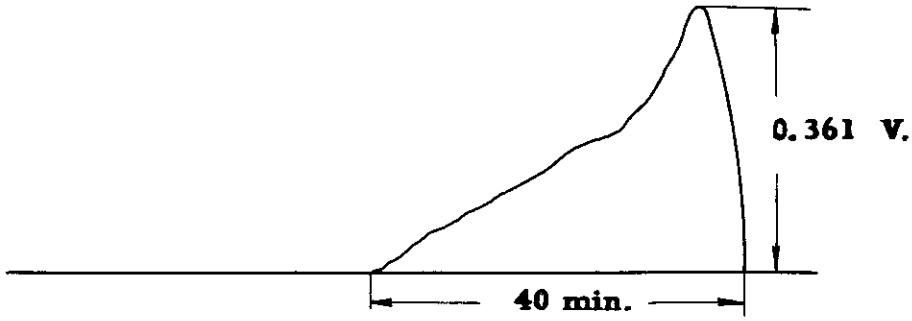
*** t_o = Time in minutes to reach zero voltage.

TABLE NO. 6 (Cont'd)

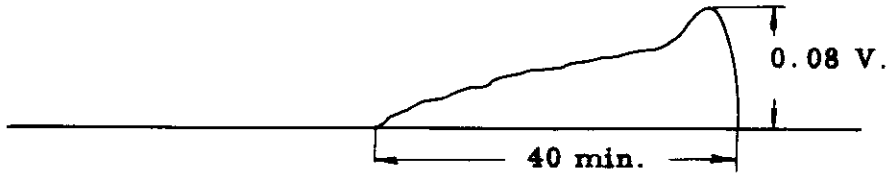
OPEN CIRCUIT POTENTIAL MEASUREMENTS

FS-1 SPECIMENS

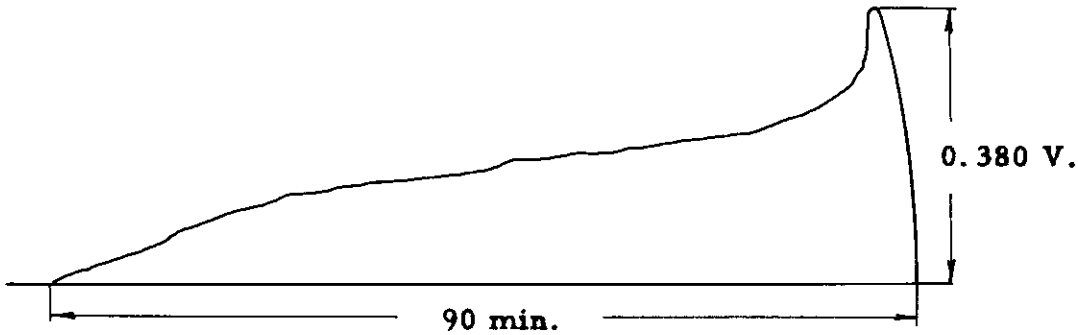
Specimen No.	Specimen Treatment	Reference Electrode	Electrolyte	E_o * (volts)	E_5 ** (volts)	t_o *** (min.)
0089	Dow #7 pH-5.4	Clean FS-1	Sat. K_2SO_4	0.03	0.005	-
0124	Dow #7 pH-5.2	Clean FS-1	0.001M K_2SO_4	0.214	0.150	60
0123	Dow #7 pH-5.2	Clean FS-1	0.001M K_2SO_4	0.159	0.153	98
0126	Dow #7 pH-5.2	Clean FS-1	0.001M K_2SO_4	0.189	0.108	38
0244	Dow #7 pH-4.0-4.6	Clean FS-1	0.001M K_2SO_4	0.340	-	72
0255	Dow #7 pH-4.0-4.6	Clean FS-1	0.001M K_2SO_4	0.340	-	91
0245	Dow #7 pH-4.0-4.6	Clean FS-1	0.001M K_2SO_4	0.375	-	73
0247	Dow #7 pH-4.0-4.6	Clean FS-1	0.001M K_2SO_4	0.398	-	75
0248	Dow #7 pH-4.0-4.6	Clean FS-1	0.001M K_2SO_4	0.380	-	90
0120	Iridite #15	Clean FS-1	0.001M K_2SO_4	0.361	-	49
0118	Iridite #15	Clean FS-1	0.001M K_2SO_4	0.361	-	40
0057	Dow #7 pH-4.6	Clean FS-1	Sat. KCl	0.004	-	1
0034	Clean FS-1	Nickel	1.0N KCl	0.70	1.0	-
0037	Clean FS-1	Nickel	1.0N KCl	0.78	1.18	-
87	Dow #7 pH-4.1	Nickel	1.0N KCl	0.80	1.22	-
0046	Dow #7 pH-4.6	Nickel	0.01N KCl	1.22	-	
0039	Clean FS-1	Nickel	0.01N KCl	1.0	-	-
0252	Dow #7 pH-4.0-4.6	Clean FS-1	0.1N KCl	0.230	-	-



Iridite #15 (0.001 M K_2SO_4) Specimen 0118



Dow #7 (Satd. K_2SO_4) Specimen 0122



Dow #7 (0.001 M K_2SO_4) Specimen 0248

Figure 12. Typical Open Circuit Potential-Time Curves for FS-1 Specimens.

The clean specimens were anodic to Dow #7 treated specimens. However, as the protective film was penetrated by the ions of the electrolyte, the potential difference decreased. Simultaneously, corrosion products built up on the untreated electrode and it became less anodic. This explains the decrease in potential to zero which occurred with this series of specimens over a time interval.

Additional tests were made to ascertain the value of "time to zero potential" (t_o) measurements. The saturated potassium sulfate electrolyte was replaced by a dilute solution since the potential decreased too rapidly to obtain a good curve, and also because the K_2SO_4 concentration in saturated solutions is dependent on temperature.

Results varied considerably with the potential differences inherent in each untreated and treated specimen electrode. This is illustrated by the variations in values for initial potential, "E_o",and "t_o" for specimens 0244, 0255, 0247, 0248, 0120, and 0118.

In general, the heavier and more protective the treatment (or film) under investigation, the higher the initial potential difference and the longer the time interval to zero potential. With the Dow #7 treatment "t_o" was consistently longer than with the Iridite #15 treatment.

Specimen 0057 (Dow #7) in saturated potassium chloride was reduced to equal potential with untreated metal within one minute. This emphasizes the rapid penetration of the gelatinous type Dow #7 coatings by chloride ion. Specimen 0252 in 0.1N KCl, however, showed a slower potential change, due to the lower chloride ion concentration.

2. Open Circuit Potentials of Cast Alloys

a. Potentials of Untreated Cast Alloys Versus Saturated Calomel

The open circuit potentials of untreated "C" and "H" cast alloys versus a saturated calomel electrode in various electrolytes are shown in Table No. 7. Little difference was noted between the potentials of the two cast alloys.

TABLE NO. 7

POTENTIALS OF CAST ALLOYS VERSUS SATURATED CALOMEL IN VARIOUS ELECTROLYTES

Electrolyte	Potential (volts)	
	"C" Alloy/Saturated Calomel	"H" Alloy/Saturated Calomel
1.0N KCl	1.58 - 1.60	1.55
Saturated KCl	1.60	1.60
3% NaCl	1.50 - 1.52	1.52
0.001M K_2SO_4	1.40	1.40 - 1.42
0.5N K_2SO_4	1.50	1.54

b. Potential Change of Treated Versus Untreated Cast Alloys

The potential change of treated (Dow #7 or #12) versus untreated specimens of the same alloy in 0.001N KCl or 3% NaCl solution was measured over a period of 169 hours. The Dow #12 treated specimens used in this test were in the rough unmachined state, and consequently the submerged area was considerably larger than for the other specimens. Therefore, the weight losses as shown in Table No. 8 are only relative between specimens with the same treatment.

The Dow #7 specimens lost soluble chromate to the test solution. In this solution the soluble chromate continued to function in a protective manner with consequent low weight losses.

The data in Table No. 8 indicate that a cathodic potential was maintained longer by the Dow #12 specimens in 0.001N KCl than by the Dow #7 specimens. (The weight losses were less for the Dow #7 treated specimens under these circumstances, however). The Dow #7 "C" alloy specimen became anodic to the untreated specimen in 97 hours.

TABLE NO. 8

POTENTIAL CHANGE OF TREATED VERSUS UNTREATED CAST ALLOYS

Time (hr.)	Potential (volts) (Treated Specimen Versus Untreated Specimen)					
	"C" Alloy Dow #7 0.001N KCl	"C" Alloy Dow #12 0.001N KCl	"C" Alloy Dow #12 3% NaCl	"H" Alloy Dow #7 0.001N KCl	"H" Alloy Dow #12 0.001N KCl	"H" Alloy Dow #12 3% NaCl
Immersion	0.127	0	0.020	0.083	0.048	0.021
2	0.005	0.030	0.015	0.014	0.054	0.032
66	0.006	0.046	0.011	0.027	0.068	0.020
73	0.004	0.030	0.014	0.020	0.052	0.010
97	-0.002	0.028	0.007	0.032	-	0.014
169	-0.006	0.006	-0.005	0.0196	0.049	0.003
Wt. loss untreated specimen (grams)	0.0092	0.0107	0.3238	0.0023	0.0087	0.3255
Wt. loss treated specimen (grams)	0.0075	0.0516	0.3323	0.0045	0.0743	0.2310

NOTES: Electrodes immersed to equal depth in 100 ml. electrolyte, with upper shank projecting above solution. Porous Lucite partition placed between electrodes to prevent contact. Solutions unstirred; 25°C.

Change in polarity indicated by minus sign.

The Dow #12 "H" alloy maintained a cathodic potential longer than the "C" alloy in 3% NaCl and also in 0.001N KCl.

Additional data were obtained on the open circuit potentials of treated (Dow #12 or #7) specimens versus untreated (alkaline cleaned and acetic-nitrate "pickled") specimens of the same alloy using 0.001N KCl or 0.001M K_2SO_4 as the electrolyte (Table No. 9). The Dow #12 specimens were unmachined. The Dow #12 "H" alloy again showed better resistance to 0.001N KCl than the Dow #12 "C" alloy.

c. Potential Change of Treated Cast Alloys in 0.01N KCl

Dow #7 "C" and "H" cast specimens were tested in the treated, primed, and lacquered stages against both saturated calomel and untreated alloy reference electrodes in 0.01N KCl.

The specimens were immersed in individual stoppered containers to a depth of one inch in the electrolyte (59 milliliters). The electrode protruded through the stopper in such a fashion that electrical connection could be made to the potentiometer. A second opening in the stopper allowed insertion of a salt bridge which made contact in another container also containing 0.01N KCl. The reference electrode was placed in this second container at the time of measurement. The test was continued for 121 hours.

Tables 10 and 11 show that the potentials of the treated "H" and "C" alloys (specimens H0605 and C0629) when compared with the calomel electrode were very similar over the 121 hour period. When compared with untreated alloy, however, the potential of the Dow #7 "H" alloy increased, whereas the potential of the Dow #7 "C" alloy decreased to zero and changed in polarity.

The potentials of the primed "H" and "C" alloys (specimens H0506 and C0530) against the calomel electrode were also similar over the test period. When compared with untreated specimens, the "H" specimen again showed continued positive potential difference, whereas the "C" primed specimen became anodic.

The lacquered "H" and "C" alloys (specimens H0542 and C0555) maintained perfect insulation during this test period indicating the absence of flaws or pin-holes in the lacquer.

TABLE NO. 9

POTENTIALS OF TREATED VERSUS UNTREATED CAST ALLOYS

Specimen Electrode	Reference Electrode	Electrolyte	Initial Potential (volts)	Time to Zero Potential
"H" Alloy Dow #12	Cleaned "H" Alloy	0.001 M K_2SO_4	0.215	120 min.
"H" Alloy Dow #12	Cleaned "H" Alloy	0.001 M K_2SO_4	0.200	24 hr. V* = 0.10
"H" Alloy Dow #12	Cleaned "H" Alloy	0.001N KCl	0.100	105 min. V = 0.030 20 hr. V = 0.026
"H" Alloy Dow #7	Cleaned "H" Alloy	0.001 M K_2SO_4	0.128	130 min.
"H" Alloy Dow #7	Cleaned "H" Alloy	0.001N KCl	0.240	40 min.
"C" Alloy Dow #12	Cleaned "C" Alloy	0.001 M K_2SO_4	0.135	90 min. V = 0.068 5 hr. V = 0.048 17 hr. V = 0.020
"C" Alloy Dow #12	Cleaned "C" Alloy	0.001 M K_2SO_4	0.072	4 hr. V = 0.10 24 hr. V = 0.02
"C" Alloy Dow #12	Cleaned "C" Alloy	0.001N KCl	0.100	75 min. 24 hr. V = 0.005
"C" Alloy Dow #7	Cleaned "C" Alloy	0.001 M K_2SO_4	0.120	4.5 hr. V = 0.01 16 hr. V = 0.15
"C" Alloy Dow #7	Cleaned "C" Alloy	0.001N KCl	0.060	190 min. 6 hr. V = 0.010
"C" Alloy Dow #7	Cleaned "C" Alloy	0.001N	0.270	105 min. 10 hr. V = 0.015

* V = Potential of time shown

TABLE NO. 10

TREATED "C" ALLOY POTENTIAL CHANGE IN 0.01N KCl

Time (hr.)	Potential (volts) Dow #7 Treated "C" Alloy Versus Saturated Calomel			Potential (volts) Dow #7 Treated Versus Untreated "C" Alloy		
	C0629 Dow #7	C0530 Primed	C0555 Lacquered	C0629 Dow #7	C0530 Primed	C0555 Lacquered
Immersion	-1.51	-1.20	∞*	+0.0195	0	∞
2	-1.55	-1.50	∞	+0.0140	+0.0194	∞
4	-1.60	-1.71	∞	+0.0121	+0.0109	∞
23	-1.55	-1.70	∞	+0.0100	+0.0294	∞
28	-1.55	-1.72	∞	+0.0101	+0.0282	∞
46	-1.58	-1.71	∞	+0.0100	+0.0216	∞
52	-1.55	-1.72	∞	-	-	∞
69	-	-	-	+0.0178	+0.0155	∞
75	-1.54	-1.70	∞	+0.0188	+0.0152	∞
91	-1.53	-1.59	∞	-	-	-
99	-1.52	-1.59	∞	-0.0060	-0.0036	∞
121	-1.52	-1.56	∞	+0.0023	-0.0027	∞

*Electrode resistance infinite.

TABLE NO. 11

TREATED "H" ALLOY POTENTIAL CHANGE IN 0.01N KCl

Time (hr.)	Potential (volts) Dow #7 Treated "H" Alloy Versus Saturated Calomel			Potential (volts) Dow #7 Treated Versus Untreated "H" Alloy		
	H0605 Dow #7	H0506 Primed	H0542 Primed	H0605 Dow #7	H0506 Primed	H0542 Primed
Immersion	-1.50	-1.21	∞ *	+0.0108	+0.0125	∞
2	-	-	-	+0.0109	+0.0130	∞
4	-1.50	-1.70	∞	+0.0105	+0.0166	∞
6	-1.50	-1.69	∞	-	-	-
23	-	-	-	+0.0166	+0.0154	∞
25	-1.54	-1.72	∞	-	-	-
28	-1.58	-1.70	∞	+0.0189	+0.0156	∞
46	-1.54	-1.68	∞	+0.0203	+0.0375	∞
52	-1.54	-1.70	∞	-	-	-
69	-	-	-	+0.0194	+0.0225	∞
75	-1.55	-1.64	∞	+0.0201	+0.0219	∞
91	-1.54	-1.58	∞	-	-	-
99	-1.55	-1.54	∞	+0.0219	+0.0337	∞
121	-1.54	-1.51	∞	+0.0229	+0.2780	∞

* Electrode resistance infinite.

3. Open Circuit Potentials of FS-1 Wrought Alloy

a. Potentials of Dow #12 Treated Versus Untreated FS-1 Alloy

Open circuit potentials of Dow #12 treated versus cleaned untreated FS-1 specimens in 0.001M K_2SO_4 and 0.001N KCl are shown in Table No. 12. These specimens increased in potential (cathodic) within the test period of several hours. This would seem to indicate that the Dow #12 has a protective capacity superior to Dow #7, since Dow #7 specimens were reduced to zero potential difference in about 90 minutes (in 0.001M K_2SO_4). Considerable variation in the initial potentials for the Dow #12 specimens was noted, however.

b. Potential Change with Electrolyte Concentration for Treated versus Untreated FS-1 Alloy

Tests were made to obtain an insight into the protective capacity of Dow #7 and #12 treatments in various concentrations of electrolyte.

Treated FS-1 specimens were compared with an untreated specimen in KCl of one concentration, then removed, washed with water, and immersed in KCl of another concentration. The initial voltages and voltages after short intervals are shown in Table No. 13.

The cathodic potential of Dow #12 specimens decreased at a slower rate in chloride electrolytes than that of Dow #7 treated specimens. This was particularly true in concentrations of 1.0N KCl and higher. The potential of Dow #7 treated specimens in such solutions quickly dropped to 0.015-0.020 volt, whereas the Dow #12 treated specimens maintained a protective potential of 0.040-0.050 volt. The high protective potentials were recovered by both Dow #7 and #12 treated specimens when they were removed from concentrated solutions (1.0N and over) and placed in the 0.001N solution.

The recovery of a higher protective potential by the Dow #7 in the 0.001N KCl indicates the presence of a protective chromate envelope resulting from solubilization of the Dow #7 itself. The Dow #12 is unable to do this.

Much of the potential change when a treated specimen is opposed to an untreated electrode occurs at the untreated surface. The untreated electrode is also individual in its corrosion rate at a given time. Because of this individuality, the value of potential readings for treated versus untreated specimens is uncertain.

TABLE NO. 12

POTENTIALS OF DOW #12 TREATED VERSUS UNTREATED FS-1 ALLOY

Specimen Electrode	Reference Electrode	Electrolyte	Potential * (volts)	Potential (volts) after Indicated Time Interval
0284 Dow #12	Acetic-nitrate "pickled" FS-1	0.001N KCl pH = 6.6	0.380	0.100 after 3.5 hr. 0.150 after 24 hr. 0.100 after 48 hr.
0292 Dow #12	Acetic-nitrate "pickled" FS-1	0.001N KCl pH = 6.6	0.520	0.180 after 3 hr. 0.240 after 15 hr.
0295 Dow #12	Acetic-nitrate "pickled" FS-1	0.001 M K_2SO_4	0.450	0.270 after 2 hr. 0.245 after 24 hr. 0.150 after 48 hr.
0293 Dow #12	Acetic-nitrate "pickled" FS-1	0.001 M K_2SO_4	0.530	0.140 after 1 hr. 0.220 after 4 hr.

* Initial potential.

TABLE NO. 13

POTENTIAL CHANGE OF DOW # 7 & 12 TREATED SPECIMENS WITH AN ELECTROLYTE CONCENTRATION CHANGE

Electrolyte	Specimen 0444 Dow #7 vs. FS-1	Specimen 0244 Dow #7 vs. FS-1	Specimen 0294 Dow #12 vs. FS-1	Specimen 0288 Dow #12 vs. FS-1
1.0N KCl pH = 7.0		E_o=0.3 + $E_{10\ min.}$=0.012	$E_{10\ min.}$=0.046	E_o=0.25 $E_{10\ min.}$=0.040
0.001N KCl pH = 6.6	E_o=0.490 $E_{5\ min.}$=0.330	E_o=0.3 + $E_{10\ min.}$=0.22	$E_{10\ min.}$=0.150	E_o=0.155 $E_{10\ min.}$=0.220
1.0N KCl	E_o=0.150 $E_{5\ min.}$=0.015	E_o=0.015 $E_{10\ min.}$=0.020 $E_{90\ min.}$=0.018	$E_{10\ min.}$=0.055 $E_{30\ min.}$=0.058	E_o=0.20 $E_{10\ min.}$=0.049
Saturated KCl pH = 6.5	E_o=0.009 $E_{5\ min.}$=0.017		$E_{10\ min.}$=0.040	
0.001N KCl	E_o=0.075 $E_{30\ min.}$=0.150 $E_{48\ hr.}$=0.165		E_o=0.070 $E_{120\ min.}$=0.120 $E_{48\ hr.}$=0.070	

NOTES: Treated and untreated electrodes immersed in electrolyte solutions in order shown.

E_o = Initial open circuit potential (volts).

$E_{5\ min.}$, $E_{30\ min.}$, etc. = Voltage after indicated time interval.

c. Potentials of Treated FS-1 Alloy Versus Saturated Calomel

The relative potentials of untreated and treated FS-1 specimens were checked against a saturated calomel electrode. The short circuit current cells shown on page 54 were used except that a salt bridge was inserted in the stirrer opening. Table No. 14 gives the potentials in 0.1N KCl and 0.1N K_2SO_4.

The Dow #12 treatment gave the lowest potentials in both the KCl and K_2SO_4. The addition of detergent (Tween 20, Atlas Powder Co.) and hydrogen peroxide as depolarizers caused little potential change in the K_2SO_4. In the KCl the potential difference between the various treatments was smaller than in the K_2SO_4, and with the two additives no appreciable difference existed.

C. Short Circuit Currents

A rapid, accurate corrosion test was developed which is easily standardized. It depends primarily on the immersion of a test specimen in an electrolyte and short circuiting it through a one ohm resistor to a reference electrode of approximately the same dimensions immersed in the same vessel. The short circuit current during the test is recorded with a photoelectric potentiometer. The dimensions and initial weight of the specimen are recorded before testing. The weight loss is calculated after corrosion product removal and is calculated as grams per hour per square inch of electrode surface.

The original potentiometer and cell hook-up used in the short circuit tests is shown in Figure 13. At "A" is shown a Lucite vessel with an FS-1 test specimen and a nickel reference electrode immersed to a depth of one inch and short circuited with an accurately wound wire resistor. The Lucite cell was leveled on an adjustable platform mounted in a constant temperature bath. The electrodes were held in grooves one inch apart. The potentiometer terminals were connected by clip contacts to cleaned bare areas.

At "B" a cell is shown for holding cast bar specimens. A Lucite holder was used to hold the specimens one inch apart.

A second type of short circuit current cell was also constructed, but will be described later.

1. Initial Short Circuit Current Determinations

In initial short circuit current tests, untreated (acetic-nitrate "pickled"), Dow #7 and #12 treated, and primed FS-1 specimens were tested. A high purity nickel electrode 1.475" wide and 0.025" thick was used as the reference electrode. The electrolyte was 1.0N KCl, pH = 5.7, made with Reagent Special Grade KCl. The tests were run for two hours, and the short circuit currents at two hours are listed in Table No. 15.

TABLE NO. 14

POTENTIALS OF FS-1 ALLOY VERSUS SATURATED CALOMEL

Specimen No.	Treatment	Electrolyte	Maximum Potential Values* (volts)		
			Initial (E_o)	With Tween 20	With Tween 20 and H_2O_2
1109	Untreated	0.1N K_2SO_4	1.80	1.80	1.70
1430	Heavy Dow #7	0.1N K_2SO_4	1.60-1.65	1.63	1.70
1391	Light Dow #7	0.1N K_2SO_4	1.58	1.58	1.58
0890	Dow #12	0.1N K_2SO_4	1.49	1.49	1.48
1109	Untreated	0.1N KCl	1.72	-	1.50
1430	Heavy Dow #7	0.1N KCl	1.55	-	1.53
1391	Light Dow #7	0.1N KCl	1.54	-	1.53
0890	Dow #12	0.1N KCl	1.53	-	1.55

* Electrolyte stirred. 5 drops each of Tween 20 and 30% hydrogen peroxide added to the electrolyte.

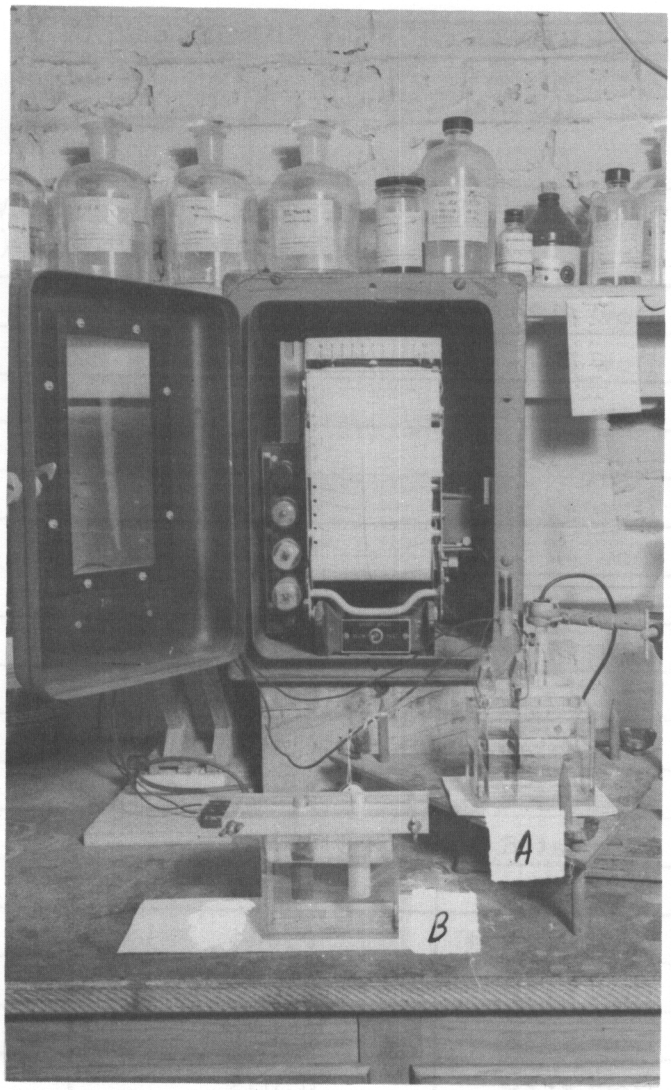


Figure 13. Equipment for Measuring Short Circuit Currents. "A" shows an FS-1 specimen in a typical one ohm short circuit set up. "B" illustrates the method of handling cast specimens.

TABLE NO. 15

SHORT CIRCUIT CURRENTS OF FS-1 SPECIMENS IN 0.1N KCl

(Nickel Reference Electrode)

Specimen No.	Treatment	Current at 2 hr. (amp.)	Wt. Loss Rate ($gm./hr./in.^2$)
0353	Dow #12	0.100	2.66×10^{-2}
0355	Dow #12	0.090	2.55×10^{-2}
0849*	Dow #12	0.104	2.29×10^{-2}
0818*	Dow #12	0.096	1.81×10^{-2}
0721	Dow #7	0.103	2.75×10^{-2}
0943	Dow #7	0.105	2.78×10^{-2}
0718	Dow #7	0.110	2.60×10^{-2}
0738*	Dow #7	0.108	2.75×10^{-2}
0938*	Dow #7	0.103	2.76×10^{-2}
0743	Untreated	0.100	2.68×10^{-2}
0758	Untreated	0.103	2.56×10^{-2}
0744*	Untreated	0.104	2.71×10^{-2}
0745*	Untreated	0.106	2.66×10^{-2}
0316	Dow #12P**	0.044	7.64×10^{-3}
0370	Dow #12P	0.075	20.7×10^{-3}
0314	Dow #12P	0.075	14.5×10^{-3}
0899*	Dow #12P	0.053	9.0×10^{-3}
0487	Dow #7P	0.050	11.3×10^{-3}
0453	Dow #7P	0.048	9.8×10^{-3}
0443	Dow #7P	0.040	6.7×10^{-3}
0787*	Dow #7P	0.042	7.64×10^{-3}

* Specimens with electroplater's tape marking off one inch immersion. Results more accurate.
** P= treated with primer.

The first tests were made by immersion of the specimens to a depth of one inch in 115 milliliters of electrolyte. Examination of the corroded specimen at the end of the two hour test revealed an irregular electrolyte-air interface corrosion line. Weight losses varied considerably in these experiments.

To expose an accurately predetermined area of the active electrodes, pressure-sensitive electroplater's tape was applied so that a depth of 1.000 inch ± 0.001 inch was exposed regardless of small variations in electrolyte volume. A volume of 135 milliliters of electrolyte was used in these tests, and the tests were made a prevailing room temperatures.

Taping the specimens eliminated the irregular liquid corrosion line and weight losses were then more reproducible. The taped specimens are indicated by an asterisk (*) in Table No. 15.

For taped specimens 0899 (Dow #12P) and 0787 (Dow #7P), the weight losses were also calculated per 0.1 mil of primer thickness. The weight losses for these specimens on this basis are:

$$\text{Dow \#12} = 1.12 \times 10^{-3}$$
$$\text{Dow \#7} = 0.96 \times 10^{-3}$$

For unprimed specimens, the weight losses and short circuit currents were greatest for Dow #7 specimens, less for untreated FS-1 specimens, and least for the Dow #12 treated specimens. Weight losses for the Dow #12 specimens were subject to some variation, and these values should not be taken as absolute values. With primed specimens the Dow #12 treated specimens had higher weight losses and currents.

The higher weight loss of Dow #7 unprimed specimens compared with untreated specimens and Dow #12 unprimed specimens may have been due to:

(1) Immediate wetting and diffusion of the electrolyte to the base metal, as indicated by high initial current readings. There was a lower surface tension between the Dow #7 surface and electrolyte than between bare alloy and electrolyte.

(2) Higher current drains perimitted by the lower resistivity of the Dow #7 coating. The Dow #12 coating is impervious, granular, and has high resistivity as compared with the gel-type Dow #7.

2. Short Circuit Currents in 1.0N and 0.1N KCl

Both wrought and cast alloy specimens were tested in 1.0N and 0.1N KCl (pH = 5.7 - 6.7) using the original short circuit current equipment and procedure.

All specimens were taped with electroplater's tape for a one inch immersion in 135 milliliters of solution. For the FS-1 specimens, a high purity nickel electrode 1.475" wide and 0.025" thick was used as the reference electrode. For the cast alloys a commercial nickel electrode of the following composition was used:

99.4%	Nickel
0.1%	Copper
0.15%	Iron
0.2%	Manganese
0.1%	Carbon
Trace	Cobalt

It was machined to the same diameter (0.6700 inch) as the test bar specimens. The electrodes unless otherwise specified were positioned one inch apart. The short circuit currents were recorded for 120 minutes after which the specimens were removed from the KCl solution.

Several determinations were also made by agitating the solution or using a silver electrode (1.5" x 0.040").

The areas under the recorded current-time curves for these specimens were measured with a compensating planimeter and from this area, an average current was calculated in milliamperes per square inch of test surface. These values along with weight loss data are presented in Tables 16, 17, and 18.

Untreated FS-1 alloy specimens exhibited an average current slightly less than that for Dow #7 treated FS-1 specimens (Table No. 16), as noted previously. The Dow #12 treatment again appeared more protective than the Dow #7, although not generally in the primed condition. Weight losses were not so consistent with average current values as would be considered desirable. The weight of the Dow #12 (MgO) varied from sample to sample, and consequently influenced the weight losses. The variation in current apparent between specimens could be due to polarization and (or) inherent individual specimen differences.

In the short circuit current tests, the "C" alloy was more reactive than the "H" alloy (Tables 17 and 18), which correlates well with pH increase data. For the cast alloys, the most promising method involved stirring the 1.0N KCl between the electrodes so that the hydrogen bubbles were removed and corrosion products prevented from accumulating.

TABLE NO. 16

SHORT CIRCUIT CURRENTS

FS-1 ALLOY

Specimen No.	Treatment	Current Drain (milliamp./in.^{2})	Electrolyte	Weight Loss (gm./in.^{2}/hr.
1101	Untreated	25.95	1.0N KCl	0.0168
1091	Untreated	5.27	0.1N KCl	0.0011
1103	Untreated	2.69	0.1N KCl Stirred*	0.0023
1108	Untreated	5.73	0.1N KCl	0.0013
1134	Dow #7	33.10	1.0N KCl	0.0242
1137	Dow #7	5.32	0.1N KCl	-
1139	Dow #7	5.74	0.1N KCl	0.0047
1135	Dow #7	5.28	0.1N KCl	0.0038
1267	Dow #7	2.95	0.1N KCl Stirred*	0.0026
1266	Dow #7	6.07	0.1N KCl Stirred*	0.0038
1133	Dow #7	1.64	0.1N KCl**	0.0011
0826	Dow #12	3.07	0.1N KCl Stirred*	0.0050
0811	Dow #12	4.67	0.1N KCl	0.0069
0848	Dow #12	4.75	0.1N KCl	-
0808	Dow #12	5.09	0.1N KCl	0.0036
0872	Dow #12	4.74	0.1N KCl Stirred***	0.0060
0866	Dow #12	30.50	1.0N KCl	0.0227

NOTES: Nickel reference electrode unless otherwise noted.
* Electrodes two inches apart, stirring between the electrodes.
** Silver reference electrode.
*** Stirring behind the nickel electrode, not between the nickel and specimen.

TABLE NO. 16 (Cont'd)

SHORT CIRCUIT CURRENTS

FS-1 ALLOY

Specimen No.	Treatment	Current Drain (milliamp./in.^{2})	Electrolyte	Weight Loss (gm./in./hr.)
0871	Dow #12	1.34	0.1N KCl	0.0029
1140	Dow #7P	6.25	1.0N KCl	0.0050
1147	Dow #7P	1.12	1.0N KCl	0.0019
1144	Dow #7P	2.05	1.0N KCl	0.0035
0820	Dow #12P	3.78	1.0N KCl	0.0057
0807	Dow #12P	4.00	1.0N KCl	0.0044
0856	Dow #12P	3.71	1.0N KCl	0.0041
0923	Iridite #15	4.27	0.1N KCl	0.0037

TABLE NO. 17

SHORT CIRCUIT CURRENTS

"C" ALLOY

Specimen No.	Treatment	Current Drain (milliamp./in.^{2})	Electrolyte	Weight Loss (gm./in.^{2}/hr.)
C1243	Untreated	5.10	0.1N KCl Stirred	0.0027
C1286	Untreated	4.73	0.1N KCl	0.0023
C1235	Untreated	39.20	1.0N KCl	0.0171
C1181	Dow #7	29.10	1.0N KCl Stirred	0.0116
C0980	Dow #7	32.90	1.0N KCl	0.0177
C0977	Dow #7	4.37	0.1N KCl	0.0018
C0986	Dow #7	-	1.0N KCl	0.0127
C1260	Dow #12	28.30	1.0N KCl	-
C1259	Dow #12	27.10	1.0N KCl	0.0140
C1256	Dow #12	29.50	1.0N KCl	0.0164
C1262	Dow #12	4.26	0.1N KCl	0.0012
C0988	Dow #7P	0.61	1.0N KCl Stirred	0.0003
C0978	Dow #7P	2.35	1.0N KCl	0.0013
C0983	Dow #7P	5.78	1.0N KCl	0.0041
C1002	Dow #12P	2.79	1.0N KCl	0.0024
C1315	Dow #12P	1.69	1.0N KCl Stirred	0.0025
C1310	Dow #12P	4.47	1.0N KCl	0.0027

NOTE: Nickel (commercial grade) reference electrode.

TABLE NO. 18

SHORT CIRCUIT CURRENTS

"H" ALLOY

Specimen No.	Treatment	Current Drain (milliamp./in.^{2})	Electrolyte	Weight Loss (gm./in.^{2}/hr.)
H1207	Untreated	4.24	0.1N KCl	-
H1214	Untreated	4.34	0.1N KCl Stirred	0.0025
H1217	Untreated	38.50	1.0N KCl	0.0154
H1168	Dow #7	25.70	1.0N KCl Stirred	0.0132
H0958	Dow #7	27.60	1.0N KCl	0.0199
H0959	Dow #7	33.70	1.0N KCl	0.0138
H1177	Dow #7	4.62	0.1N KCl	0.0020
H1247	Dow #12	20.50	1.0N KCl	0.0110
H1246	Dow #12	27.85	1.0N KCl	0.0186
H1252	Dow #12	3.44	0.1N KCl	0.0017
H0967	Dow #7P	1.81	1.0N KCl	0.0012
H1158	Dow #7P	1.03	1.0N KCl	0.0016
H0952	Dow #7P	0	1.0N KCl Stirred	0
H1297	Dow #12P	5.10	1.0N KCl Stirred	0.0040
H0996	Dow #12P	2.66	1.0N KCl	0.0020
H0993	Dow #12P	3.93	1.0N KCl	0.0032
NOTE: Nickel (commercial grade) reference electrode.				

Primed "C" and "H" alloy specimens in stirred 1.0N KCl had the following rating in order of increasing current and weight loss: H Dow #7P, C Dow #7P, C Dow #12P, and H Dow #12P.

3. Short Circuit Currents in 0.1N KCl and 0.1N K_2SO_4

(With New Type Cells)

New short current cells were constructed from Lucite as shown in Figure 14. These specimen holders permit adjustment of each electrode to the desired height and distance apart. FS-1 specimens were positioned two inches and cast specimens one inch from a nickel electrode of approximately the same size and shape as the specimens. A stirrer was inserted between the electrodes. All electrodes were masked with electroplater's tape so that only a one inch depth was exposed in the electrolyte (135 milliliters of 0.1N KCl or 0.1N K_2SO_4). Measurements with these new cells were made in a constant temperature bath at 25° ± 0.1°C rather than at room temperature as with the original short circuit current cells.

In initial experiments the electrodes were shorted (one ohm short) for one and two hour periods, and the current was recorded on the recording potentiometer. The trend of the current during this period was observed, and from the recorded current-time curve, average current values were obtained.

The current reached a maximum value at the beginning of the test and gradually decreased to approximately equal values for all treatments. The Dow #12 treated specimens reached this maximum value more slowly than the Dow #7 treated specimens, but generally the maximum was attained within 15 minutes of the short. Since this initial current (C_o) varied with each treatment, in subsequent experiments only the C_o value was determined, which eliminated the necessity of measuring the areas under the current-time curves and calculating average currents.

The decrease in current from the maximum C_o value was due mainly to hydrogen polarization as shown by the change in current with change in the rate of stirring and addition of depolarizer (H_2O_2) and/or detergent. This C_o value therefore represents the actual current drain possible from the cell combination before any appreciable polarization occurs.

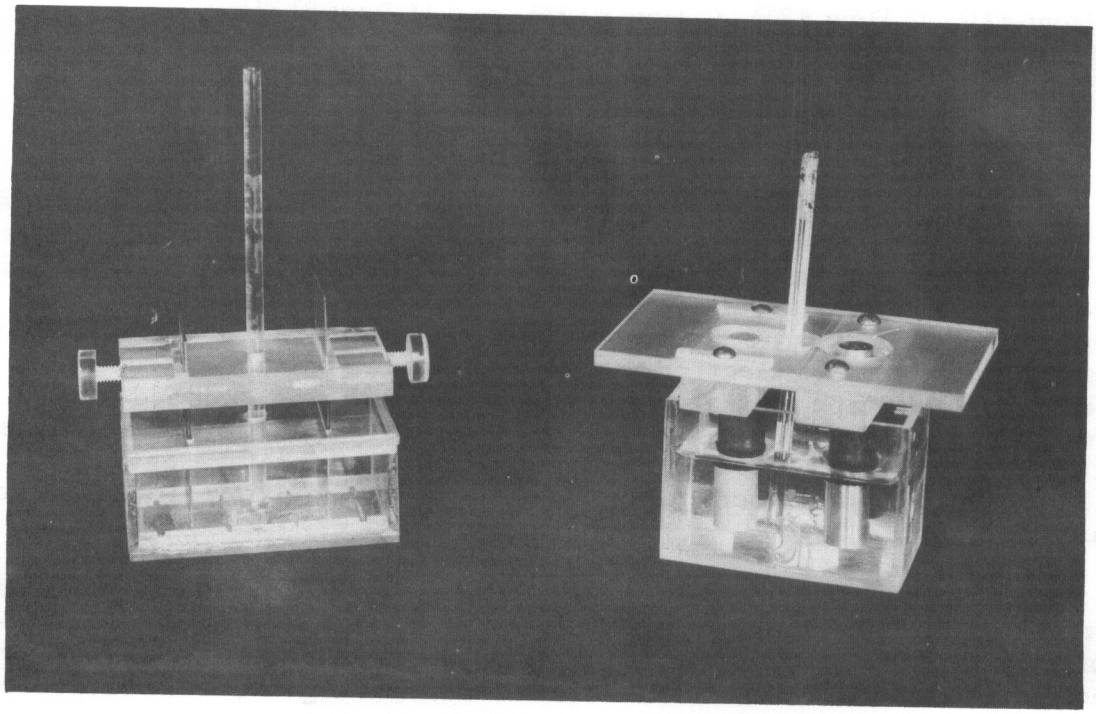


Figure 14. Short Circuit Current Cells. In the cell for FS-1 alloy specimens (left) the electrodes were positioned two inches apart. In the cell for cast specimens (right) the electrodes were one inch apart. A stirrer was inserted between the electrodes in each cell. All electrodes were masked with an insulating tape so that only a one inch depth was exposed to the electrolyte.

The data in Table No. 19 were obtained from one hour short circuits of treated and untreated FS-1 specimens. Average current values, in milliamperes per square inch of test surface, were calculated from the areas under the recorded current-time curves. Higher average current values were obtained with the 0.1N KCl than with the 0.1N K_2SO_4; however, higher initial current readings and lower final currents were observed with the 0.1N K_2SO_4.

Generally, the Dow #7 and the untreated FS-1 specimens showed similar average currents. Somewhat lower values were obtained for the Dow #12 specimens. The Iridite #15 gave somewhat higher rates than either the Dow #7 or #12. Average values in 0.1N K_2SO_4 were:

Dow #12	1.82 milliamp./sq. in.
Dow #7	2.44 milliamp./sq. in.
Iridite #15	2.58 milliamp./sq. in.
Untreated FS-1	2.49 milliamp./sq. in.

Table No. 20 presents the data obtained on treated and untreated specimens of cast "C" and "H" alloy in 0.1N KCl and 0.1N K_2SO_4. Polarization was difficult to control on these curved specimens, and resulted in some variation in currents. The addition of Tween 20 (Atlas Powder Co.) and hydrogen peroxide did not completely eliminate this variation.

The average currents in 0.1N K_2SO_4 for the Dow #12 specimens of "C" and "H" alloys were slightly lower than those for Dow #7 specimens:

Dow #7 "C" alloy	5.41 milliamp./sq. in.
Dow #7 "H" alloy	4.79 milliamp./sq. in.
Dow #12 "C" alloy	4.81 milliamp./sq. in.
Dow #12 "H" alloy	3.90 milliamp./sq. in.

The "H" alloy generally gave lower currents than the "C" alloy in all treatment conditions.

Short circuit current values for a group of specimens subjected to several degrees of polarization are presented in Table No. 21. Maximum currents were obtained with stirring and the addition of 30% hydrogen peroxide. Even with these influences the Dow #12 specimens did not reach so high a current drain as the Dow #7 specimens. The light Dow #7 FS-1 specimen produced a higher current than the heavy Dow #7 FS-1 specimen before stirring.

Another group of specimens (FS-1) were tested consecutively in 0.1N K_2SO_4, 0.1N KCl, and 1.0N KCl (Table No. 22). Characteristic currents were recorded in the 0.1N K_2SO_4 with measurable current differences corresponding to degree of treatment. In the chloride solutions the currents were subjected to more rapid change and variation especially between the light and heavy Dow #7 treatments.

TABLE NO. 19

SHORT CIRCUIT CURRENTS

FS - 1 ALLOY

Specimen No.	Treatment	Electrolyte	Initial Current-C_o (amp.)	Final Current (amp.)*	Average Current (milliamp./in.^{2})
1424	Dow #7	0.1N KCl	0.0122	0.0090	-
0883	Dow #12	0.1N KCl	0.0096	0.0088	2.69
1092	Untreated	0.1N KCl	0.0120	0.0095	2.89
1094	Untreated	0.1N KCl	0.0126	0.0075	2.86
1096	Untreated	0.1N K_2SO_4	0.0165	0.0060	2.55
1098	Untreated	0.1N K_2SO_4	0.0146	0.0076	2.56
1104	Untreated	0.1N K_2SO_4	0.0150	0.0066	2.35
1456	Dow #7	0.1N K_2SO_4	0.0092	0.0056	2.24
1694	Dow #7	0.1N K_2SO_4	0.0120	0.0063	2.51
1675	Dow #7	0.1N K_2SO_4	0.0104	0.0064	2.47
1437	Dow #7	0.1N K_2SO_4	0.0094	0.0068	2.55
0895	Dow #12	0.1N K_2SO_4	0.0080	0.0048	1.83
0873	Dow #12	0.1N K_2SO_4	0.0075	0.0056	1.94
0896	Dow #12	0.1N K_2SO_4	0.0087	0.0062	1.69
0924	Iridite #15	0.1N K_2SO_4	0.0101	0.0078	2.61
0922	Iridite #15	0.1N K_2SO_4	0.0110	0.0072	2.55

NOTES: FS-1 specimen two inches from nickel electrode; stirring between electrodes.

* Final currents for specimen Nos. 1424, 0883, 1092, and 1094 determined after two hours; all others determined after one hour.

TABLE NO. 20

SHORT CIRCUIT CURRENTS

"C" AND "H" CAST ALLOYS

Specimen No.	Treatment	Electrolyte	Initial Current-C_o (amp.)	Final Current (amp.)	Average Current (milliamp./in.^{2})
C1237	Untreated	0.1N K_2SO_4	0.0150	0.0130	5.56
H1211	Untreated	0.1N K_2SO_4	0.0130	0.0116	5.28
C1242	Untreated	0.1N K_2SO_4	0.0150	0.0110	4.72
C1212	Untreated	0.1N K_2SO_4	0.0122	0.0108	-
H1206	Untreated	0.1N K_2SO_4 + Tween 20*	0.0146	0.0106	4.97
H1169	Dow #7	0.1N K_2SO_4	0.0110	0.0110	-
C1192	Dow #7	0.1N K_2SO_4	0.0130	0.0144	5.85
H1167	Dow #7	0.1N K_2SO_4	0.0118	0.0110	4.79
C0920	Dow #7	0.1N K_2SO_4	0.0122	0.0110	4.79
H1220	Dow #7	0.1N K_2SO_4	0.0130	0.0118	-
H1171	Dow #7	0.1N K_2SO_4 + Tween 20*	0.0122	0.0106	-
C1258	Dow #12	0.1N K_2SO_4	0.0120	0.0120	4.71
H1253	Dow #12	0.1N K_2SO_4	0.0094	0.0098	3.90
H1210	Untreated	0.1N KCl	0.0168	0.0110	-
H1176	Dow #7	0.1N KCl	0.0144	0.0112	-
H1222	Untreated	0.1N KCl + Tween 20*	0.0170	0.0107	5.34
H1164	Dow #7	0.1N KCl + Tween 20*	0.0163	0.0112	5.20

NOTES: Cast alloy specimen one inch from nickel electrode; stirring between electrodes.

* Five drops of Tween 20 added to 135 milliliters of electrolyte.

TABLE NO. 21

SHORT CIRCUIT CURRENTS

FS-1 AND "H" ALLOYS IN 0.1N K_2SO_4

Specimen No.	Treatment	Maximum Current Values (amp.)		
		Initial (C_o), no stirring	With H_2O_2 added*	With stirring and H_2O_2*
FS-1 1102	Untreated	0.0150	0.0170	0.0190
FS-1 1444	Heavy Dow #7	0.0096	0.0164	0.0190
FS-1 1386	Light Dow #7	0.0100	0.0174	0.0190
FS-1 0887	Dow #12	0.0070	0.0120	0.0152
"H" alloy	Untreated	-	0.0305	0.0380
"H" alloy	Dow #7	-	0.0300	0.0380

* Five drops of 30% hydrogen peroxide added to the 135 milliliters of electrolyte.

TABLE NO. 22

SHORT CIRCUIT CURRENTS

FS-1 ALLOY

Specimen No.	Treatment	Maximum Current Values * (amp.)		
		In 0.1N K_2SO_4	In 0.1N KCl	In 1.0N KCl
1109	Untreated	0.0126	-	0.0770
1430	Heavy Dow #7	0.0088	-	0.0730
1391	Light Dow #7	0.0102	-	0.0690
0890	Dow #12	0.0063	-	0.0530
1718	Untreated	0.0150	0.0123	0.0750
0916	Iridite #15	0.0102	0.0135	0.0723
1706	Heavy Dow #7	0.0082	0.0124	0.0660
1701	Light Dow #7	0.0100	0.0135	0.0610
1516	Dow #12	0.0052	0.0100	0.0610

* Moderate stirring. Maximum values recorded with photoelectric potentiometer.

4. Short Circuit Currents in 1.0N KCl (With New Type Cells)

The short circuit currents of a group of untreated and treated FS-1 specimens were determined with 1.0N KCl as the electrolyte and a nickel reference electrode. After the initial maximum current (C_o) had been recorded, the specimens were washed with distilled water and dried at 37°C. These specimens were primed in the conventional (two-spray) manner followed by a three day air-drying period. Initial short circuit currents and also the current after 30 minutes were recorded for the primed specimens.

The specimens were washed and dried again, and shear adhesion values determined from specimen pairs using Plastilock #601 (B. F. Goodrich Co.) as the adhesive (see page 94 for shear adhesion test). The data from these tests are presented in Table No. 23.

The unprimed specimens rated in the following order of increasing current: heavy Dow #12, heavy Dow #17, specification Dow #12, light Dow #12, heavy Dow #7, light Dow #7, and untreated FS-1. The electrical insulat value of the anodic types of treatments is apparent in the above series.

After a 30 minute short the primed specimens had the following order of increasing current: heavy Dow #17, heavy Dow #12, specification Dow #12, heavy Dow #7, light Dow #7, light Dow #12, and untreated FS-1.

The shear adhesion of the zinc chromate primer was rated in the following decreasing order: untreated FS-1, light Dow #7, light Dow #12, heavy Dow #7, heavy Dow #17, specification Dow #12, and heavy Dow #12.

Two opposing characteristics were apparent. The treatment having the highest adhesion value had the highest corrosion rate in the short cirucit current test. The best overall performance was obtained from the Dow #7 and heavy Dow #17 treatments.

The short circuit currents of unprimed treated specimens cannot be directly correlated with corrosion rates, since the electrical resistivity of the Dow #12 greatly exceeds that of the Dow #7. This test, however, could be utilized to measure the thickness of the treatment.

For primed specimens it was a convenient test for showing paint failure in a two hour test period.

TABLE NO. 23

SHORT CIRCUIT CURRENTS - SHEAR ADHESION

FS - 1 ALLOY

Specimen No. and Treatment	Initial Current*(amp.) Unprimed	Initial Current*(amp.) Primed	Current after 30 Minutes (amp.)	Primer Thickness (mil)	Shear Adhesion (psi)	Average Adhesion (psi)
Heavy Dow #12						
1572	0.046	0	0.0045	0.75)	94)	90
1570	0.047	0.003	0.009	0.85)		
1569	0.042	0	0.006	0.85)	85)	
1568	0.041	0	0	0.65)		
Spec. Dow #12						
1540	0.060	0	0.022	0.65)	184)	231
1607	0.061	0	0.001	0.80)		
1560	0.063	0	0.004	0.80)	279)	
1612	0.061	0	0.012	0.80)		
Light Dow #12						
1482	0.066-0.063	0	0.022	0.75)	563)	581
1473	0.067-0.063	0	0.024	0.60)		
1470	0.070-0.066	0.007	0.022	0.60)	600)	
1475	0.065-0.062	0.005	0.025	0.65)		
Heavy Dow #17						
1583	0.059	0	0	-)	281)	281
1587	0.058	0	0	-)		
Heavy Dow #7						
1747	0.072-0.064	0.0015	0.0015	0.80)	470)	574
1744	0.072-0.064	0.005	0.005	0.70)		
1742	0.074-0.066	0.006	0.019	0.70)	678)	
1745	0.070-0.064	0.013	0.022	0.65)		
Light Dow #7						
1714	0.074-0.066	0.011	0.0225	0.65)	588)	645
1705	0.074-0.066	0.007	0.018	0.80)		
1395	0.075-0.065	0	0.002	0.80)	702)	
1394	0.078-0.068	0.009	0.025	0.75)		
Untreated						
1752	0.076-0.070	0.015	0.030	0.65)	773)	813
1754	0.074-0.060	0.009	0.025	0.80)		
1794	0.076-0.069	0.010	0.025	0.80)	853)	
1793	0.078-0.067	0.008	0.029	0.75)		

* Currents recorded initially and at two minutes; moderate stirring.

D. Hydrogen Evolution Rates - Gasometric Methods

Hydrogen is the principal gaseous product formed when magnesium alloys corrode in salt solutions. Measurement of the rate of hydrogen evolution, as indicated by enclosed volume changes, will disclose the initiation and rate of corrosion. Several prototype gasometric cells were developed for this purpose.

1. Initial Gasometric Equipment

The first gasometric apparatus we developed consisted of a glass corrosion vessel attached by a side arm to a three-way stopcock, then to a 10 milliliter microburette (Figure 15). A leveling bulb (containing same electrolyte solution) was attached to the lower end of the burette.

The specimens were immersed in the electrolyte, and the cell was sealed with a stopper. The liquid in the measuring burette was adjusted to zero, then lowered slightly as the reaction proceeded. Successive readings were made by leveling the burette and leveling bulb liquid levels. The complete assembly was maintained at 25° ± 0.5°C in a constant temperature room, and barometric pressure was recorded with each volume reading.

A principal advantage of this system was that hydrogen bubbles which adhered to the surface did not have to be detached by stirring. As the bubbles formed the enclosed volume increased accordingly.

Trial runs were made with FS-1 specimens immersed in 3% NaCl solution (Figure 16). Clean FS-1 alloy, Dow #7 treated, and Dow #7 primed specimens were compared. Untreated alloy corroded approximately 10 times faster than Dow #7 treated specimens and Dow #7 treated specimens 10 times faster than primed specimens.

2. Hydrogen Evolution Rates-Closed, Unstirred Cell

The first gasometer was extremely sensitive to small room temperature fluctuations. The large volume of enclosed air (approximately 100 milliliters) responded to such temperature changes sufficiently to introduce a marked source of error in the measurements. Consequently, the apparatus was redesigned to eliminate these effects.

In the improved gasometer, a ground glass stopper with a three-way capillary outlet attached to the top replaced the original stopper (Figure 17). This allowed the vessel to be filled with the corrosive medium up to the capillary outlet. The three-way stopcock was attached directly to the top of the measuring microburette.

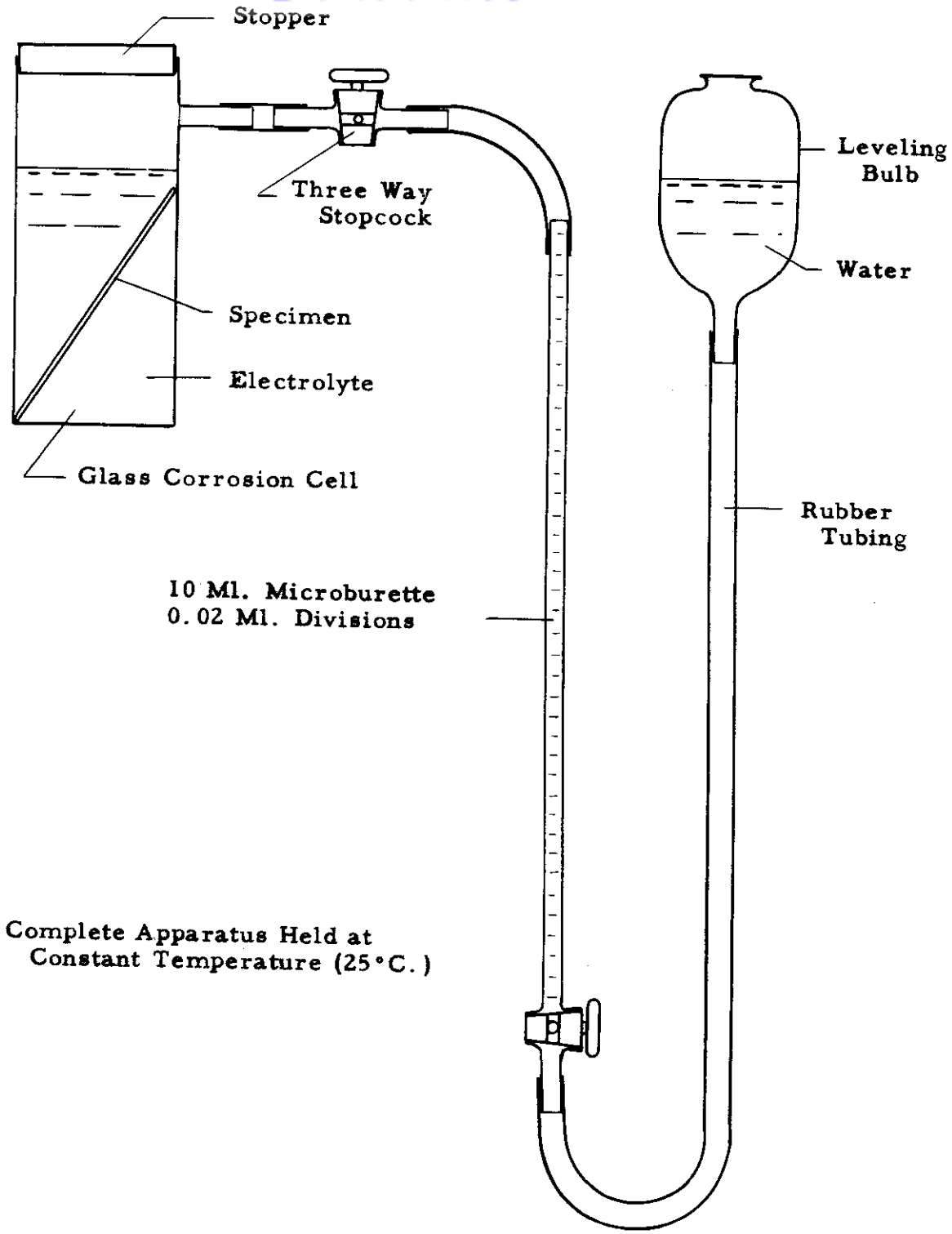


Figure 15. Gasometer for Magnesium Alloy Corrosion Rate Studies.

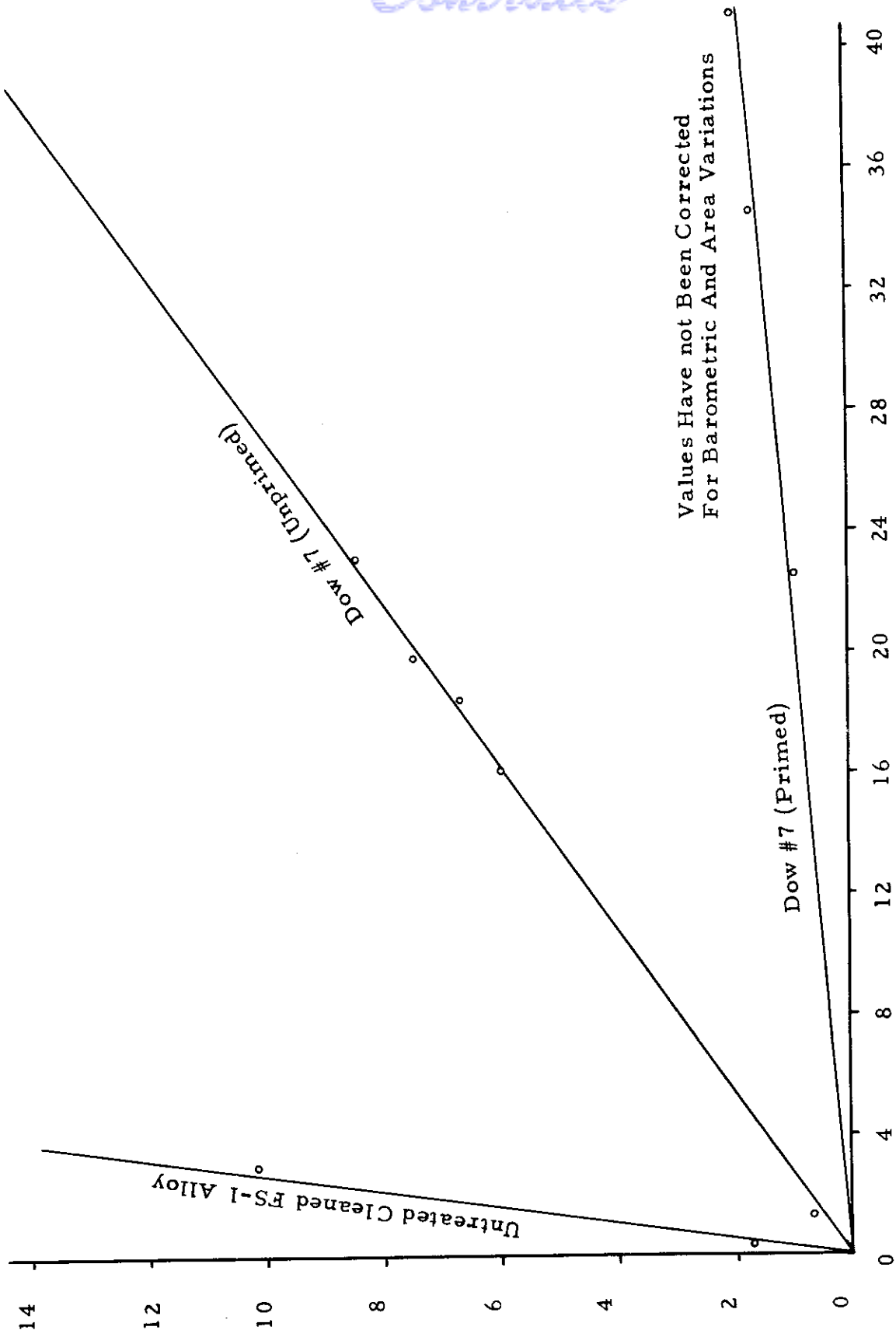


Figure 16. Relative Gas Evolution Rates of FS-1 Specimens in 3% NaCl.

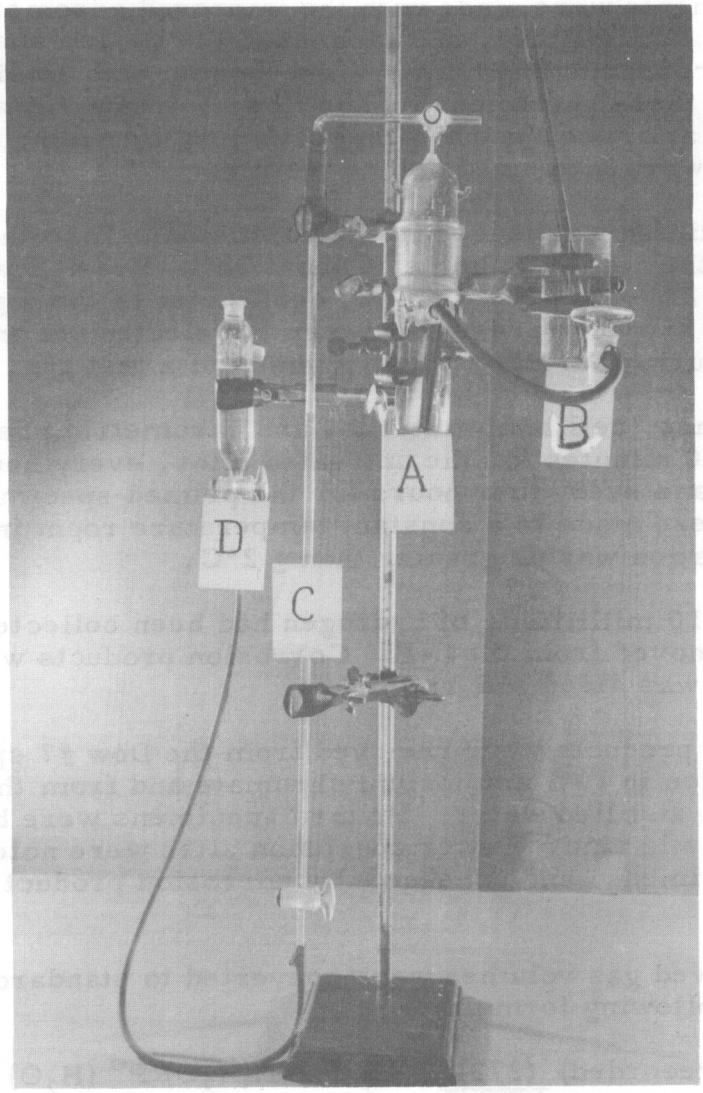


Figure 17. Gasometric Apparatus. "A" is the corrosion cell which has a 275 milliliter capacity. A Dow #7 FS-1 specimen is in the cell. "B" is a Beckman thermometer for temperature measurement in the attached vessel. This container also serves to fill and empty the corrosion cell. "C" is a 10 milliliter microburette calibrated in 0.02 milliliter divisions and "D" a leveling bulb containing distilled water.

Measurements were made with the improved gasometer (Figure 17) on untreated, treated, primed, and lacquered FS-1 alloy specimens with 1.0N KCl as the corroding medium. Vinyl lacquer was applied around the 9/64 inch hole of these specimens. (The Dow #7 treatment was missing at the immediate area around the hole.) The length, width, and weight of these specimens were measured before testing.

Each specimen was placed in the corrosion cell so that it rested on the bottom of the cell at an angle of about 76°. The cell was filled with 1.0N KCl at 23° - 25° C within one centimeter of the top, so that two milliliters of air were present between the electrolyte and the liquid level in the measuring burette at the beginning of a test run.

Gas volumes, cell temperatures, and barometric pressures were recorded every 30 minutes for the untreated alloy, every hour for the Dow #7 and #12, and every four hours for the primed specimens. All determinations were made in a constant temperature room in which the temperature variation was no greater than ± 2°C.

After 8 - 10 milliliters of hydrogen had been collected, each specimen was removed from the cell. Corrosion products were removed and the specimen was dried and reweighed.

Corrosion products were removed from the Dow #7 specimens by 12 hours immersion in 10% ammonium chromate and from the Dow #12 by gentle brushing in distilled water. Primed specimens were brushed briefly in 0.1N acetic acid. Fewer corrosion sites were noted than on short circuit specimens, and consequently corrosion product removal was easier.

The observed gas volumes were converted to standard dry conditions by means of the following formula:

$$V = (\text{vol. recorded}) \frac{(273)}{(273+t)} \left(\frac{P - N(H_2O)\, P^{o}(H_2O)}{760} \right)$$

Where: t = temperature °C

P = barometric pressure (in millimeters)

$$N(H_2O) = \frac{n(H_2O)}{n(H_2O) + n(KCl)} = 0.982 \text{ for 1.0N KCl}$$

$P^{o}(H_2O)$ = vapor pressure of water (in millimeters) at observed temperature

$n(H_2O)$ = moles of H_2O $n(KCl)$ = moles of KCl.

Weight losses were calculated as gm./hr./10 sq. in. and are reported in Table No. 24. Average gas evolution rates for each specimen were calculated on the basis of the last observed reading as ml. H_2/min./10 sq. in. Final evolution rates were also calculated between the times indicated. The following formulas were used in these calculations:

$$\text{Average rate} = \frac{V_n}{t_n}$$

$$\text{Final rate} = \frac{V_n - (V_{n-1})}{t_n - (t_{n-1})}$$

Where: V = volume.

t = time of immersion.

n = final reading.

n-1 = next to final reading.

From the data in Table No. 24, average weight loss and hydrogen evolution rates were calculated for each treatment and are reported in Table No. 25. Hydrogen evolution rates are shown graphically in Figure 18 for unprimed specimens and in Figure 19 for primed specimens.

The evolution rates varied with time of immersion. The rate for Dow #12 specimens increased slowly over a longer period than the rate for Dow #7 specimens. The Dow #7 rate was higher initially, but after 7 to 8 hours it was lower than the Dow #12 rate. The rate for the Iridite #15 specimens was the highest initially, but it decreased rapidly with time until at 7 hours it was comparable to the rate for the Dow #7 specimens. (Data beyond 3 hours for Iridite #15 specimens are not plotted in Figure 18, but the decrease in rate with time is indicated by the dotted arrows at the end of the curves for these specimens.)

Considerable variation in gasometric rates was apparent with the primed specimens, which undoubtedly indicates the variability from specimen to specimen, due mainly to variation in surface coverage by the primer. However, the Dow #7P combination was generally more corrosion resistant.

Additional Dow #7 and #12 primed specimens were carefully prepared so that all specimens had a primer film thickness of 0.7 mil. These specimens were examined microscopically for primer flaws before testing and for loss of primer after testing.

TABLE NO. 24

GASOMETRIC RATES FOR FS-1 ALLOY IN 1.0N KCl

CLOSED CELL - NO STIRRING

Specimen No.	Treatment	Average Hydrogen Evolution Rate (ml./min./10 in.^{2})	Final Evolution Rate at Time Indicated (ml./min./10 in.^{2})	Wt. Loss Rate (gm./hr./10 in.^{2})
0360	Dow #12	1.17×10^{-2}	7.05×10^{-3} at 9-10 hours	1.86×10^{-3}
0354	Dow #12	1.17×10^{-2}	1.03×10^{-2} at 8 - 9 hours	2.67×10^{-3}
0829	Dow #12	1.59×10^{-2}	1.36×10^{-2} at 6 - 8 hours	1.65×10^{-3}
0784	Dow #7	1.31×10^{-2}	5.32×10^{-3} at 7 - 8 hours	6.15×10^{-4}
0786	Dow #7	2.05×10^{-2}	2.73×10^{-2} at 5 - 6 hours	7.14×10^{-4}
0785	Dow #7	1.33×10^{-2}	6.97×10^{-3} at 5 - 7 hours	1.12×10^{-3}
0741	Untreated	1.10×10^{-1}	8.23×10^{-2} at 0 - 1.5 hours	7.10×10^{-3}
0760	Untreated	1.13×10^{-1}	10.00×10^{-2} at 0.5 - 1.5 hours	6.95×10^{-3}
0748	Untreated	1.02×10^{-1}	9.90×10^{-2} at 1 - 1.5 hours	5.60×10^{-3}
0911	Iridite #15	5.35×10^{-2}	4.36×10^{-2} at 1 - 3 hours	2.48×10^{-3}
0901	Iridite #15	3.64×10^{-2}	2.17×10^{-2} at 2 - 4 hours	2.37×10^{-3}
0893	Dow #12P *	1.74×10^{-3}	2.39×10^{-3} at 53 - 79 hours	3.55×10^{-4}
0319	Dow #12P	2.79×10^{-3}	3.43×10^{-3} at 23 - 48 hours	3.68×10^{-4}
0364	Dow #12P	1.87×10^{-3}	9.66×10^{-4} at 48 - 68 hours	2.80×10^{-4}
0932	Dow #7P	5.53×10^{-4}	5.28×10^{-4} at 142 - 165 hours	9.50×10^{-5}
0437	Dow #7P	1.07×10^{-3}	1.23×10^{-3} at 91 - 94 hours	1.14×10^{-4}
0483	Dow #7P	1.00×10^{-3}	9.66×10^{-4} at 48 - 68 hours	1.17×10^{-4}
0450	Dow #7L **	No corrosion in 14 days.		

* P = Primed. ** L = Lacquered.

TABLE NO. 25

AVERAGE GASOMETRIC RATES FOR

FS-1 ALLOY IN 1.0N KCl

(Calculated from data in Table No. 24)

Treatment	Average Hydrogen Evolution Rate ($ml./min./10\ in.^2$)	Average Weight Loss Rate ($gm./hr./10\ in.^2$)	Immersion Time
Untreated	1.10×10^{-1}	6.55×10^{-3}	55 min.
Iridite #15	2.07×10^{-2}	2.43×10^{-3}	4 hr.
Dow #7	1.69×10^{-2}	8.16×10^{-4}	5 hr.
Dow #12	1.51×10^{-2}	2.06×10^{-3}	5 hr.
Dow #7P	8.73×10^{-4}	1.09×10^{-4}	165 hr.
Dow #12P	2.13×10^{-3}	3.34×10^{-4}	79 hr.
* P= Primed.			

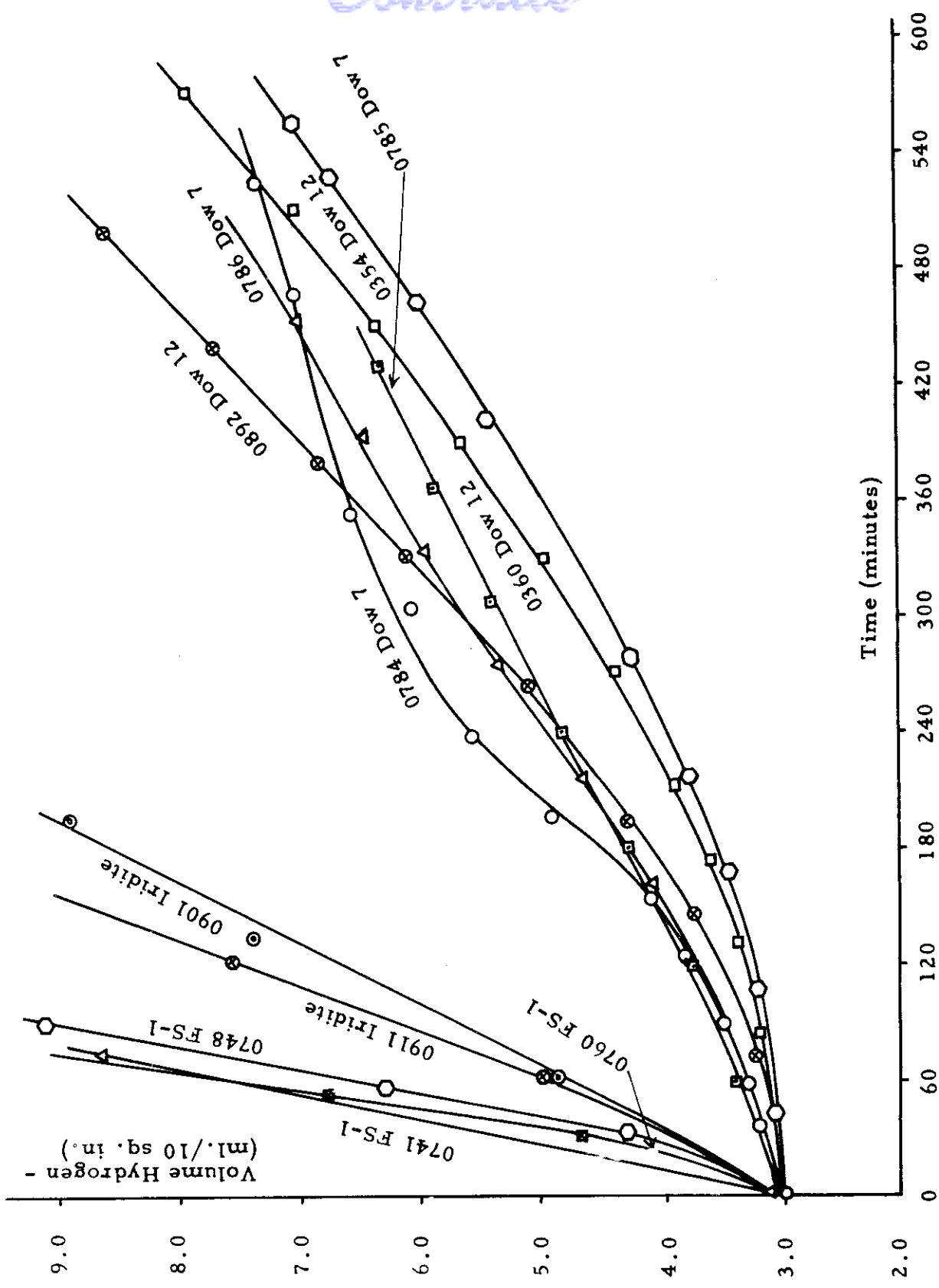


Figure 18. Rate of Hydrogen Evolution for Unprimed FS-1 Alloy in 1.0N KCl. (Closed Cell - No Stirring.)

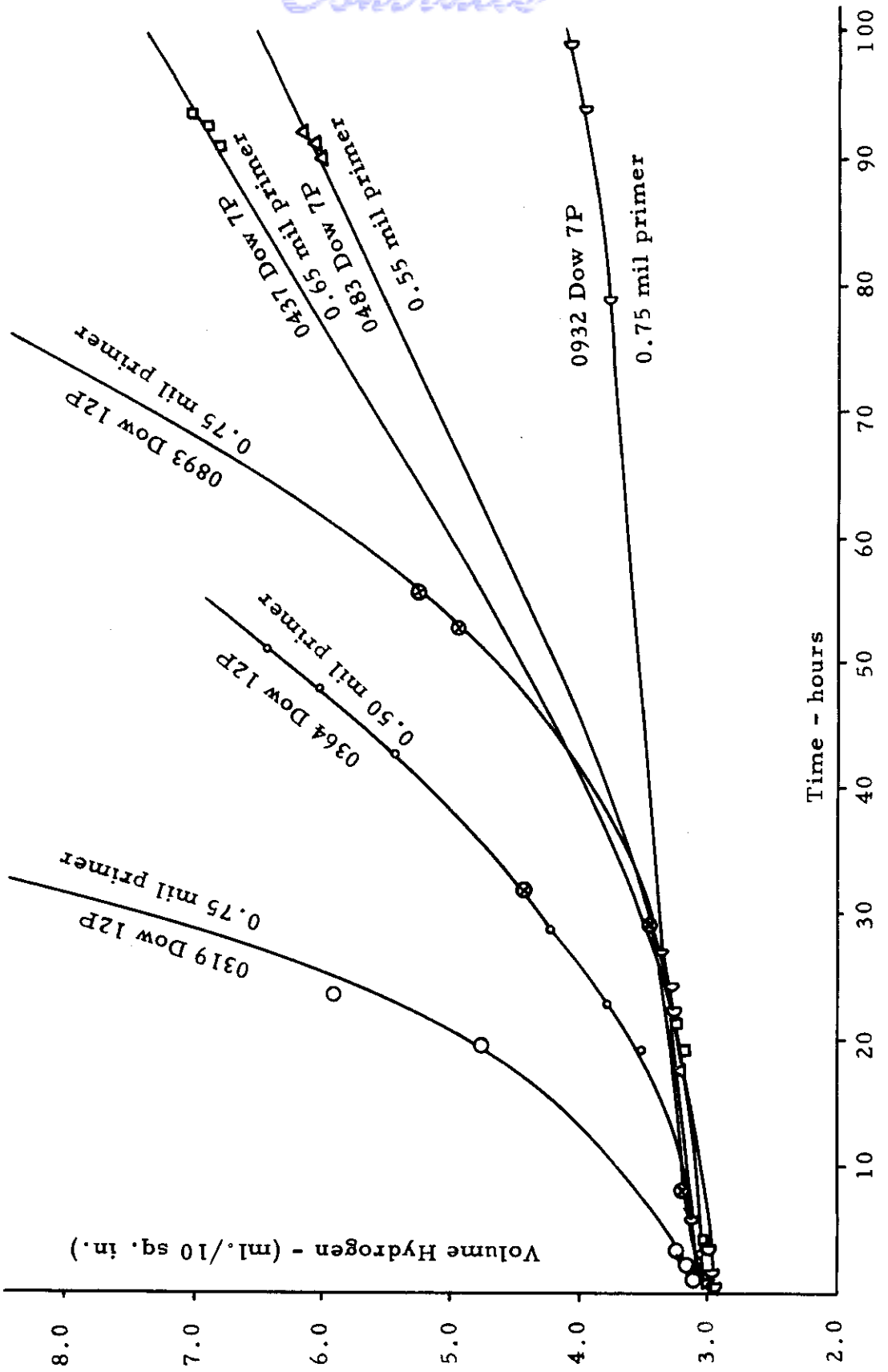


Figure 19. Rate of Hydrogen Evolution for Primed FS-1 Alloy in 1.0N KCl. (Closed Cell - No Stirring.)

For testing these specimens, the corrosion cell was immersed in a constant temperature bath held at 25° ± 0.1°C. (Some of the irregularity noted in the previous tests was attributed to the expansion of the electrolyte during the day as the temperature increased 2°C in the controlled temperature room.)

The following hydrogen evolution rates for the four samples tested were determined from the curves in Figure 20.

Sample No.	Average Rate ($ml./min./10\ in.^2$)	Final Rate ($ml./min./10\ in.^2$)	Weight Loss Rate ($gm./hr./10\ in.^2$)
1154 Dow #7P	3.37×10^{-4}	1.54×10^{-4}	3.15×10^{-5}
1143 Dow #7P	3.97×10^{-4}	3.34×10^{-4}	5.46×10^{-5}
0805 Dow #12P	2.37×10^{-3}	3.37×10^{-3}	3.25×10^{-4}
0851 Dow #12P*	3.29×10^{-4}	2.10×10^{-4}	7.07×10^{-5}
* Additional data for this specimen are given in Appendix B.			

The rates for Dow #7 specimens agreed fairly well, but the rates for the Dow #12 specimens varied markedly. One Dow #12 specimen, No. 0851 Dow #12P, had a lower rate than the Dow #7P specimens. (This specimen had a greater weight loss, however, than No. 1154 Dow #7P with a comparable evolution rate.) The difference between the Dow#12P specimens was probably due to variation in the primer on the individual specimens. Under the microscope Dow #12P specimens showed a loss of primer over greater areas than the Dow #7P specimens indicating deterioration of primer adhesion for the Dow #12 treatment.

3. Hydrogen Evolution Rates - Magnetic Stirrer Type Cell

The gasometric set-up for hydrogen evolution rate determinations was further improved. Figure 21 shows the corrosion cell with attached measuring burette and a suspended FS-1 specimen in the cell. Figure 22 shows the complete unit immersed in a constant temperature bath. A magnetic stirrer was employed to agitate the electrolyte (350 milliliters of 1.0N KCl) in the cell.

Readings were taken by leveling the liquid level in the cell with that in the measuring burette. These readings indicated the positive liquid displacement due to formation of hydrogen bubbles in the corrosion cell. Complete removal of hydrogen bubbles from the specimen or from the cell sides was difficult with the mild stirring afforded by the magnetic stirrer. However, the relative error due to the hydrostatic volume effect on the bubbles was considered comparatively small.

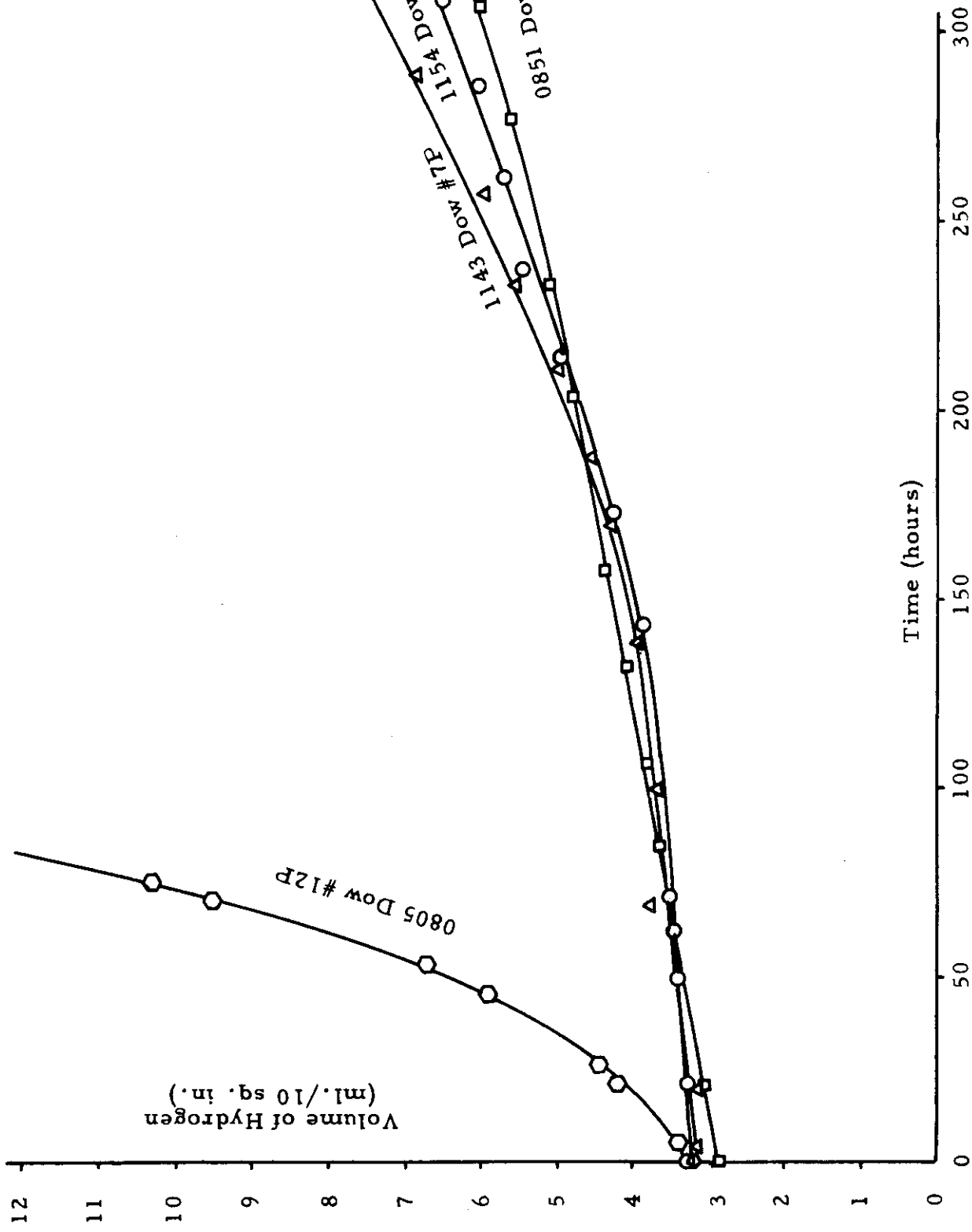


Figure 20. Rate of Hydrogen Evolution of Primed FS-1 Alloy in 1.0N KCl. (Closed Cell - No Stirring.)

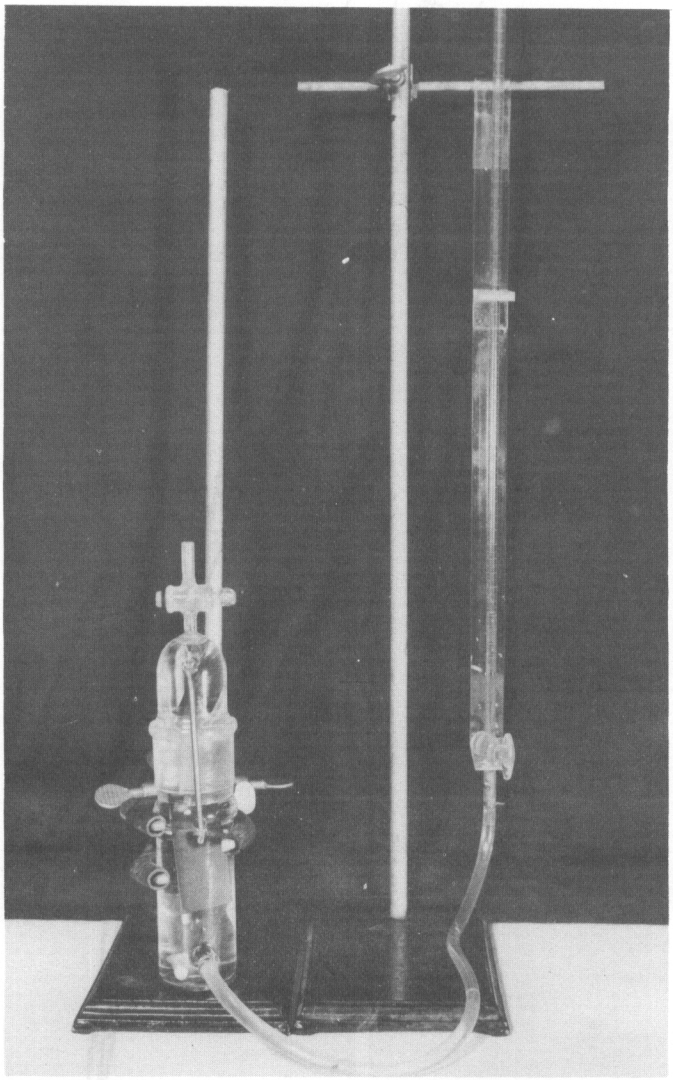


Figure 21. Gasometric Apparatus. The corrosion cell with attached measuring burette is shown. An FS-1 specimen is suspended in the cell above the magnetic stirrer.

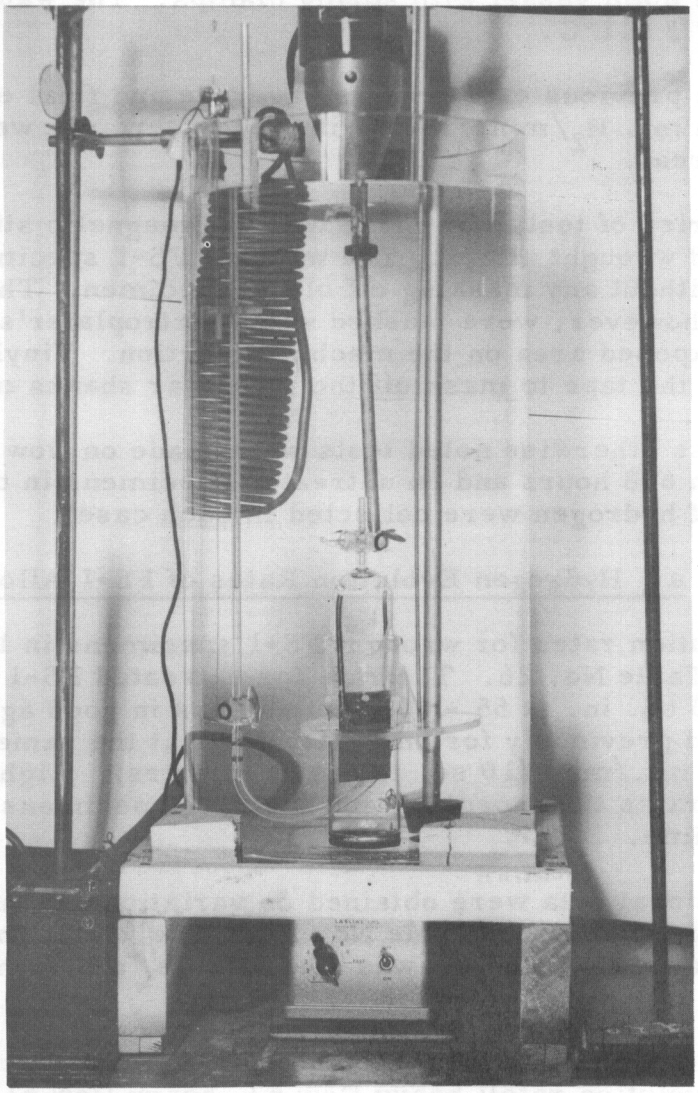


Figure 22. Gasometric Apparatus. The gasometer is shown in operation in a constant temperature bath which permits complete immersion of the cell and burette.

The specimen was suspended from a nylon filament attached to a supporting member in the top of the cell. The ground glass joint (50/50) in the top of the cell was greased with silicone vacuum grease and clamped firmly to the main vessel with spring clamps. The water bath was maintained at 25° ± 0.1°C.

As in previous experiments, average and final evolution rates were calculated in ml. H_2/min./10 sq. in. (edge surfaces were included in the calculated area).

A series of tests was made with the magnetic stirrer type cell on both cast and wrought alloys. The wrought FS-1 specimens were completely immersed without any masking off of the specimen. The tensile bar cast specimens, however, were masked with electroplater's tape to allow only a one inch exposed area on the machined portion. Vinyl lacquer was also utilized with the tape to mask off the irregular shanks of the cast alloy specimens.

Unless otherwise noted tests were made on Dow #7 and #12 treated specimens in 6-8 hours and on untreated specimens in two hours (5 to 10 milliliters of hydrogen were collected in each case).

a. Hydrogen Evolution Rates of FS-1 Alloy

Evolution rates for wrought FS-1 specimens in 1.0N KCl are reported in Table No. 26. The rate for untreated FS-1 alloy (11.4×10^{-2} ml./min./10 sq. in. at 55 - 60 minutes) was in good agreement with the rate reported previously for untreated FS-1 at the same immersion time (1.10×10^{-1} ml./min./10 sq. in. at 55 minutes). Light Dow #7 specimens gave higher rates than specification Dow #12 specimens at 5-6 hours immersion time.

Additional data were obtained on variations of the Dow #7 and #12 treatments on FS-1 alloy (Table No. 27). The variation in evolution rate with thickness treatment was measurable, although actual differences were small.

The following rating was obtained for these specimens (in order of increasing evolution rate): heavy Dow #7, heavy Dow #12, heavy Dow #17, light Dow #12, specification Dow #12, and light Dow #7. Actually, all treatments were very close in evolution rate, and this rating is applicable only for this particular series of specimens.

The short circuit currents (C_E) recorded at the end of the test were inversely proportional to the treatment thickness for each type of treatment, but they did not correlate well with the gasometric corrosion rates. The current values had the following increasing order: heavy Dow #12, specification Dow #12, heavy Dow #17, light Dow #12, heavy Dow #7, and light Dow #7. The lower currents for the Dow #12 are due to its greater electrical resistance.

Hydrogen evolution rates are shown graphically in Figure 23 for unprimed FS-1 specimens.

TABLE NO. 26

GASOMETRIC RATES FOR FS-1 ALLOY IN 1.0N KCl

MAGNETIC STIRRER TYPE CELL

Specimen No.	Treatment	Average Rate ($ml./min./10\ in.^2$)	Immersion Time	Final Rate at Time Indicated ($ml./min./10\ in.^2$)
1426	Spec. Dow #7	6.88×10^{-3}	8 hr.	5.5×10^{-3} at 7 - 8 hr.
1673	Spec. Dow #7	1.01×10^{-2}	9 hr.	1.35×10^{-2} at 8 - 9 hr.
1387 *	Light Dow #7	1.89×10^{-2}	7 hr.	2.04×10^{-2} at 6 - 7 hr.
1387	Light Dow #7	1.75×10^{-2}	5 hr.	-
1443	Light Dow #7	1.69×10^{-2}	6 hr.	1.46×10^{-2}
1443	Light Dow #7	1.73×10^{-2}	5 hr.	-
0889 *	Spec. Dow #12	1.39×10^{-2}	8 hr.	1.67×10^{-2} at 7 - 8 hr.
0889	Spec. Dow #12	1.22×10^{-2}	4 hr.	-
0892	Spec. Dow #12	1.10×10^{-2}	6 hr.	1.37×10^{-2} at 4 - 6 hr.
1099	Untreated	14.57×10^{-2}	45 min.	-
1110 *	Untreated	12.35×10^{-2}	45 min.	-
1110	Untreated	11.44×10^{-2}	60 min.	-

* Additional data for these specimens are given in Appendix B.

TABLE NO. 27

GASOMETRIC RATES FOR FS-1 ALLOY IN 1.0N KCl

MAGNETIC STIRRER TYPE CELL

Specimen No. and Treatment	Average Hydrogen Evolution Rate (ml./min./10 in.^{2})	Final Hydrogen Evolution Rate (ml./min./10 in.^{2})	E_o-Open Circuit Potential (volts)	C_o-Initial Short Circuit Current (amp.)	C_E-Current after Experiment (amp.)	Test Time (min.)
1501 Heavy Dow #17	1.52×10^{-2}	1.42×10^{-2}	1.53	0.053	0.068	225
1574 Heavy Dow #12	8.55×10^{-3}	1.35×10^{-2}	1.55	0.050	0.057	285
1463 Spec. Dow #12	1.65×10^{-2}	2.10×10^{-2}	1.55-1.56	0.059	0.063	240
1485 Light Dow #12	1.73×10^{-2}	1.64×10^{-2}	1.56	0.060	0.069	210
1713 Light Dow #7	2.43×10^{-2}	4.55×10^{-2}	1.58	0.067	0.073	240
1709 Heavy Dow #7	1.05×10^{-2}	1.15×10^{-2}	1.60	0.073	0.071	240

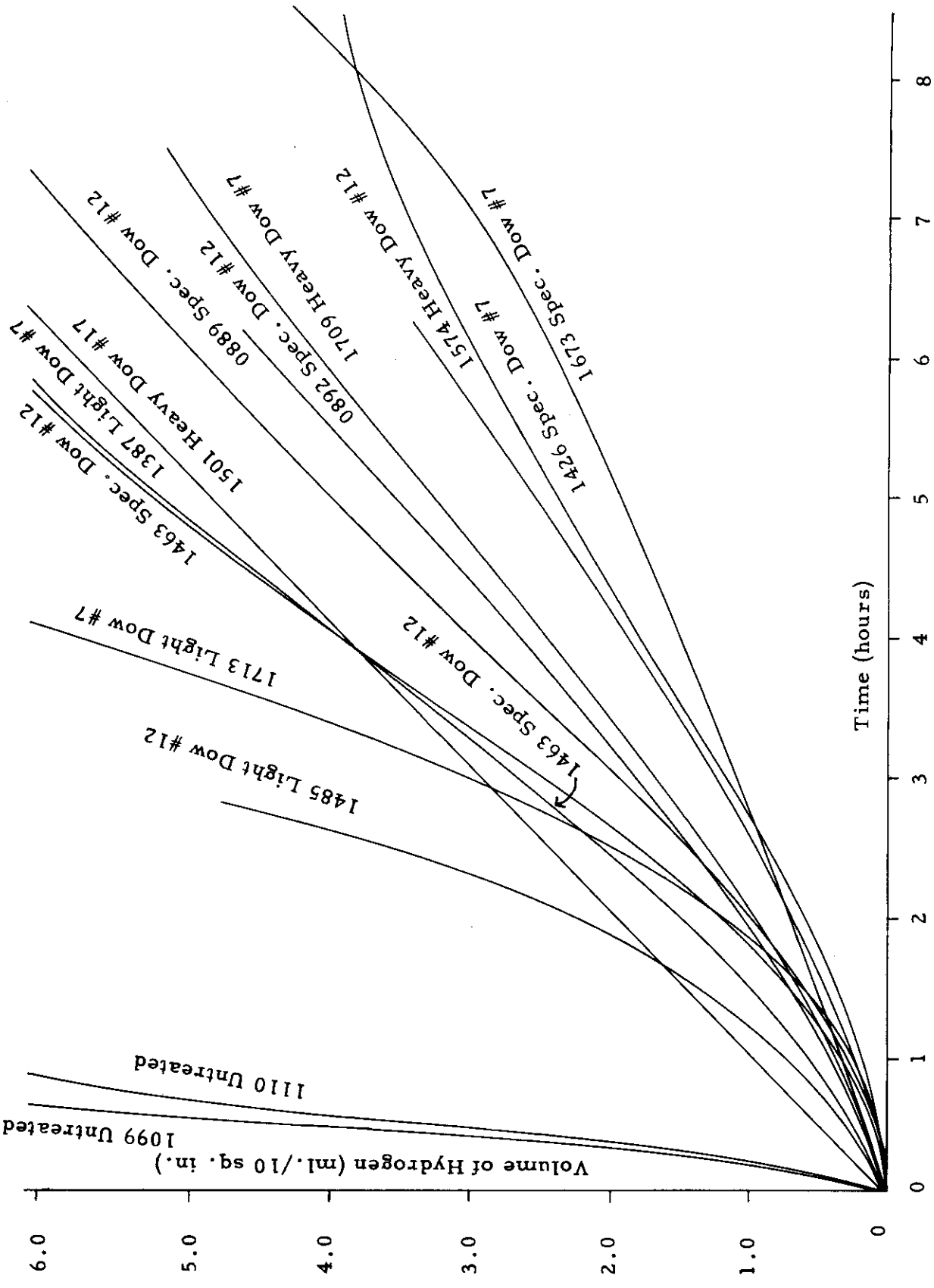


Figure 23. Rate of Hydrogen Evolution for Unprimed FS-1 Alloy in 1.0N KCl. (Magnetic Stirrer Type Cell.)

b. Hydrogen Evolution Rates of Cast Alloys

On cast alloys the Dow #12 was always inferior to the Dow #7 (Table No. 28). The Dow #12 "H" alloy appeared to be the least corrosion resistant, since it gave high evolution rates at an earlier immersion time than the Dow #12 "C" alloy. Some variation in the thickness of the Dow #12 treatment was noted from specimen to specimen with the "C" and "H" alloys. The untreated and Dow #7 treated "C" alloy specimens had higher corrosion rates in 1.0N KCl than the corresponding "H" alloy specimens.

For comparison, the short circuit currents of the cast alloy specimens at the conclusion of the test are included in Table No. 28. No direct correlation can be made between these currents and the evolution rates for the treatments (e.g., the Dow #12 "H" alloy specimens had the highest evolution rates but had low short circuit currents).

Additional gasometric data on cast "C" and "H" alloy specimens are given in Table No. 29. As in the previous tests, the Dow #7 treatment was considerably more corrosion resistant on both alloys than the Dow #12, and the Dow #12 "H" alloy was the most susceptible to corrosion. Additional data are necessary to verify the lower rate for the Dow #7 "C" alloy than for the Dow #7 "H" alloy. Previous gasometric tests and other corrosion resistance tests, i.e., pH increase and short circuit currents, have indicated that the Dow #7 "H" alloy is more resistant to corrosion.

Gasometric rates on untreated "C" and "H" alloys cleaned with the acetic-nitrate "pickle" are given in Table No. 30. The "H" alloy had the lower corrosion rate during the test period, which correlates with pH increase data, the weight losses during salt spray exposure (shown later in Table No. 45), and the short circuit currents. The corrosion rate of the "H" alloy specimen (H1161) increased from 1.66×10^{-2} at 3 hours to 18.5×10^{-2} at 68 hours.

Hydrogen evolution rates are shown graphically in Figure 24 for unprimed "C" and "H" alloy specimens.

4. Hydrogen Evolution Rates - Fermentation Shaker Cell Apparatus

The fermentation shaker cell apparatus shown in Figures 25 and 26 was constructed for additional testing and for comparison with the other types of gasometric apparatus. This apparatus was constructed so that two determinations could be made simultaneously. Two corrosion cells attached to a reciprocating shaft were connected to microburettes and leveling bulbs. The cells were agitated in a bath regulated at $25° \pm 0.1°C$.

The fermentation shaker cell apparatus is best suited for operation in a constant temperature room. Otherwise, because the measuring burettes are above the constant temperature bath, the measured gas volume will require correction for variations in room temperature.

TABLE NO. 28

GASOMETRIC RATES FOR CAST ALLOYS IN 1.0N KCl

MAGNETIC STIRRER TYPE CELL

Specimen No.	Treatment	Average Rate for Total Immersion Time (ml./min./10 in.^{2})	Total Immersion Time (hr.)	Average Rate for Time Indicated (ml./min./10 in.^{2})	Final Rate at Time Indicated (ml./min./10in.^{2})	Short Circuit Current (amp.)
H1165	Untreated	10.45×10^{-2}	2	-	8.20×10^{-2} at 1 - 2 hr.	0.084
C1227	Untreated	13.28×10^{-2}	3	-	12.82×10^{-2} at 2.5 - 3.0 hr.	0.082
H1209*	Dow #7	1.36×10^{-2}	23	9.9×10^{-3} at 5 hr.	1.76×10^{-2} at 14 - 23 hr.	0.083
C0975	Dow #7	2.35×10^{-2}	12	2.88×10^{-2} at 5 hr.	1.93×10^{-2} at 7 - 12 hr.	0.085
H1178	Dow #7	1.57×10^{-2}	10	1.62×10^{-2} at 7 hr.	1.43×10^{-2} at 8 - 10 hr.	0.081
C0969	Dow #7	1.78×10^{-2}	10	1.44×10^{-2} at 7 hr.	2.53×10^{-2} at 7 - 10 hr.	0.077
H1251	Dow #12	5.38×10^{-2}	6	6.97×10^{-2} at 5.5 hr.	9.33×10^{-2} at 5.5 - 6 hr.	0.065
H1254	Dow #12	6.07×10^{-2}	4	-	6.75×10^{-2} at 3 - 4 hr.	0.064
C1264	Dow #12	2.57×10^{-2}	7	2.61×10^{-2} at 5 hr.	2.46×10^{-2}	0.076
C1201	Dow #12	6.54×10^{-2}	7	-	8.00×10^{-2} at 6 - 7 hr.	0.075

* Additional data for this specimen are given in Appendix B

TABLE NO. 29

GASOMETRIC RATES FOR CAST ALLOYS IN 1.0N KCl

MAGNETIC STIRRER TYPE CELL

Specimen No. and Treatment	Average Hydrogen Evolution Rate (ml./min./10 in.^{2})	Final Hydrogen Evolution Rate (ml./min./10 in.^{2})	E_o - Open Circuit Potential (volts)	C_o-Initial Short Circuit Current (amp.)	C_E-Current after Experiment (amp.)	Test Time (min.)
H1804 Light Dow #7	1.49×10^{-2}	1.58×10^{-2}	1.58	0.069	0.073-0.075	480 min.
C1872 Light Dow #7	1.43×10^{-2}	1.47×10^{-2}	1.57	0.081	0.080-0.084	480 min.
H1249 Spec. Dow #12	5.13×10^{-2}	6.40×10^{-2}	1.50	0.056-0.058	-	480 min.
C1257 Spec. Dow #12	3.39×10^{-2}	4.06×10^{-2}	1.55	0.064-0.067	0.068-0.070	300 min.
C1308 Spec. Dow #12P*	2.01×10^{-3}	4.50×10^{-3}	0	0	-	133 hr.
H1298 Spec. Dow #12P*	5.58×10^{-3}	8.74×10^{-3}	0	0	-	52 hr.
"H" Alloy Spec. Dow #7P**	0.96×10^{-3}	-	-	-	-	176 hr.
"C" Alloy Spec. Dow #7P**	0.11×10^{-3}	-	-	-	-	165 hr.

* Primed specimens each with 0.55 mil of primer.

** These values represent single determinations which were terminated after 2-7 milliliters of hydrogen were collected.

TABLE NO. 30

GASOMETRIC DETERMINATIONS

UNTREATED CAST ALLOYS

Specimen No. and Type	Average Hydrogen Evolution Rate ($ml./min./10\ in.^2$)	Final Hydrogen Evolution Rate ($ml./min./10\ in.^2$)	Test Time (hr.)
C1229 Acetic-nitrate "pickled"	15.05×10^{-2}	18.80×10^{-2}	3
H1156 Acetic-nitrate "pickled"	5.88×10^{-2}	6.82×10^{-2}	4
C1233 Acetic-nitrate "pickled"	7.32×10^{-2}	8.67×10^{-2}	2
H1161 Acetic-nitrate "pickled"	2.27×10^{-2} (for 3 hr.)	1.66×10^{-2} 18.5×10^{-2}	3 68

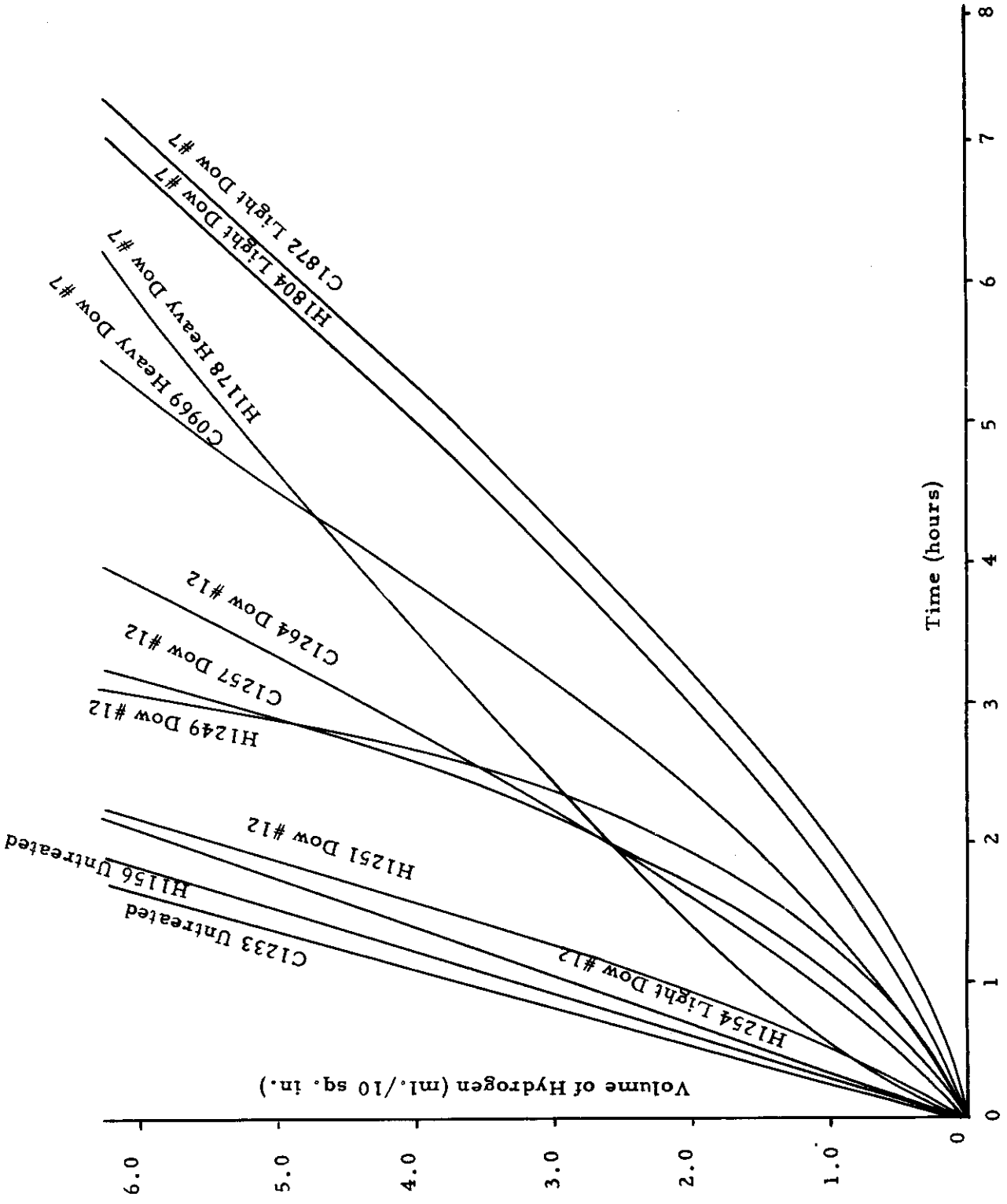


Figure 24. Rate of Hydrogen Evolution for Unprimed Cast Alloys in 1.0N KCl. (Magnetic Stirrer Type Cell.)

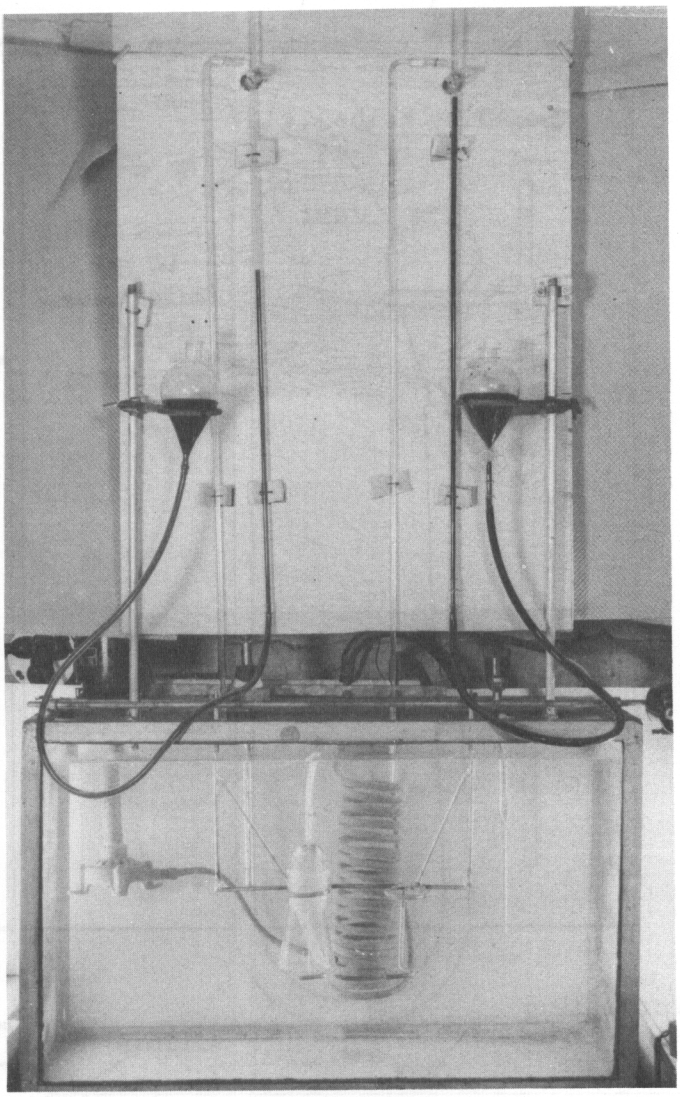


Figure 25. Fermentation Shaker Cell Apparatus. Two determinations can be made simultaneously with this apparatus, although only one cell is shown in the constant temperature bath.

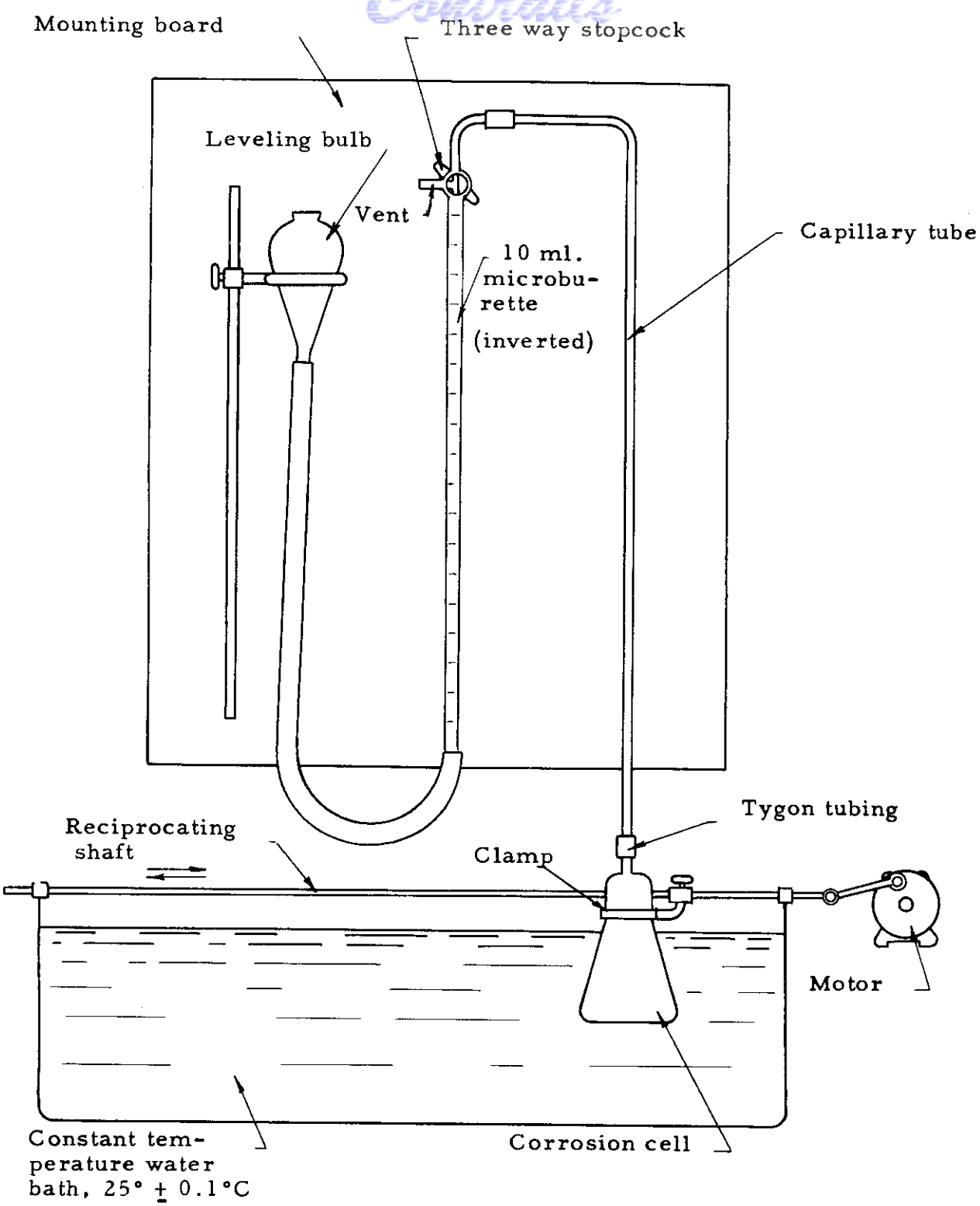


Figure 26. Fermentation Shaker Cell Apparatus - Single Unit.

Gasometric corrosion rates for FS-1 specimens obtained with the fermentation shaker cell apparatus are presented in Table No. 31 and are shown graphically in Figure 27. The values for the Dow #12 and #7 treatments compare favorably with previous data obtained with other types of gasometric cells.

Several variations were included for each treatment and two specimens were tested simultaneously. Test times were varied unintentionally. However, a 6 or 8 hour limit was established for each determination, and all rates were calculated at that time. The rates decreased with time.

The corrosion rates of a number of Iridite #15 specimens were also determined with the shaker cell equipment. The rates compared favorably with rates for the Dow #7 and #12 treatments when calculated at the 5 hour immersion time. They also agreed closely with previous gasometric rates for Iridite #15 specimens when calculated at the 5 hour immersion time. The Iridite #15 specimens also gave decreasing rates with time.

In gasometric tests, the rate of stirring or agitation of the electrolyte was a definite factor in determining the gas evolution rate for a treatment at a given time. For example, gasometric values obtained in initial experiments with a stagnant corrosion cell (closed cell-no stirring) were larger at a given time than those obtained with the magnetic stirrer or shaker types of cell. Stirring would therefore have to be standardized in the approved method.

In stirred 1.0N KCl the Dow #7 gave lower corrosion rates than the Dow #12 at a given time. Both treatments had a short induction period with low rates, followed by several hours of increasing rates and ending (on long exposures) with decreasing rates. The more violent the agitation the shorter was the induction period.

Generally, the gasometric rate was directly proportional to the thickness of the treatment.

5. Linearity of Gasometric Corrosion Rates

The linearity of the corrosion rates from the gasometric method was determined on FS-1 Dow #7 and #12 specimens for a 97 hour immersion in 1.0N KCl (Table No. 32). The magnetic stirrer type of cell was used.

Both specimens showed a decrease in corrosion rate with time. The Dow #7 rate was initially lower than the Dow #12 rate. After 50 hours the rate for the Dow #7 specimen began to increase. If this rate increase were assumed to continue, it would confirm the corrosion rate rise noted for salt spray exposure specimens (shown later in Tables 45 and 46). However, an increase in gasometric rate for Dow #7 after long exposure was observed only in this particular experiment.

TABLE NO. 31

GASOMETRIC DETERMINATIONS - FS-1 ALLOY

FERMENTATION SHAKER CELL

Specimen No. and Treatment *	Average Hydrogen Evolution Rate ($ml./min./10\ in.^2$)	Final Hydrogen Evolution Rate ($ml./min./10\ in.^2$)	Test Time (min.)
1528 Spec. Dow #12	1.27×10^{-2}	1.20×10^{-2}	300
1537 Spec. Dow #12	1.34×10^{-2}	1.67×10^{-2}	360
1538 Spec. Dow #12	1.34×10^{-2}	1.67×10^{-2}	360
1131 Spec. Dow #7	7.71×10^{-3}	1.20×10^{-2}	480
1138 Spec. Dow #7	7.98×10^{-3}	1.17×10^{-2}	480
1967 Spec. Dow #7	1.0×10^{-2}	8.3×10^{-3}	300
1334 Light Dow #7	1.41×10^{-2}	2.31×10^{-2}	570
1710 Heavy Dow #7	9.57×10^{-3}	1.63×10^{-2}	570
1462 Light Dow #12	2.13×10^{-2}	2.15×10^{-2}	360
1461 Spec. Dow #12	2.25×10^{-2}	2.60×10^{-2}	360
1933 Iridite #15	2.03×10^{-2}	1.83×10^{-2}	300
1940 Iridite #15	2.20×10^{-2}	1.55×10^{-2}	300
1931 Iridite #15	1.05×10^{-2}	1.5×10^{-3}	420
1932 Iridite #15	1.07×10^{-2}	3.8×10^{-3}	420

* Additional data for all specimens are given in Appendix B.

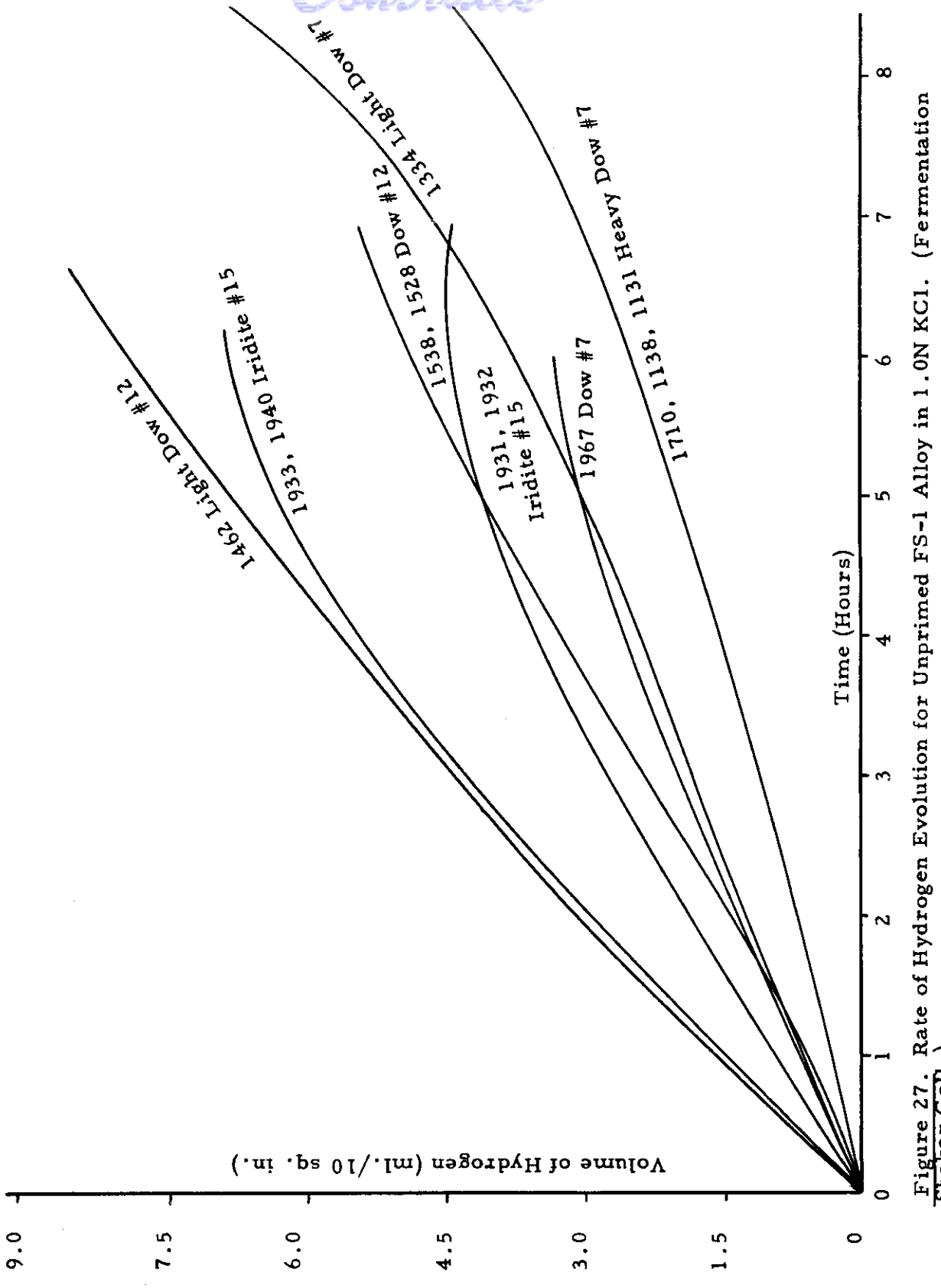


Figure 27. Rate of Hydrogen Evolution for Unprimed FS-1 Alloy in 1.0N KCl. (Fermentation Shaker Cell.)

TABLE NO. 32

GASOMETRIC RATE LINEARITY CHECK

FS-1 ALLOY

Specimen No. 1966 Spec. Dow #7		Specimen No. 1640 Spec. Dow #12	
Hydrogen Evolution Rate (ml./min./10 in.^{2})	Time (hr.)	Hydrogen Evolution Rate (ml./min./10 in.^{2})	Time (hr.)
8.12×10^{-3}	7	1.28×10^{-2}	7
8.15×10^{-3}	10	1.03×10^{-2}	24
7.17×10^{-3}	31	1.17×10^{-2}	48
6.07×10^{-3}	50	7.95×10^{-3}	72
7.02×10^{-3}	72	7.40×10^{-3}	96
7.66×10^{-3}	97	-	-

E. Polarographic Analysis of Corrosion Products

We planned to make a preliminary investigation of existing polarographic methods pertinent to the analysis of magnesium alloy corrosion products. A prototype polarograph (Figure 25) was constructed for this purpose.

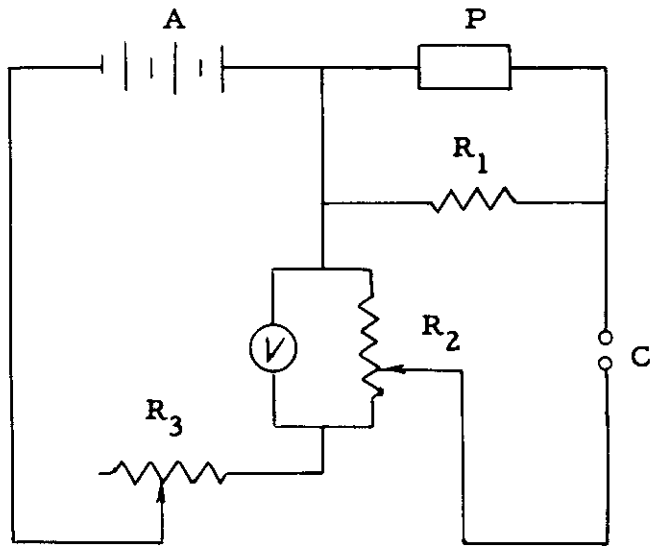
One method considered fo investigation was analysis of the corrosion products resulting from immersion of magnesium alloys in 1.0N KCl and determination of the corrosion rate change over several time intervals. Another method which was considered involved complexing or buffering the several ions to be analyzed.

For use in calibrating the polarograph, a standard solution containing $MgCl_2$ (1.0×10^{-3}M), $ZnCl_2$ (1.0×10^{-5}M), and $AlCl_3$ (3.0×10^{-5}M) dissolved in 0.1M KCl was prepared. Bromophenyl blue was added as a maximum suppressor following the method of H. C. Gull.[1] Several polarograms of the above ions were made. These showed fair correspondence with literature values.[2]

Some difficulty was experienced, however, on obtaining sharp breaks between the curves for the aluminum and magnesium diffusion currents, thus making calculation of half-wave potentials difficult.

The determination of metal ions formed during corrosion depends largely on a method for complete or representative removal of these corrosion products from the surface of the specimens. Ammonium chromate and chromic acid are commonly used to remove corrosion products from the surface of the specimens. Ammonium chromate and chromic acid are commonly used to remove corrosion products, but the effect of these reagents on polarographic curves has not been investigated. We therefore postponed further work on the polarograph and concentrated on more practical and more easily interpreted methods.

1/ H. C. Gull, J. Soc. Chem. Ind., 56, 177-183 (1937).
2/ I. M. Kolthoff and J. J. Lingane, Polarography, 2nd. Ed. Vol. I, p. 189, Interscience, New York.



A - Radio "A" - Battery; 4.5 Volts

P - Potentiometer; Range 0 to 1.11 Volts

R_1 - Fixed Resistor; 10,000 Ohms

R_2 - "Helipot" (Rheostat); 100 Ohms, 0.1% Linearity

R_3 - Rheostat, 50 Ohms

V - Voltmeter; Range 0 to 3 Volts, 0.25% Accuracy

C - (Dropping Mercury Electrode
(Saturated Calomel Electrode
(Salt (KCl) Bridge

Figure 28. Circuit Diagram for Manual Polarograph.

III ADHESION TESTS

The second phase of our test evaluation program was directed toward the development of tests capable of differentiating the adhesion of zinc chromate primer (Specification MIL-P-6889A) to the various treatments.

Several qualitative adhesion tests were made initially. On the basis of these tests, a search was made for an adhesive material which would remove the primer completely from all treated surfaces. A number of adhesive tapes and films were evaluated in shear adhesion tests with lap joint specimens of primed FS-1 alloy.

The rectangular cast alloy specimens obtained for adhesion testing had rough "as cast" surfaces and could not be used for shear tests. A tension adhesion test was therefore devised for them.

A. Qualitative Adhesion Tests

The following types of qualitative adhesion tests were made:

(1) Pressure sensitive tape tests.
(2) Impact and deformation tests.
(3) Ultrasonic vibratory tests.

1. Pressure Sensitive Tape Tests

The stripping of pressure sensitive adhesive tape (Specification UU-T-106) from scribed FS-1 alloy specimens after immersion in a corrosion environment was investigated as a qualitative test of primer adhesion.

Dow #7 primed and lacquered FS-1 specimens were scribed with a modified Mears and Ward Scriber (Figure 29) into areas 1/16" - 1/2" square. These specimens were immersed in 3% NaCl, 0.1N $CaCl_2 \cdot 2H_2O$, and 0.2N $ZnCl_2$ (pH = 1.79 with HCl) solutions for varying periods. Pressure sensitive tape was applied to specimens after removal from the corrosion environment and stripped off in accordance with the Anchorage Test Method of Specification MIL-P-6889A.

No appreciable primer or lacquer was removed on the tape from specimens immersed in 3% NaCl solution for 7, 14, and 20 days. Primed specimens immersed for 6 weeks showed little loss of primer adhesion.

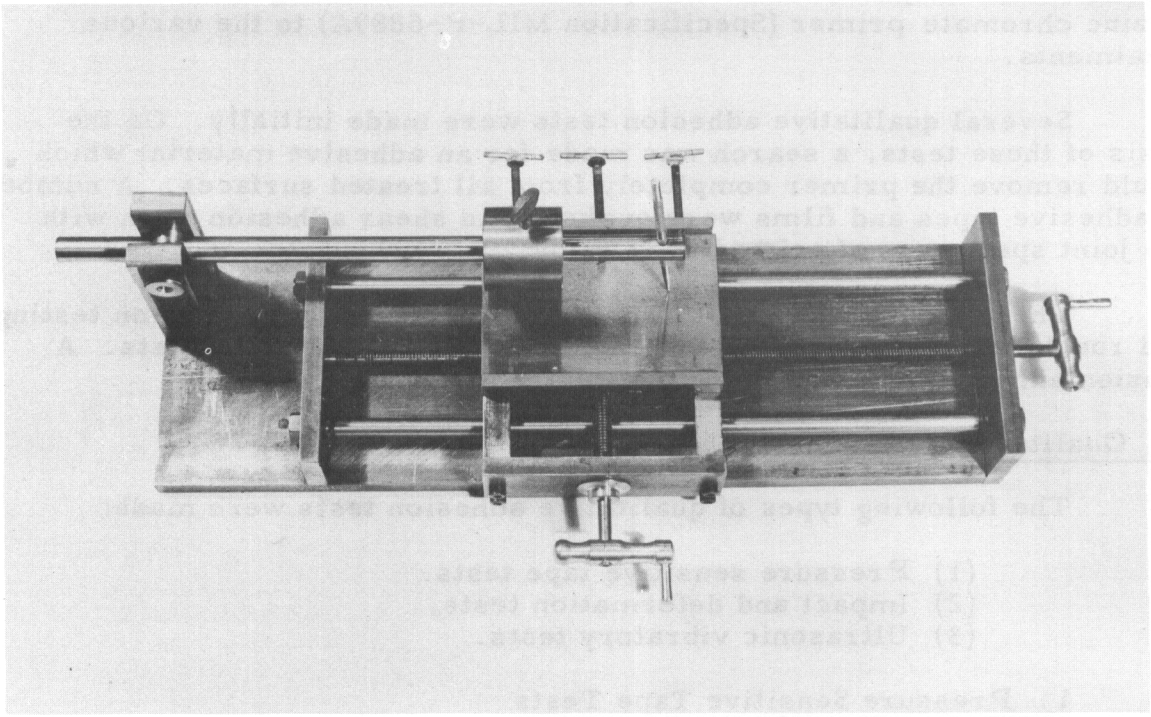


Figure 29. Calibrated Scriber. The Carballoy scribing point is at the center on the sample mounting table. The mounting table may be moved to the left or right by the handle at the right, and forward or backward by the handle at the front.

Specimens immersed in 0.1N $CaCl_2$ for seven days did not show adhesive failure.

The specimens immersed in the acidic $ZnCl_2$ solution corroded rapidly at the scratch lines. After two days immersion there was deep cavitation at the scratches and occasional deep pitting on the unscratched areas. The tape, however, did not remove any area of film 1/16" or larger since there was no undercutting or blistering of the paint film on the unscratched areas. This series was discontinued because of excessive corrosion at the pits and scratches.

Lacquered Dow #7 specimens (scribed) were also tested after immersion in 3% NaCl containing 25 and 50% of methanol or acetone. Adhesion was unimpaired after 14 days in the NaCl-methanol solutions. Considerable swelling of the lacquer was evident after 7 days in NaCl-acetone solutions, but no loss of adhesion between the primer and the treatment was observed.

Since the adhesion specified for study was primarily that between the Dow #7 or #12 treatment and the zinc chromate primer, succeeding tests were confined to primed specimens without the lacquer top coat.

Dow #7 and #12 primed specimens were immersed in ethylene glycol and in boiling water. The specimens in ethylene glycol were tape tested after three days immersion and showed little loss of adhesion.

Specimens in the boiling water were removed after eight hours. Some primer was removed on both types with the pressure sensitive tape. These specimens were placed in the boiling water for an additional four hours and then tested. Additional pressure was applied to the tape and on stripping, the Dow #12 lost considerably more primer than the Dow #7 (film thicknesses were the same at the start for both treatments). Specimens heated at 100°C in ethylene glycol also showed the same removal characteristics, with the Dow #7 retaining more primer than the Dow #12.

The pressure sensitive tape used in these tests had insufficient adhesion to the zinc chromate to remove it from the treated surfaces in any measurable amount. Furthermore, since the primer formed a hard, almost crystalline film it was not suited to the scribing technique and subsequent stripping with a pressure sensitive tape. Microscopic examination of the scribed lines also revealed considerable tearing and the presence of ragged edges.

2. Impact and Deformation Tests

The following impact and deformation tests were applied to primed FS-1 specimens:

Test No. 1, Impact Hammer - 60 strokes per minute with a two pound hammer; test time 10 minutes.

Test No. 2, Falling Ball - a one pound steel ball falling 16 feet onto the specimen.

Test No. 3, Bend Test - test panel bent 90°.

After each test the test panel was tape tested with pressure sensitive tape (Spec. UU-T-106).

The following observations were made:

For Sample No. 1883, Untreated FS-1 Specimens:

Test No. 1 - Only a small area of primer was removed on the side opposite the point of impact.

Test No. 2 - Only a small area of primer was removed.

Test No. 3 - No primer was removed.

For Sample No. 1116, Dow #7 FS-1 Specimens:

Test No. 1 - The area of primer removed was slightly larger than for untreated specimens.

Test No. 2 - About one inch of primer was removed.

Test No. 3 - No primer was removed.

For Sample No. 1655, Dow #12 FS-1 Specimens:

Test No. 1 - There was extensive primer removed around point of impact.

Test No. 2 - Primer was removed on both sides of the specimen.

Test No. 3 - There was extensive removal on both sides along bend.

3. Ultrasonic Vibratory Method

An ultrasonic vibrator was constructed utilizing a nickel magnetostrictive element (Figure 30). The theory back of this instrument was that primed specimens subjected to a frequency of up to 20 kilocycles per second while immersed in water would have weight losses (due to erosion) proportional to the adhesion of the primer to the treatment.

Initial tests were made by bolting 1.5" x 3" or 0.5" x 3" FS-1 specimens to the vibrating nickel element and immersing the specimens in water. Frequencies of 6 and 12.8 kilocycles per second were applied for up to 8 hours without appreciably lowering the primer adhesion for either the Dow #7 or #12 treatment. Weight losses were negligible for this exposure time.

Since considerable research would be entailed in standardizing the ultrasonic equipment, finding a suitable frequency, and determining the critical specimen mass for best results, this method was abandoned in favor of shear and tension tests.

B. Adhesion in Shear - Lap Joint Method

Since the qualitative adhesion tests showed that a larger adhesive force was required to remove the zinc chromate primer from the treated magnesium surfaces, a search for such an adhesive material was made.

A number of adhesive films and tapes were evaluated by a shear test method using lap joint specimens. This method eliminated scribing of ruled areas and gave more adhesion than the pressure sensitive tape method.

Two primed FS-1 specimens of the same type were placed together so as to form a one inch lap into which was placed the adhesive film or tape. The lap joints were cured in a press under conditions suitable for the particular adhesive. The cured lap joint specimens were pulled apart in a direction parallel to their long axis (longitudinal pull) in a Dillon dynamometer (Figure 31) with an applied force of 600 pounds per minute.

The rectangular cast alloy specimens obtained for adhesion tests were unsuitable for shear tests of this type because they had rough "as cast" surfaces.

1. Adhesion in Shear - Film Adhesives

Thin adhesive films of polyvinylbutyral were applied to Dow #7 and Dow #12 FS-1 primed specimens by dipping the specimens in a 10% polyvinylbutyral (Butacite-Du Pont) solution in 90% ethanol-10% toluene and withdrawing them at a rate of three inches per minute. After drying, the specimens were overlapped (one inch), cured in a Carver press at 100°C, 20 pounds platen pressure, and cooled. When the lap joint specimens were tested in shear, the primer separated from the Dow #12 but not from the Dow #7.

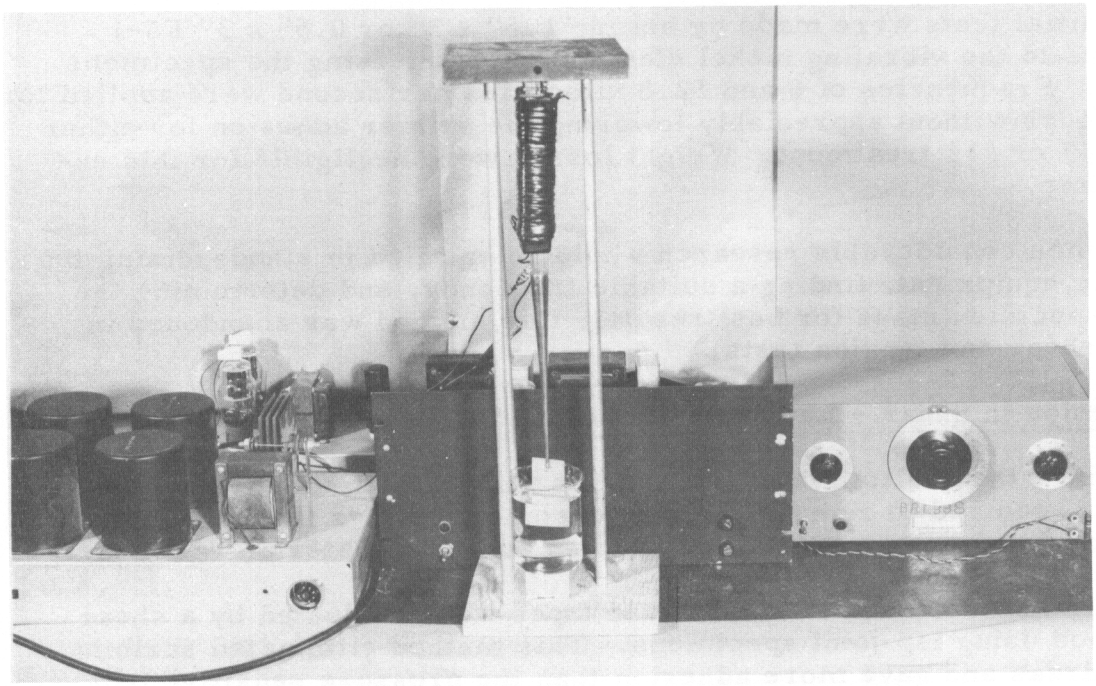


Figure 30. Ultrasonic Vibrator. Magnetostrictive nickel rod with 1.5" x 3" specimen attached is shown. Power supply and oscillator are also shown.

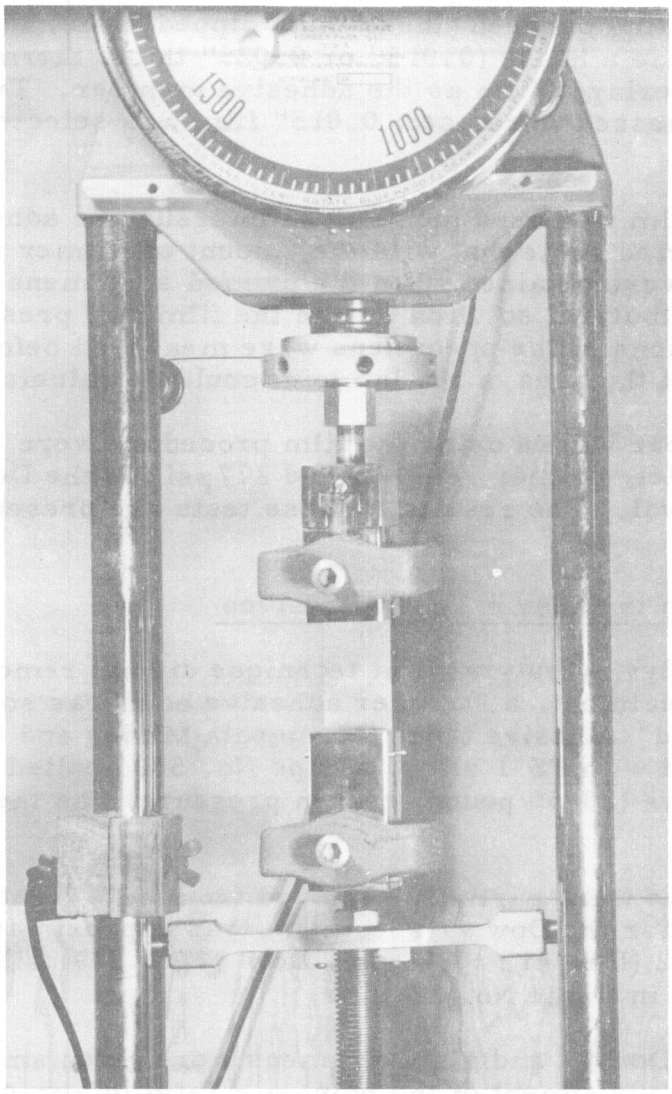


Figure 31. Shear Adhesion Testing with Dynamometer.

Since minor surface irregularities could interfere with the interfacial adhesion existing between these thin, dipped films, the procedure was altered to include a heavy (0.015" or 0.025" thick) thermoplastic polyvinylbutyral interlayer film as the adhesive member. Two film compositions and thicknesses were used; 0.015" film was selected as most promising.

When this film was used alone as an intersurface adhesive the shear adhesion values varied somewhat with the amount of primer removed. More consistent results were obtained when the primed specimens were dip coated in the 10% polyvinylbutyral solution before the film was pressed between them. The dimensions of the specimens were measured before the specimens were joined, so that the area of the lap joint could be calculated.

Average shear values using the film procedure were 227 psi for the Dow #12 with complete primer removal and 277 psi for the Dow #7 with little or no primer removal. The results of these tests are presented in Table No. 33.

2. Adhesion in Shear - Tape Adhesives

Since the polyvinylbutyral film technique did not remove any primer from the Dow #7 treatment, a stronger adhesive bond was sought. Several types of "Scotchweld" adhesive tapes (Minnesota Mining and Manufacturing Co.) were evaluated with FS-1 alloy. Tape No. 588 applied with heat (142°C) and pressure (20-50 pounds platen pressure) was the most satisfactory.

Primer films were partially removed from both treatments, but the adhesion at failure for the Dow #7 specimens was approximately 600 psi more than for the Dow #12 (Dow #12 = 278 psi, Dow #7P = 879 psi). Data for this work are presented in Table No. 34.

A series of Dow #7 and #12 specimens were given smooth or rough primer coatings by adjustment of the paint-air ratio in spray application. These specimens were air dried two days followed by a two hour conditioning at 37°C. Lap joints were made with these primed specimens using Scotchweld Adhesive Tape No. 588, 1" x 0.006", and tested for adhesion in shear.

As in previous tests the Dow #7 surface gave greater adhesion to the MIL-P-6889A primer than the Dow #12 surface (Table No. 35). Average adhesion values of 721 psi and 284 psi were obtained for the Dow #7 and #12 treatments, respectively. Smooth primer applications gave better values than rough, improperly applied primer.

TABLE NO. 33

ADHESION IN SHEAR - FILM ADHESIVES

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesive	Width Singly (in.)	Length Singly (in.)	Length Pair (in.)	Lap Joint Area ($in.^2$)	Adhesion in Shear (psi)	Removal of Primer
0411 0424	Dow #7P	25 mil PVB*	1.498 1.500	3.027 3.032	5.088	1.455	233.5	None removed
0420 0413	Dow #7P	25 mil PVB	1.496 1.495	3.032 3.025	5.121	1.405	266.5	None removed
0343 0840	Dow #12P	25 mil PVB	1.503 1.500	3.030 3.019	5.126	1.387	252.0	Removed
0831 0865	Dow #12P	25 mil PVB	1.505 1.502	3.013 3.012	5.076	1.429	231.5	Removed
0934 ** 0945	Dow #7P	25 mil PVB	1.500 1.503	3.032 3.020	5.110	1.414	237.0	2/3 removed
0905 0939	Iridite #15P. Dow #7P	25 mil PVB	1.498 1.500	3.005 3.032	5.107	1.392	273.0	2/3 removed

NOTES: * 25 mil polyvinylbutyral film plasticized with 23% dibutyl sebacate.
** These specimens were primed 24 hours before testing; solvent retention allowed primer to be 2/3 removed.

All specimens were pressed two minutes with 50 pounds pressure at 125°C.

TABLE NO. 33 (Cont'd)

ADHESION IN SHEAR - FILM ADHESIVES

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesive	Width Singly (in.)	Length Singly (in.)	Length Pair (in.)	Lap Joint Area ($in.^2$)	Adhesion in Shear (psi)	Removal of Primer
0726 0730	Dow #7P (dipped)*	25 mil PVB	1.495 1.495	3.031 3.016	5.035	1.512	225	1/3 removed
0346 0344	Dow #12P (dipped)	25 mil PVB	1.502 1.502	3.032 3.029	5.060	1.502	146	1/2 removed
0782 0937	Dow #7P	15 mil PVB**	1.500 1.498	3.032 3.029	5.077	1.475	244	Removed
0844 0816	Dow #12P	15 mil PVB	1.505 1.505	3.012 3.030	5.065	1.473	227	Removed
0801*** 0882	Dow #12P	15 mil PVB	1.504 1.500	3.018 3.028	5.052	1.492	191	Removed
0931 0933	Dow #7P	15 mil PVB	1.495 1.500	3.014 3.016	5.015	1.518	218	1/10 removed
0941 0942	Dow #7P	15 mil PVB	1.502 1.502	3.027 3.030	5.105	1.430	213	None removed
0486 0489	Dow #7P	15 mil PVB	1.500 1.502	3.022 3.028	5.012	1.558	247	None removed
0863 0828	Dow #12P	15 mil PVB	1.508 1.507	3.006 3.028	5.060	1.470	223	Removed

NOTES:
* Primer applied by dip method, rather than spraying.
** 15 mil polyvinylbutyral plasticized with 23% 3GH (Monsanto Chemical Co.).
*** These and following specimens heated 1/2 hour at 80°C before adhesive interlayer was pressed between them.

TABLE NO. 33 (Cont'd)

ADHESION IN SHEAR - FILM ADHESIVES

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesive	Width Singly (in.)	Length Singly (in.)	Length Pair (in.)	Lap Joint Area (in.)	Adhesion in Shear (psi)	Removal of Primer
0415* 0412	Dow #7P- smooth**	15 mil PVB	1.502 1.502	3.010 3.032	5.072	1.458	267	None removed
0414 0417	Dow #7P - smooth	15 mil PVB	1.497 1.498	3.033 3.028	5.058	1.502	269	None removed
0268 0247	Dow #7P - smooth	15 mil PVB 3GH	1.498 1.496	3.012 3.015	5.017	1.510	234	None removed
0944 0946	Dow #7P - rough	15 mil PVB 3GH	1.502 1.502	3.030 3.012	5.050	1.490	282	1/10 removed
0918 0919	Dow #7P rough	15 mil PVB 3GH	1.500 1.499	3.023 3.022	5.020	1.538	325	None removed
0418 0427	Dow #7P- smooth	15 mil PVB 3GH	1.496 1.494	3.018 3.028	5.057	1.480	213	None removed
0789 0790	Dow #7P	15 mil PVB 3GH	1.500 1.500	3.020 3.015	5.040	1.493	345	1/10 removed
0341 0841	Dow #12P	15 mil PVB 3GH	1.504 1.502	3.032 3.002	5.017	1.528	232	Removed
0832 1861	Dow #12P	15 mil PVB 3GH	1.502 1.504	3.030 3.030	5.063	1.497	250	2/3 removed
0802 0817	Dow #12P	15 mil PVB 3GH	1.503 1.502	3.026 3.010	5.010	1.540	192	Removed

NOTES: * These and following specimens all dipped in 10% PVB solution, air dried 12 hours, and oven cured one hour at 80°C before adhesive interlayer was pressed between them.

** Smooth or rough primer surfaces obtained by adjustment of the paint-air ratio in spray application.

TABLE NO. 34

ADHESION IN SHEAR - TAPE ADHESIVES

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesive	Lap Joint Area ($in.^2$)	Cure Conditions	Adhesion in Shear (psi)	Removal of Primer
1278 1275	Dow #7P	3M-#588	1.175	142°C, 40 lb. for 10 min.	890	1/4 removed
1276 1277	Dow #7P	3M-#588	1.140	142°C, 40 lb. for 10 min.	860	1/2 removed
1279 1283	Dow #7P	3M-#588	1.100	142°C, 40 lb. for 10 min.	802	1/4 removed
1285 1284	Dow #7P	3M-#588	1.103	142°C, 40 lb. for 10 min.	863	1/4 removed
1282 1280	Dow #7P	3M-#588	1.168	142°C, 40 lb. for 10 min.	980	1/3 removed
0940 0935	Dow #7P	15 mil PVB** PVB dip	1.445	120°C, 20 lb. for 5 min.	297	None removed
0846 0864	Dow #12P	15 mil PVB PVB dip	1.460	120°C, 20 lb. for 5 min.	189	Removed
0940 0935	Dow #7P	3M-#583*	-		615	None removed
0936 0788	Dow #7P	3M-#588	1.130	145°C, 50 lb. for 15 min.	707	1/3 removed

* 3M - #588 and 3M - #583 = Scotchweld (Minnesota Mining & Manufacturing Co.) tapes, 3/4" wide, 0.006" thick.

** PVB = polyvinylbutyral.

TABLE NO. 34 (Cont'd)

ADHESION IN SHEAR - TAPE ADHESIVES

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesive	Lap Joint Area ($in.^2$)	Cure Conditions	Adhesion in Shear (psi)	Removal of Primer
0894 0884	Dow #12P	3M-#588	1.160	145°C, 50 psi for 15 min.	259	Removed
1126 1151	Dow #7P	3M-#588	1.140	140°C, 40 psi for 5 min.	790	1/5 removed
0813 0815	Dow #12P	3M-#588	1.150	140°C, 40 psi for 5 min.	535	All removed
0853 0852	Dow #12P	3M=#588	1.162	142°C, 40 psi for 10 min.	271	2/3 removed
0837 0803	Dow #12P	3M-#588	1.155	142°C, 40 psi for 10 min.	199	1/2 removed
0838 0879	Dow #12P	3M-#588	1.160	142°C, 40 psi for 10 min.	276	2/3 removed
0860 0857	Dow #12P	3M-#588	1.158	142°C, 40 psi for 10 min.	384	2/3 removed
0804 0876	Dow #12P	3M-#588	1.073	142°C, 40 psi for 10 min.	261	1/2 removed

TABLE NO. 35

ADHESION IN SHEAR

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment*	Adhesion in Shear (psi)	Removal of Primer
1589 1611	Dow #12P- rough	161.5	2/3 removed
1578 1619	Dow #12P- rough	620.0	4/5 removed
1423 1436	Dow #7P- rough	630.0	1/5 removed
1428 1447	Dow #7P- rough	730.0	1/4 removed
1297 1289	Dow #7P- smooth	501.0	1/2 removed
1292 1290	Dow #7P- smooth	661.0	3/4 removed
1511 1521	Dow #12P- smooth	139.9	Poor adhesive cure
1425** 1533	Dow #12P- smooth	216.5	1/2 removed
1294 1288	Dow #7P- smooth	821.0	1/3 removed
1668 1695	Dow #7P- smooth	985.0	1/3 removed

NOTES: Adhesive in all cases was Scotchweld No. 558 (Minnesota Mining and Manufacturing Co.).
* Smooth or rough characterizes nature of primer surface.
** Cure temperature increased from 140° to 150°C.

Data for variations of the Dow #7 and #12 treatments on primer specimens conditioned as above are shown in Table No.36. Dow #12 and Iridite #15 treated specimens and untreated FS-1 cleaned with acetic-nitrate "pickle" were also included in these tests.

The shear adhesion values obtained from these tests indicated that untreated FS-1 alloy offered considerable adhesion to the primer. The heavier treatments tended to lower the adhesion, with the exception of the heavy Dow #17 which gave good adhesion.

3. Effect of Aging on Adhesion in Shear

The effect of aging on the adhesion of the primer to the treatment was investigated with several series of FS-1 alloy specimens. Since Scotchweld No. 588 did not completely remove the primer from the Dow #7, other adhesives were included in these tests. Plastilock #601 (B. F. Goodrich) completely removed the primer from both Dow #7 and #12, but gave somewhat lower adhesion values than Scotchweld No. 588 (Table No. 37). In some cases it removed the treatment, if the interfacial adhesion between the treatment and base metal was lower than that of the primer to the treatment.

a. Weatherometer Exposure

The aging test for one series of FS-1 specimens consisted of exposing primed specimens for 100 hours in the weatherometer, which had a sun-rain cycle of 15 and 3 minutes, respectively. At the end of the exposure the specimens were dried at room temperature for 24 hours, followed by a two hour drying period at 37°C. Lap joints were made with these aged specimens.

With the Dow #12 specimens adhesion was completely lost after aging (Table No. 37). The Dow #7 and Dow #17 specimens were far superior, although adhesion was lowered after aging. The cleaned, untreated FS-1 alloy specimens retained fair adhesion after 100 hours' exposure. Most of the primer was removed from the untreated FS-1 with the Scotchweld #588 adhesive, indicating a rapid lowering of adhesion.

b. Accelerated Aging Tests

The following methods for accelerating adhesion failure were evaluated:

(1) Immersion in water (at room temperature) for 100 hours.
(2) Immersion in water (at room temperature) for 100 hours.
(3) Heating at 121°C for 100 hours.
(4) Immersion in boiling water for one hour.

TABLE NO. 36

ADHESION IN SHEAR

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Adhesion in Shear (psi)	Removal of Primer
1736 1741	Heavy Dow #7	861.0	1/5 removed
1725 1726	Acetic-nitrate "pickled"	1046.0	3/4 removed
0908 0921	Iridite #15	1000.0	2/3 removed
1551 1553	Heavy Dow #17	747.0	9/10 removed
1614 1617	Light Dow #12	108.0	1/2 removed
1573 1577	Heavy Dow #12	167.0	All removed
1703 1704	Light Dow #7	1085.0	None removed
1555 1628	Spec. Dow #12	248.0	All removed
NOTE: Adhesive in all cases was Scotchweld No. 588 (Minnesota Mining and Manufacturing Co.)			

TABLE NO. 37

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesive*	Adhesion in Shear (psi)	Primer Removal
1530 1631	Spec. Dow #12	None	Scotchweld #588	258	Almost complete
1738 1740	Heavy Dow #7	None	Scotchweld #588	875	Little removed
1550 1555	Dow #17	None	Scotchweld #588	769	Most removed
0805 0851	Spec. Dow #12	Immersed 7 days in 1.0N KCl	Scotchweld #588	89	All removed
0437 0483	Spec. Dow #7	Immersed 7 days in 1.0N KCl	Scotchweld #588	635	1/2 removed
1728 1723	Acetic-nitrate "pickled"	40 hr. in weathero-meter**	Scotchweld #588	900	1/8 removed
1733 1734	Heavy Dow #7	100 hr. in weathero-meter	Scotchweld #588	558	1/5 removed
0907 0920	Iridite #15	100 hr. in weathero-meter	Scotchweld #588	339	Complete removal
1579 1598	Heavy Dow #12	100 hr. in weathero-meter	Scotchweld #588	17	Complete removal
1554 1552	Dow #17	100 hr. in weathero-meter	Scotchweld #588	387	1/3 removed

* All lap joint specimens cured for 10 minutes at 152°C, 40 pounds platen pressure.

** Weatherometer - 3 minute rain cycle, 15 minute arc; afterwards specimens dried at room temperature plus 2 hours at 37°C.

TABLE NO. 37 (Cont'd)

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesive	Adhesion in Shear (psi)	Primer Removal
1650 1551	Dow #17	100 hr. in weathero-meter	Scotchweld #588	458	1/4 removed
1782 1778	Acetic-nitrate "pickled"	100 hr. in weathero-meter	Scotchweld #588	510	1/2 removed
1779 1788	Acetic-nitrate "pickled"	100 hr. in weathero-meter	Scotchweld #588	677	4/5 removed
1145 1142	Spec. Dow #7	None	Plastilock #601***	653	Complete removal
1604 1459	Spec. Dow #12	None	Plastilock #601***	134	Complete removal

*** Plastilock #601 (B. F. Goodrich Co.) tape, 0.012" x 1.0".

Shear adhesion values of Dow #7, Dow #12, and untreated FS-1 specimens aged under the above conditions are given in Table No. 38. No appreciable reduction in adhesion after aging was noted on the Dow #7 surface. However, the Dow #12 values were lower after 8 months of aging (decreased from 200-300 psi to 100-150 psi).

The light Dow #7 treatment (10 minutes in dichromate at pH 5.0) gave the highest shear adhesion values. Iridite #15 gave shear values comparable with those of the Dow #7 treatments. Untreated FS-1 specimens cleaned with acetic-nitrate "pickle" had higher primer adhesion than specimens with the Dow #12 specification treatment.

The adhesion failure in heavy treatment resulted from a separation of the granular treatment or a complete removal of the treatment, as with the heavy Dow #7. With the light treatments, the primer was removed from the treatment.

Pairs of Dow #7 and Dow #12 lacquered specimens were tested for adhesion in shear. The thermoplastic lacquer, however, squeezed out of the lap joint, and effective adhesion was not obtained.

The effects of each accelerated aging test on primer adhesion are discussed below.

(1) Immersion in Water at Room Temperature

Immersion in water at room temperature for 50 hours had little effect on primer adhesion.

After immersion for 100 hours the Iridite #15, Dow #7, and untreated FS-1 specimens showed an increase in shear adhesion. Dow #12 and #17 specimens showed no appreciable change.

After immersion for 200 hours some adhesion was lost by all specimens. However, this exposure was too mild to bring out any characteristic weakness in the primer-treatment system.

(2) Heating at 121°C for 100 Hours

The adhesion of the zinc chromate primer increased on both the Dow #7 and #12 after this exposure. The Dow #12 showed the larger increase. The acetic-nitrate "pickled" specimens showed a slight decrease in primer adhesion.

Since both the Dow #7 and #12 treatment-primer systems showed an increase in shear adhesion resulting from this exposure, it appears likely that little deterioration of these systems occurred during the cure (10 minutes at 150°C) of the adhesive (Plastilock #608) in the lap-joint.

TABLE NO. 38

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesion in Shear (psi)	Remarks
0428 0421	Heavy Dow #7P	Air dried 11 months	582	Primer and Dow #7 completely removed
0259 0243	Heavy Dow #7P	Air dried 11 months	662	Primer and Dow #7 completely removed
0256 0260	Heavy Dow #7P	Air dried 11 months	612	Primer and Dow #7 completely removed
1141 1155	Heavy Dow #7P	Air dried 7 months	894	Primer and Dow #7 completely removed
0795 0792	Heavy Dow #7L	Air dried 7 months	None	Thermoplastic lacquer squeezed out of lap joint
0827 0843	Spec. Dow #12P	Air dried 8 months	136	Primer completely removed
0850 0830	Spec. Dow #12P	Air dried 8 months	104	Primer completely removed
0331 0333	Spec. Dow #12L	Air dried 7 months	-	Thermoplastic lacquer squeezed out of lap joint
1324 1323	Light Dow #7P	Air dried 6 days	902	Primer and some of Dow #7 removed
1768 1399	Heavy Dow #7P	Air dried 6 days	875	Primer and Dow #7 removed
0914 0928	Iridite #15P	Air dried 6 days	884	Primer and Iridite #15 removed

NOTES: P= primed; L= lacquered.
Adhesive in all cases was Plastilock #608 (B. F. Goodrich Co.).

TABLE NO. 38 (Cont'd)

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesion in Shear (psi)	Remarks
1435 1440	Spec. Dow #12P	Air dried 6 days	282	Primer and some Dow #12 removed
1342 1340	Acetic-nitrate "pickled", primed	Air dried 6 days	507	Primer completely removed
1403 1396	Heavy Dow #7P	50-hour water immersion	820	Primer completely removed
1419 1356	Light Dow #7P	50-hour water immersion	827	Primer completely removed
1566 1563	Heavy Dow #12P	50-hour water immersion	98	Primer completely removed
1446 1454	Spec. Dow #12P	50-hour water immersion	315	Primer completely removed
1467 1445	Light Dow #12P	50-hour water immersion	544	Primer completely removed
1776 1341	Acetic-nitrate "pickled", primed	50-hour water immersion	553	Primer completely removed
1622 1623	Heavy Dow #17P	100-hour water immersion	568	Primer and 1/2 Dow #17 removed
0909 0926	Iridite #15P	100-hour water immersion	1042	Primer and 1/2 Iridite #15 removed
1322 1333	Light Dow #7P	100-hour water immersion	1145	Dow #7 not removed
1762 1770	Heavy Dow #7P	100-hour water immersion	1028	Primer and Dow #7 removed
1565 1567	Heavy Dow #12P	100-hour water immersion	97	Primer and 1/2 Dow #12 removed

TABLE NO. 38 (Cont'd)

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesion in Shear (psi)	Remarks
1491 1443	Spec. Dow #12P	100-hour water immersion	230	Primer and 1/2 Dow #12 removed
1465 1466	Light Dow #12P	100-hour water immersion	576	Primer removed
1416 1343	Acetic-nitrate "pickled", primed	100-hour water immersion	883	Primer removed
0910 0929	Iridite #15P	200-hour water immersion	977	Primer and 1/2 Iridite #15 removed
1335 1777	Acetic-nitrate "pickled", primed	200-hour water immersion	487	Primer removed
1400 1464	Heavy Dow #7P	200-hour water immersion	747	Primer and Dow #7 removed
1524 1525	Spec. Dow #12P	200-hour water immersion	180	Primer removed
1439 1451	Spec. Dow #12P	100 hours at 121°C	667	Primer removed
1765 1767	Spec. Dow #7P	100 hours at 121°C	1008	Primer and Dow #7 removed
1321 1341	Light Dow #7P	100 hours at 121°C	1003	Dow #7 not removed
1339 1771	Acetic-nitrate "pickled", primed	100 hours at 121°C	373	Primer removed
1920 1402	Spec. Dow #7P	1 hour in boiling water	485	Primer removed

TABLE NO. 38 (Cont'd)

ADHESION IN SHEAR - EFFECT OF AGING

LAP JOINTS OF PRIMED FS-1 SPECIMENS

Specimen No.	Treatment	Aging Condition	Adhesion in Shear (psi)	Remarks
2003 2008	Light Dow #7P	1 hour in boiling water	788	Primer removed
1438 1434	Spec. Dow #12P	1 hour in boiling water	181	Primer removed
1342 1339	Acetic-nitrate "pickled", primed	1 hour in boiling water	None	Primer removed
1322 1352	Light Dow #7P	1 hour in boiling water	463	Primer removed
0454 0490	Spec. Dow #7P	262 days in tropical humidity cabinet	80	Primer removed
-	Spec. Dow #12P	262 days in tropical humidity cabinet	-	Insufficient primer remaining for test
2000 2005	Light Dow #17P	Air dried 5 days	796	Primer removed; no Dow #17 removed
2011 2009	Light Dow #17P	Air dried 5 days	813	Primer removed; no Dow #17 removed
2004 2007	Light Dow #17P	Air dried 5 days	775	Primer removed; no Dow #17 removed
2001 2006	Light Dow #17P	Air dried 5 days	847	Primer removed; no Dow #17 removed
2002 2010	Light Dow #17P	Air dried 5 days	790	Primer removed; no Dow #17 removed

(3) Immersion in Boiling Water for One Hour

This test was effective for lowering the adhesion of a primer-treatment system with an inherent weakness. The primer-bare metal system, for example, failed completely with all primer loosened from the base metal. The Dow #7 treatment also showed about a 400 psi reduction in adhesion. The light Dow #7 withstood the test as well as the heavy Dow #7, indicating that heavy treatments may be unnecessary. The light Dow #17 and the Dow #12 adhesion values were reduced somewhat. The Dow #17 was the best of all treatments.

Specimens of Dow #7 and #12 primed FS-1 alloy from a 262 day exposure in a tropical humidity cabinet were also tested. The primer remaining on the Dow #12 surface was completely nonadherent, whereas a residual shear adhesion of 80 psi was found for the Dow #7 specimens.

No steam corrosion or discoloration resulting from the Plastilock #608 was observed on the metal surfaces upon examination after testing.

4. Effect of Curing Conditions on Adhesion in Shear

The effect of the press curing temperature on Dow #7 was checked by heating unprimed FS-1 specimens (1670 - 1672; 1960 - 1965, Table No. 39) at 150°C for 5 minutes before lap joints were made with Plastilock #608. Increased adhesion of the treatment to the base metal resulted from this heating, with shear values of about 1300 psi being obtained.

Pressure, time, and temperature of cure were varied for lap joints made from primed FS-1 specimens. Shear adhesion values for these specimens are also given in Table No. 39.

Considerable variation in cure conditions was possible without greatly affecting the shear adhesion of the primer. At a temperature of 125°C Plastilock #608 was cured sufficiently to remove the primer. A cure time of 5 minutes was also sufficient. A reduction of the platen pressure to 20 pounds caused some reduction in primer adhesion to the light Dow #7 and an increase in adhesion to clean metal.

The following curing conditions were considered most suitable for preparing lap joints of FS-1 specimens:

Time: 10 minutes.
Pressure: 40 pounds platen pressure or 330 psi.
Temperature: 150° $\pm$ 2°C.

TABLE NO. 39

ADHESION IN SHEAR - EFFECT OF CURING CONDITIONS

LAP JOINTS OF FS-1 SPECIMENS

Specimen No.	Treatment	Press Cure Conditions *	Adhesion in Shear (psi)	Remarks
1670 1672	Spec. Dow #7 unprimed	Preheated to 150°C	1391	No color change in Dow #7
1960 1965	Spec. Dow #7 unprimed	Preheated to 150°C	1270	Dow #7 removed
1401 1764	Spec. Dow #7P	5 min. at 150°C, 40 lb.	884	Primer and Dow #7 removed
1923 1405	Spec. Dow #7P	10 min. at 150°C, 20 lb.	747	Primer and Dow #7 removed
1921 1922	Spec. Dow #7P	10 min. at 125°C, 40 lb.	825	Primer partially removed
0925 0927	Iridite #15P	10 min. at 150°C, 40 lb.	817	Primer and 1/2 Iridite #15 removed
1773 1774	Acetic-nitrate "pickled", primed	5 min. at 150°C, 40 lb.	520	-
1351 1355	Light Dow #7P	10 min. at 150°C, 40 lb.	925	Dow #7 not removed

NOTES: Adhesive used was Plastilock #608.

* P = Primed.

* All cure pressures given are platen pressures.

40 lb. = 330 psi on specimen.

TABLE NO. 39 (Cont'd)

ADHESION IN SHEAR - EFFECT OF CURING CONDITIONS

LAP JOINTS OF FS-1 SPECIMENS

Specimen No.	Treatment	Press Cure Conditions	Adhesion in Shear (psi)	Remarks
1711 1702	Light Dow #7P	10 min. at 150°C, 20 lb.	706	Primer and part of Dow # 7 removed
1712 1715	Light Dow #7P	10 min. at 150°C, 20 lb.	757	Primer and part of Dow #7 removed
1393 1388	Light Dow #7P	10 min. at 150°C, 20 lb.	725	Primer and part of Dow #7 removed
1615 1492	Light Dow #12P	10 min. at 150°C, 20 lb.	802	Primer removed
1472 1487	Spec. Dow #12	10 min. at 150° C, 20 lb.	206	Primer removed
1293 1291	Spec. Dow #7P	10 min. at 150°C, 20 lb.	623	Dow #7 removed with primer
1783 1785	Acetic-nitrate "pickled", primed	10 min. at 150°C, 20 lb.	733	Primer removed
1753 1787	Acetic-nitrate "pickled", primed	10 min. at 150° C, 20 lb.	733	Primer removed
1786 1781	Acetic-nitrate "pickled", primed	10 min. at 150°C, 40 lb.	637	Primer removed
1789 1780	Acetic-nitrate "pickled", primed	10 min. at 150°C, 40 lb.	701	Primer removed

5. Adhesion of Treatment to Base Metal

A group of unprimed specimens with treatments in various thicknesses were tested to determine the adhesion between the treatment and the base metal. Five variations of the Dow #7 treatment were tested, including specimens recycled in potassium acid fluoride after the dichromate treatment.

Highest adhesion values were obtained for the acetic-nitrate "pickled," the light Dow #7, and the light Dow #17 specimens (Table No. 40). The light Dow #7 and the light Dow #17 treatments were not removed by the Plastilock #608. The other Dow #7's, the heavy Dow #17, and some of the Dow #12, however, were removed with the adhesive. This same effect was noted on primed specimens (Table No. 39).

C. Adhesion in Tension - Perpendicular Pull Method

The adhesion of the zinc chromate primer to treated magnesium alloys was also evaluated by a tension method. In this method the specimens (Figure 32) were pulled by a force perpendicular to their long axis, rather than parallel to this axis as in shear adhesion tests (compare Figures 31 and 33).

Specimens for tension adhesion tests were prepared and tested as follows:

Cast aluminum "T" blocks were machined as shown in Figure 32. The facial dimensions were 1" x 1" or 1.5" x 0.75" and the leg dimensions 0.3" x 1" (for attachment in the chuck of the dynamometer). These blocks were sealed with Scotchweld No. 588 (FS-1 specimens), Plastilock #601, or Plastilock #608 to primed FS-1 or cast alloy specimens using the following press conditions:

Time: 10 minutes for FS-1 specimens.
15 minutes for cast specimens.
Pressure: 40 pounds platen pressure of 300 psi.
Temperature: 150° ± 2°C.

The aluminum block was pulled from the primed specimen in a dynamometer with a force applied at 600-750 pounds per minutes (Figure 33). The specimen was held in stirrups as the force was applied.

TABLE NO. 40

ADHESION OF TREATMENT TO BASE METAL

UNPRIMED FS-1 ALLOY

Specimen No.	Treatment	Adhesion in Shear (psi)	Remarks
1973 1976	Spec. Dow #7 KHF recycle	673	Dow #7 removed
1962 1968	Spec. Dow #7	520	Dow #7 removed
1950 1951	Light Dow #7	1230	Dow #7 not removed
1983 1988	Heavy Dow #7	562	Dow #7 removed
2050 2051	Powdery Dow #7	380	Dow #7 removed
1518 1498	Spec. Dow #12	104	Dow #12 partially removed
2033 2032	Acetic-nitrate "pickled"	1020	-
-	Light Dow #17	1125	Dow #17 not removed
-	Light Dow #17	898	Dow #17 not removed
-	Heavy Dow #17	462	Heavy Dow #17 removed
2023 2022	Acetic-nitrate "pickled"	1345	-

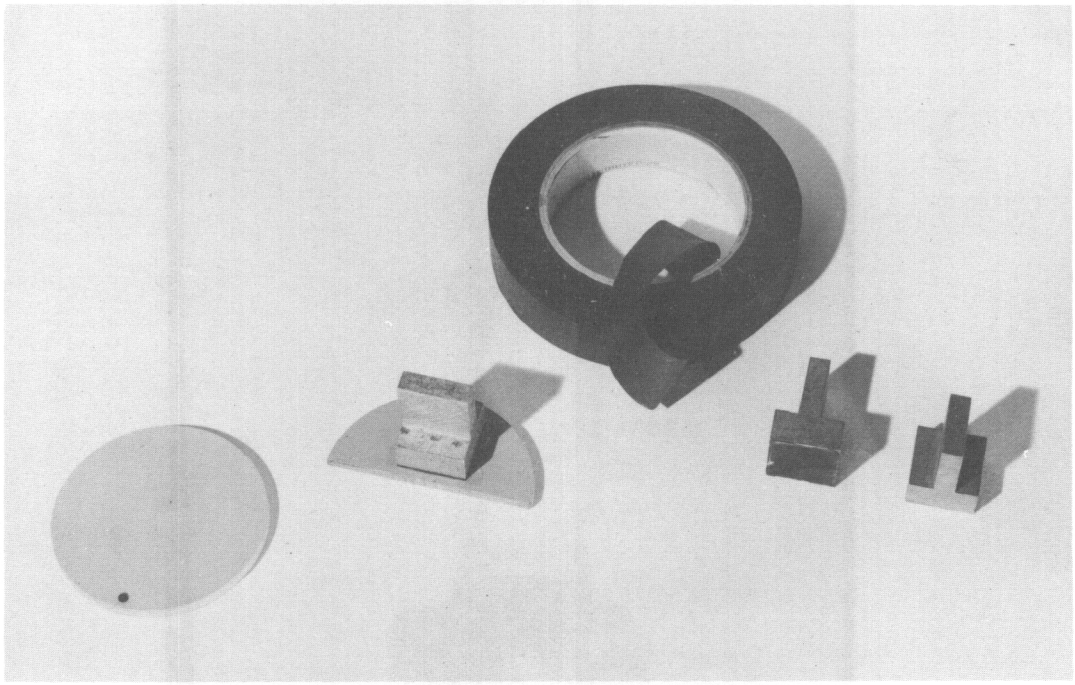


Figure 32. Adhesion in Tension Specimens. Cast aluminum blocks were attached with Plastilock #607 or #608 (B.F. Goodrich Co.) to the semi-circular cast specimens as shown above.

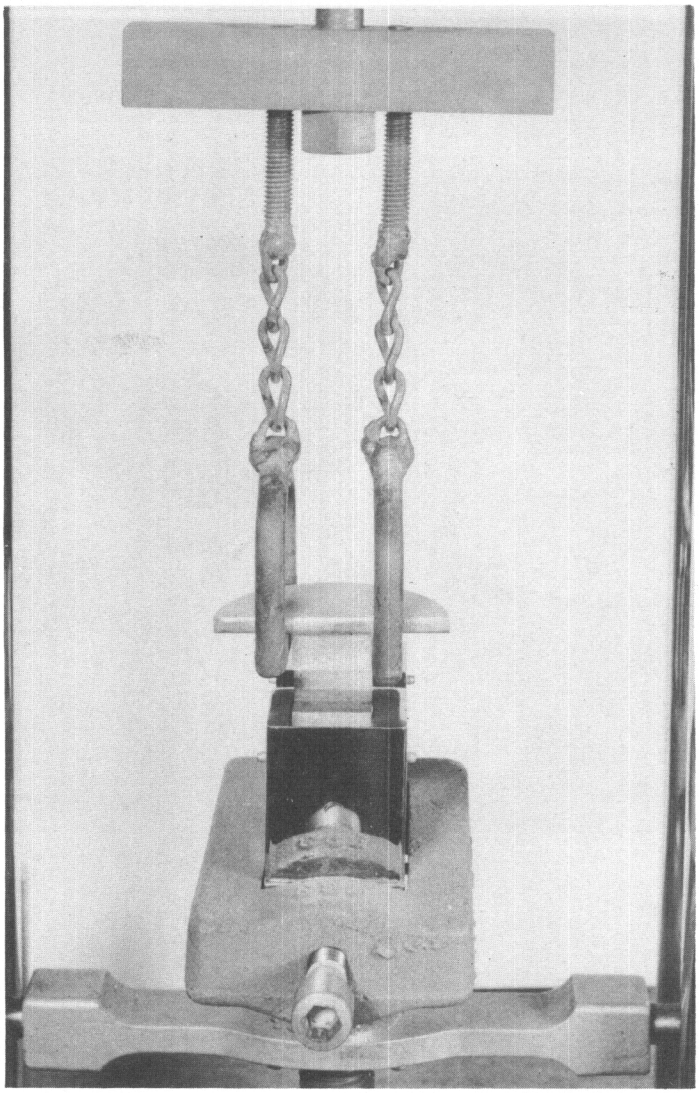


Figure 33. Tension Adhesion Testing with Dynamometer. A cast primed specimen is shown under test, before failure, in the tension jig of the dynamometer.

1. Adhesion in Tension - FS-1 Wrought Alloy

Adhesion in tension values for Dow #7 FS-1 specimens were twice as large as those for Dow #12 FS-1 specimens. However, tension values for FS-1 specimens showed considerable variation within each treatment type, due to the bending of the specimen before failure. This bending pulled the specimen away from the perimeter of the block, so that actual primer removal was concentrated in a small central area. This method was therefore considered unapplicable to the 0.040" FS-1 sheet and confined exclusively to the heavier cast forms.

2. Adhesion in Tension - Cast Alloys

The rectangular cast alloy specimens (3/8" x 1.5" x 3") with rough "as cast" surfaces were used initially in the tension adhesion tests. These specimens were air-dried five days after priming. Plastilock #601 (0.012" thick) was used as the adhesive in all tests, since it was especially suited to the irregular surfaces. It completely removed the primer in all cases.

The tension adhesion values obtained for untreated and Dow #7 and #12 treated specimens (Table No. 41) varied considerably because of the irregular surfaces involved. The "C" alloy surfaces were somewhat rougher than the "H" alloy, and this may explain the generally higher adhesion values for this alloy. In spite of the variation, the adhesion values shown in Table No. 41 indicate the superiority of the Dow #7 as an adhesive base.

The data shown in Table No. 42 were obtained from smooth, machined cast specimens. Tension values on these specimens were notably lower than those for the unmachined specimens and should therefore be more accurate. The "C" alloy when untreated was less adhesive to the primer than the "H" alloy, but when treated it was more adhesive. The lack of adhesion to the untreated "C" alloy may be due to the loose corrosion products formed during the pickling process which are especially hard to wash off on the "C" alloy.

Additional tension values were obtained using Plastilock #608. In these tests the primer was removed with the adhesive from both the Dow #7 and #12 surfaces.

The tension adhesion values shown in Table No. 43 have the same relative order of increasing adhesion as those reported previously with the Plastilock #601 adhesive: untreated "C" alloy, Dow #12 "H" alloy, Dow #12 "C" alloy, untreated "H" alloy, Dow #7 "H" alloy, and Dow #7 "C" alloy.

TABLE NO. 41

ADHESION IN TENSION

"AS CAST" "C" and "H" ALLOY SPECIMENS*

Specimen Type	Adhesion in Tension (psi)	Average Adhesion (psi)
C-Dow #7	1035	806
C-Dow #7	336	
C-Dow #7	1048	
C-Dow #12	502	499
C-Dow #12	523	
C-Dow #12	493	
C-Untreated	502	782
C-Untreated	978	
C-Untreated	867	
H-Dow #7	303	542
H-Dow #7	738	
H-Dow #7	585	
H-Dow #12	308	345
H-Dow #12	309	
H-Dow #12	418	
H-Untreated	695	590
H-Untreated	582	
H-Untreated	493	

NOTES: * Specimens 3/8" x 1.5" x 3" with rough "as cast" surfaces.

Adhesive used was Plastilock #601. It removed the primer completely from all specimens.

TABLE NO. 42

ADHESION IN TENSION

MACHINED "C" AND "H" CAST ALLOY SPECIMENS*

Specimen Type	Adhesion in Tension (psi)	Average Adhesion (psi)
H-Untreated	49	147
H-Untreated	269	
H-Untreated	122	
H-Dow #7	176	188
H-Dow #7	274	
H-Dow #7	102	
H-Dow #7	191	
H-Dow #12	44	48
H-Dow #12	22	
H-Dow #12	78	
C-Untreated	44	37
C-Untreated	22	
C-Untreated	49	
C-Untreated	34	
C-Dow #7	381	289
C-Dow #7	293	
C-Dow #7	200	
C-Dow #7	273	
C-Dow #12	176	137
C-Dow #12	147	
C-Dow #12	147	
C-Dow #12	78	

NOTES: Adhesive used was Plastilock #601. It removed the primer completely from all specimens.

* Specimens cut from 0.2" x 3" machined discs (smooth finish).

TABLE NO. 43

ADHESION IN TENSION

PRIMED "C" AND "H" CAST ALLOYS

Specimen Type	Adhesion in Tension (psi)	Remarks
Dow #7 "C" alloy	275	Primer removed
Dow #7 "C" alloy	147	Primer removed
Dow #7 "C" alloy	196	Primer removed
Dow #7 "C" alloy	166	Primer removed
Average	196	
Dow #7 "H" alloy	215	Primer removed
Dow #7 "H" alloy	152	Primer removed
Dow #7 "H" alloy	161	Primer removed
Average	176	
Dow #12 "C" alloy	113	Primer removed
Dow #12 "C" alloy	171	Primer removed
Average	142	
Dow #12 "H" alloy	132	Primer removed
Dow #12 "H" alloy	78	Primer removed
Average	105	
Untreated "C" alloy	49	Primer removed
Untreated "H" alloy	196	Primer removed
Dow #7 "C" alloy	83	Specimens from 134 day
Dow #7 "C" alloy	58	exposure in salt spray *
Dow #7 "H" alloy	108	Specimens from 134 day
Dow #7 "H" alloy	63	exposure in salt spray

NOTES: Adhesive used was Plastilock #608.

* Dow #12 primed specimens lost all of their primer in this exposure.

Dow #7 "C" and "H" alloy specimens from the 134 day salt spray exposure (p. 130) were tested for residual primer adhesion. Tension adhesion values were 85 psi for the Dow #7 "H" alloy and 71 psi for the Dow #7 "C" alloy. Cast Dow #12 specimens lost practically all of their primer in the exposure, and could not be tested.

Cast specimens immersed in water for 100 hours (Table No. 44) did not show any large reduction in tension adhesion (except the untreated "H" alloy specimen).

TABLE NO. 44

ADHESION IN TENSION - EFFECT OF WATER IMMERSION

PRIMED "C" AND "H" CAST ALLOYS

Specimen No.	Treatment	Adhesion in Tension (psi)	Remarks
H1011	Dow #7P	166	Primer removed
H1011	Dow #7P	150	Primer removed
C1061	Dow #7P	122	Primer removed
C1061	Dow #7P	195	Primer removed
H1016	Dow #12P	181	Primer removed
H1016	Dow #12P	49	Primer removed
C1054	Dow #12P	220	Primer removed
C1054	Dow #12P	156	Primer removed
H1028	Acetic-nitrate "pickled"	98	Primer removed

NOTES: Specimens were immersed for 100 hours in water at room temperature.

Adhesive used was Plastilock #608. It removed the primer completely from all specimens.

IV. WEATHERING TESTS

Three weathering tests were included in our test evaluation program for correlation with the accelerated corrosion resistance tests. The weathering exposures were:

(1) A 3% intermittent salt spray cabinet.
(2) A tropical humidity cycle cabinet.
(3) A marine atmosphere exposure in Florida.

In the salt spray cabinet, specimens were exposed to a spray of 3% NaCl solution at 35°C for five minutes per hour. (Approximately 20 milliliters of the NaCl solution was injected into the cabinet each hour.) The FS-1 specimens were supported in the cabinet with Lucite specimen holders and the cast specimens (machined discs, 3" x 0.2") with magnesium rod.

The tropical humidity cycle cabinet was maintained at 48°C and 95% relative humidity, except for two one-hour condensation periods each day when the temperature of the vapor was lowered to 23°C. The FS-1 specimens were supported by Lucite holders at an angle of 5° from vertical. No cast specimens were included in this exposure.

In the marine exposure, specimens were supported by magnesium rods above the ocean on a sailing vessel. Practically no spray came in contact with the specimens).

Specimens in each of the following four stages of preparation were included in each weathering test:

(1) Bare metal.
(2) Treated (Dow #7 or #12).
(3) Treated plus two coats of MIL-P-6889A primer.
(4) Treated plus two coats of primer plus MIL-L-7178 lacquer to specification thickness.

After exposure corrosion products were removed from the unprimed specimens with boiling 10% chromic acid and from primed and lacquered specimens with cold 10% chromic acid. (See Section I H.) Corrosion rates were determined in milligrams /day/ square decimeter (mdd.).

A. Salt Spray Exposure

1. Corrosion Rates of FS-1 Alloy

The salt spray cabinet (intermittent spray of 3% NaCl solution) was operated for 253 days. Bare and unprimed treated FS-1 specimens were removed after 182 days, since corrosion had progressed to the extent of general perforation. One primed specimen of each type was also removed at this time for comparison. The remaining primed and lacquered specimens were exposed for 253 days.

Corrosion rate averages (Table No. 45) indicated the following order of increasing corrosion resistance for unprimed specimens: untreated, Dow #7, and Dow #12. On primed specimens and lacquered specimens, however, the Dow #7 showed greater corrosion resistance than the Dow #12.

During the first several months of exposure the Dow #7 resisted corrosion better than the Dow #12. The higher final corrosion rate of the Dow #7 unprimed system (Dow #7, 16.19 mdd.; Dow #12, 9.78 mdd.) was believed due to the depletion of protective hexavalent chromium after a given time of exposure. This left the surface highly receptive to corrosion. The Dow #12 maintained a mechanical barrier throughout the exposure period and consequently maintained a more linear rate.

The lower corrosion rate of the Dow #7 primed system (Dow #7P, 1.42 mdd.; Dow #12P, 3.53 mdd.) correlates well with all other accelerated test measurements, i.e., pH increase, short circuit currents, gasometric rates, and adhesion measurements.

The superiority of the Dow #7 primed system was also shown by the lower corrosion rates of Dow #7 lacquered specimens (Dow #7L, 0.07 mdd., Dow #12L, 0.19 mdd.).

Other FS-1 specimens were removed from the salt spray at recorded intervals up to 69 days. The values in Table No. 46 show the low initial corrosion rate of the Dow #7. Apparently the corrosion rate of the Dow #7 treatment accelerates sometime after 69 days of exposure. Both Dow #12 and bare metal showed an initial increase in corrosion rate followed by a decrease which may have been caused by accumulation of corrosion products. The Dow #7 was initially about eight times more corrosion resistant than the untreated metal.

TABLE NO. 45

CORROSION RATES OF FS-1 ALLOY IN SALT SPRAY*

Specimen No.	Treatment	Corrosion Rate (mdd.)	Time of Exposure (days)
0646	Acetic-nitrate "pickled"	21.39	182
0650	Acetic-nitrate "pickled"	17.25	182
0649	Acetic-nitrate "pickled"	24.00	182
0652	Acetic-nitrate "pickled"	22.05	182
0643	Acetic-nitrate "pickled"	22.90	182
Average		21.52	
0433	Dow # 7	19.50	182
0435	Dow #7	16.80	182
0448	Dow #7	15.75	182
0434	Dow #7	15.10	182
0431	Dow #7	13.80	182
Average		16.19	
0327	Dow #12	10.10	182
0286	Dow #12	8.43	182
0289	Dow #12	7.64	182
0335	Dow #12	9.60	182
0285	Dow #12	13.10	182
Average		9.78	

* Intermittent spray of 3% NaCl solution at 35°C (5 minutes per hour).

TABLE NO. 45 (Cont'd)

CORROSION RATES OF FS-1 ALLOY IN SALT SPRAY

Specimen No.	Treatment	Corrosion Rate (mdd.)	Time of Exposure (days)
0416	Dow #7P*	1.17	182
0465	Dow #7P	1.40	253
0430	Dow #7P	1.42	253
0426	Dow #7P	1.33	253
0425	Dow #7P	1.52	253
Average (253 days)		1.42	
0303	Dow #12P	2.62	182
0282	Dow #12P	4.40	253
0296	Dow #12P	3.72	253
0281	Dow #12P	3.08	253
0338	Dow #12P	2.92	253
Average (253 days)		3.53	
0446	Dow #7L**	0	253
0455	Dow #7L	0.065	253
0447	Dow #7L	0.017	253
0436	Dow #7L	0.195	253
Average		0.070	

* P = primed.

** L = lacquered.

TABLE NO. 45 (Cont'd)

CORROSION RATES OF FS-1 ALLOY IN SALT SPRAY

Specimen No.	Treatment	Corrosion Rate (mdd.)	Time of Exposure (days)
0307	Dow #12L	0.44	253
0308	Dow #12L	0.10	253
0329	Dow #12L	0.24	253
0283	Dow #12L	0.15	253
0297	Dow #12L	0.027	253
Average		0.19	

TABLE NO. 46

CORROSION RATE CHANGE WITH TIME - FS-1 ALLOY IN SALT SPRAY

Specimen No.	Treatment	Corrosion Rate (mdd.)	Time of Exposure (days)
1749	Dow #7	3.11	14
1602	Dow #12	8.95	14
1720	Acetic-nitrate "pickled"	25.50	14
1748	Dow # 7	3.43	28
1597	Dow #12	8.53	28
1727	Acetic-nitrate "pickled"	30.60	28
1732	Dow #7	6.80	42
1457	Dow #12	11.80	42
1719	Acetic-nitrate "pickled"	29.60	42
1735	Dow #7	3.07	58
1493	Dow #12	11.40	58
1721	Acetic-nitrate "pickled"	26.20	58
1739	Dow #7	4.45	69
1479	Dow #12	7.15	69
1717	Acetic-nitrate "pickled"	21.80	69

2. Corrosion Rates of Cast Alloys

Cast alloy corrosion rates shown in Table No. 47 were obtained from a 134 day exposure. The corrosion rates indicated the following order of increasing corrosion resistance: untreated "C" alloy, untreated "H" alloy, Dow #7 "C" alloy, Dow #12 "C" alloy, Dow #12 "H" alloy, and Dow #7 "H" alloy. This rating is in good agreement with pH increase data and gasometric rates. There was not much difference in rate between the Dow #12 "C" and "H" alloys, although the "H" alloy had a slightly lower rate (as in the pH increase method).

As with the FS-1 alloy specimens, the Dow #12 primed "C" and "H" alloy specimens gave higher corrosion rates than the Dow #7 primed specimens. This result is also in agreement with all other tests.

The corrosion rates for the lacquered specimens were so low that the difference may not be especially significent. However, the Dow #12 lacquered specimens gave the highest rates.

B. Tropical Humidity Exposure

The tropical humidity cabinet was operated for 262 days. Corrosion rates (Table No. 48) obtained in this environment were small, but the order of increasing corrosion resistance of the treatments on unprimed, primed, and lacquered FS-1 specimens was the same as in the salt spray:

(1) Unprimed specimens - untreated, Dow #7, Dow #12.
(2) Primed specimens and lacquered specimens - Dow #12, Dow #7.

The loss of protective capacity by the Dow #7 on unprimed specimens was also noted in this test. Dow #12 primed specimens lost most of their primer, which accounts for their higher corrosion rates.

C. Marine Atmosphere Exposure

Cast and wrought specimens from the 160-day marine atmosphere exposure in Florida showed almost negligible corrosion. A rate of 5.58 mdd. was determined on bare FS-1. Corrosion on the other specimens was considered insufficient to measure. An exposure of one year is recommended in order to obtain measurable corrosion.

TABLE NO. 47

CORROSION RATES OF "C" AND "H" ALLOYS IN SALT SPRAY

(134-Day Exposure)

Specimen No.	Treatment	Corrosion Rate (mdd.)
C1087	Acetic-nitrate "pickled"	70.5
C1086	Acetic-nitrate "pickled"	72.4
C1088	Acetic-nitrate "pickled"	54.3
Average		65.7
H1034	Acetic-nitrate "pickled"	88.4
H1027	Acetic-nitrate "pickled"	67.0
H1035	Acetic-nitrate "pickled"	34.2
Average		63.2
C1070	Dow #7	54.6
C1074	Dow #7	51.5
C1079	Dow #7	28.9
Average		45.0
H1043	Dow #7	22.7
H1045	Dow #7	14.4
H1049	Dow #7	27.0
Average		21.3
C1055	Dow #12	107 (discarded)
C1066	Dow #12	52.6
C1065	Dow #12	32.0
Average		42.3
H1017	Dow #12	34.7
H1009	Dow #12	34.1
H1013	Dow #12	42.7
Average		37.2

TABLE NO. 47 (Cont'd)

CORROSION RATES OF "C" AND "H" ALLOYS IN SALT SPRAY

(134-Day Exposure)

Specimen No.	Treatment	Corrosion Rate (mdd.)
C1078	Dow #7P*	0.9
C1080	Dow #7P	0.9
H1042	Dow #7P	1.3
H1041	Dow #7P	0.9
C1053	Dow #12P	3.7
C1057	Dow #12P	1.6
H1014	Dow #12P	1.2
H1022	Dow #12P	11.7
C1081	Dow #7L**	0.1
C1072	Dow #7L	0.2
H1038	Dow #7L	0.4
H1036	Dow #7L	0.1
C1067	Dow #12L	0.2
C1052	Dow #12L	0.5
H1018	Dow #12L	0.8
H1025	Dow #12L	0.3

* P= primed
** L= lacquered

TABLE NO. 48

CORROSION RATES OF FS-1 ALLOY IN TROPICAL HUMDIITY

(262-Day Exposure)

Specimen No.	Treatment	Corrosion Rate (mdd.)
0751	Acetic-nitrate "pickled"	0.85
0750	Acetic-nitrate "pickled"	0.77
0757	Acetic-nitrate "pickled"	0.65
0746	Acetic-nitrate "pickled"	0.87
Average		0.78
0783	Dow #7	0.78
0781	Dow #7	0.71
0702	Dow #7	0.78
0704	Dow #7	0.70
Average		0.74
0317	Dow #12	0.70
0321	Dow #12	0.44
0324	Dow #12	0.35
0318	Dow #12	0.84
Average		0.58
0458	Dow #7P*	0.70
0454	Dow #7P	0.76
0490	Dow #7P	0.62
0442	Dow #7P	0.67
Average		0.69

* P= primed

TABLE NO. 48 (Cont'd)

CORROSION RATES OF FS-1 ALLOY IN TROPICAL HUMIDITY

(262-Day Exposure)

Specimen No.	Treatment	Corrosion Rate (mdd.)
0310	Dow #12P	2.00
0304	Dow #12P	1.69
0336	Dow #12P	1.82
0299	Dow #12P	1.85
Average		1.84
0798	Dow #7L*	0.19
0708	Dow #7L	0.31
0710	Dow #7L	0.30
0728	Dow #7L	0.32
Average		0.28
0332	Dow #12L	0.37
0290	Dow #12L	0.50
0306	Dow #12L	0.33
0301	Dow #12L	0.49
Average		0.42

*L = lacquered

V. CONCLUSIONS

The adhesion and corrosion tests included in our test evaluation program indicated that the corrosion resistance of the finished magnesium protective system, i.e., treated, primed, and lacquered, depends more on the adhesion between the primer and the treatment or the treatment and the base metal than on the corrosion rate of the particular treatment. Only small corrosion rate differences were noted for the various treatments, but large differences were noted in the paint adhesion.

The corrosion resistance afforded by a properly applied primer-lacquer system far exceeds the difference in resistance afforded by variations in the treatment.

A. Summary of Test Results

1. Corrosion Resistance Tests

Good correlation was obtained between the corrosion rates on unprimed treated magnesium alloys determined by the following accelerated laboratory tests:

(1) pH increase rate, and
(2) Hydrogen evolution rate (gasometric method).

Treated magnesium alloys which were primed with zinc chromate primer (Specification MIL-P-6889A) gave corrosion rates in accelerated laboratory tests which correlated well with rates in the weathering exposures.

The gasometric test was critical in its evaluation of unprimed treated specimens within 5 hours and of primed specimens in 7 days. The Dow #7 treatment gave lower hydrogen evolution rates in 1.0N KCl than the Dow #12 on all alloys tested. The highest evolution rates were obtained on under-treated specimens. Corrosion rates obtained with this method have the advantage of being independent of the electrical resistance properties of the treatment.

The pH increase method also gave lower values for the Dow #7 than the Dow #12. This method is convenient for qualitative studies and for correlation purposes, but it is too insensitive to distinguish between good and poor treatments, especially on unprimed specimens.

The electrical open circuit potential and short circuit current measurements on unprimed specimens gave smaller values for Dow #12 specimens than for Dow #7 specimens, due in part to the greater electrical resistivity of the Dow #12 treatment. These lower values did not correlate with the higher corrosion rate values obtained in the pH increase and gasometric tests.

The extent of failure of primed systems, however, was conveniently determined by the short circuit current test within a two hour test period.

The corrosion rate of the Dow #7 treatment in a nonconfining environment such as the salt spray exposure was nonlinear and failed to correlate with the results of tests in stagnant corrosion media. This phenomenon is due to the depletion of the protective chromium ions after a given time of exposure.

2. Adhesion Tests

The shear and tension adhesion tests showed measurable differences between the various treatments. The Dow #7 and the light Dow #17 gave the best overall adhesion values to the zinc chromate primer. Heavy alkaline anodic treatments or powdery dichromate treatments gave low adhesion values.

B. Conclusions

We recommend that additional performance tests be made on primed and finished protective systems on magnesium alloys wherein all common variations of treatment types, as well as variations resulting from commercial fabrication, are included. The data from these tests should be analyzed statistically in order to establish practical performance limits.

The performance tests should include gasometric (agitated type) or short circuit current tests for corrosion resistance and shear and tension adhesion tests.

The adhesion tests should include further investigation of the effect of aging. In this respect various aging techniques should be checked for correlation with the one hour boiling water immersion test. Perhaps in its final development, the adhesion test alone will suffice in qualifying magnesium alloy treatments.

C. Procedures for Best Test Methods

1. Gasometric Determination of Hydrogen Evolution Rates

The corrosion resistance test method considered most promising is the gasometric method. The following procedure is recommended for cast and wrought alloy specimens:

Construct a cell of type 1(Figure 34) for the magnetic stirrer method or of type 2 (Figure 34) for the shaker cell technique. Measure the dimensions of all specimens to the nearest 0.001 inch.

(Left) Type 1. With Magnetic Stirrer.

(Right) Type 2. Fermentation or Shaker Type.

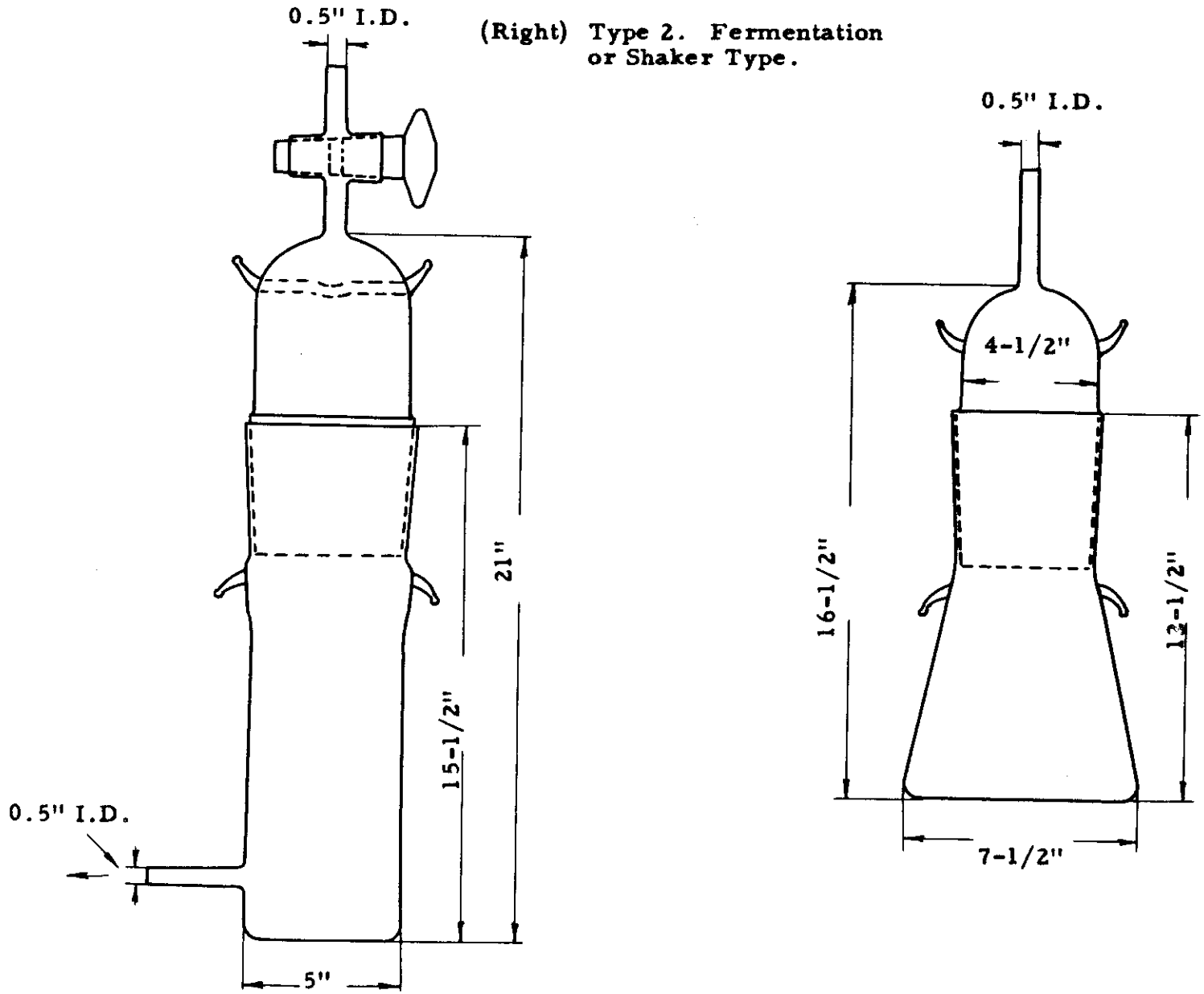


Figure 34. Gasometric Cells.

If the type 1 cell is used, attach it to a 10 milliliter microburette with Tygon plastic tubing from the bottom of the cell. Place the magnetic stirrer (Teflon covered) in the bottom of the cell. Suspend the cast or wrought alloy specimen with a nylon filament from the top of the cell. Grease the center glass ground joint thoroughly with silicone grease, and close the cell. Attach springs to hold the top and bottom together. Fill the cell by running the 1.0N KCl down the microburette, until the cell is completely full and the level of the 1.0N KCl in the microburette is near the 9.0-10.0 mark. Close the ground glass valve at the top of the cell.

Support the complete assembly in an upright position in a constant temperature water bath at 25° C. (A nine gallon battery jar is suitable for this bath.) Start the magnetic stirrer. After about 10 minutes, take a volume reading on the microburette by leveling liquid levels in the burette and the cell. Record the volume increase after 5 hours or at hourly intervals for eight hours. Record the barometric pressure with all volume readings.

If the type 2 cell is used, place the specimen in the bottom of the cell. Fill the bottom cell only to the ground glass joint. Attach the cell to a 10 milliliter microburette with Tygon tubing from the top of the cell. Clamp the cell to a reciprocating arm operating in a constant temperature water bath at 25°C. Take volume readings in the same manner as with the type 1 cell. The temperature variations in the room, as well as the barometric pressure, must be recorded with each volume reading in this method, since the microburette for measuring the hydrogen evolved is above the constant temperature bath.

Convert the measured hydrogen volumes to standard dry conditions (see p. 66). Calculate hydrogen evolution rates in ml./min./10 sq. in. with either of the following formulas:

$$\text{Average rate} = \frac{V_n}{t_n}$$

$$\text{Final rate} = \frac{V_n \quad (V_{n-1})}{t_n - (t_{n-1})}$$

Where: V - volume.

t = total time of immersion.

n = final reading.

n-1 = next to final reading.

The second formula can also be used to calculate the rate over a particular one-hour interval.

Compare the gasometric rates for different treatments at one given immersion time (usually 5 hours).

2. Shear and Tension Adhesion Tests

The following procedure is recommended for shear adhesion tests of 1.5" x 3" x 0.040" primed FS-1 wrought alloy specimens:

Dry the specimens for at least three days, preferably six days after priming. Measure the length and width of each specimen to the nearest 0.001 inch.

Place a 1.0" x 0.12" piece of Plastilock #608 adhesive tape (B. F. Goodrich Co.) between a 1.0 inch lap made with two similar specimens. Place the lapped specimens between heat resistant cellophane and press in a Carver press for 10 minutes at 150° - 152°C, 40 pounds platen pressure.

Allow the specimens to cool after removal from the press and then trim off the excess adhesive tape around the edges of the lap joint. Measure the overall length of the lapped specimens.

Place a specimen in a dynamometer and pull to failure in a direction parallel to the long axis of the specimen with an applied force of 600-1000 pounds per minute (Figure 31). Calculate shear adhesion in psi.

The following procedure is recommended for tension adhesion tests of primed cast alloy specimens:

Use specimens with smooth machined surfaces. They may be plate specimens 1.5" x 3" x 0.37" or specimens obtained by cutting 0.2 inch thick discs from cast rod stock 3 inches in diameter and cutting the discs into two semicircular pieces. The specimens should be dried for at least three days, preferably six days, after priming.

Seal a cast aluminum "T" block machined as shown in Figure 32 (facial dimensions: 1" x 1"; leg dimension: 0.3" x 1") to each primed specimen with a 1.0" x 0.12" piece of Plastilock #608 adhesive tape (B. F. Goodrich Co.). Place the specimens in a Carver press for 15 minutes at 150° - 152°C, 40 pounds platen pressure. Allow the specimens to cool after removal from the press and trim off the excess adhesive tape around the perimeter of the aluminum block.

Place the aluminum block in the chuck of a dynamometer, with the specimen held in suitable stirrups (Figure 33). (Level the stirrups with a spirit level before securing the aluminum block to the chuck.) Pull the aluminum block from the specimen with a force applied at 600-1000 pounds per minute. Calculate tension adhesion in psi.

GLOSSARY

1. FS-1 Wrought Alloy: Sheet magnesium alloy AZ-31 of Federal Specification QQ-M-44.
   Wrought FS-1-H24 sheet alloy was obtained from Dow Chemical Co.

2. "C" Cast Alloy: Sand casting magnesium alloy AZ-63 of Federal Specification QQ-M-56.
   Dowmetal "C" was obtained from Dow Chemical Co.

3. "H" Cast Alloy: Sand casting magnesium alloy AZ-92 of Federal Specification QQ-M-56.
   Dowmetal "H" was obtained from Dow Chemical Co.

4. Dow #7 Treatment: Type III acid dichromate treatment of Military Specification MIL-M-3171A (Magnesium Alloys, Processes for Corrosion Protection of). Dow Chemical Co.
   Specification Dow #7: 30 minutes in dichromate bath at pH = 4.2-5.2 ("Dow #7" in text refers to this treatment).
   Light Dow #7: 20 minutes in dichromate bath at pH = 5.2-5.4.
   Heavy Dow #7: 30 minutes in dichromate bath at pH = 3.5-4.0.

5. Dow #12 Treatment: Alkaline anodic treatment of Military Specification MIL-M-3171A (Magnesium Alloys, Processes for Corrosion Protection of); metal used as anode in treatment bath. Dow Chemical Co.
   Specification Dow #12: 20 minutes at 15 amperes per square foot (A.S.F.) in anodic treatment bath ("Dow #12" in text refers to this treatment).
   Light Dow #12: 5 minutes at 15 A.S.F. in anodic treatment bath.
   Heavy Dow #12: 35 minutes at 15 A.S.F. in anodic treatment bath.

6. Iridite #15: Acid chromate dip for magnesium alloys; similar to Dow #7. Allied Research Products Co.

7. Dow #17: Anodic treatment for magnesium alloys. Dow Chemical Co.

8. Primer: Zinc chromate primer of Military Specification MIL-P-6889A.

9. Lacquer: Top-coat aluminized lacquer of Military Specification MIL-L-7178.

10. Shear Adhesion Test: Lap joint specimens are pulled to failure in a dynamometer with a force applied parallel to their long axis.

11. Tension Adhesion Test: Specimens are pulled to failure in a dynamometer with a force applied perpendicular to their long axis.

12. Gasometric Method: Method for determining the rate of hydrogen evolution when magnesium alloys corrode in a salt solution.

APPENDIX

APPENDIX A

LITERATURE SEARCH

The following is a summary of pertinent information from the literature survey. Specific reference to the bibliography at the end is indicated by the numbers in parentheses.

General Information

Because of the wide variation in the environment to which magnesium alloys used in aircraft construction are subjected, the corrosion process itself varies greatly. Thus, such metal surfaces may be exposed to

Rainfall (inland), fog, sunshine.
Salt spray at sea coasts.
Galvanic coupling with other materials of construction.
Mechanical stress.
Erosion of corrosion products due to velocity of air movement.

It would seem unlikely, therefore, that any laboratory corrosion test could simulate all of these service conditions. Laboratory tests must also accelerate the corrosion rate beyond that usually occurring in service.

Nevertheless, early corrosion testing centered about a crude duplication of some natural environment. Consequently, the salt spray and humidity cabinet tests were developed with a great deal of effort on standardization. Sea water was used and later salt solutions replaced the natural product. At present 3% and 20% sodium chloride solutions are commonly used. These tests suffer for lack of reproducibility and represent corrosion peculiar to that environment.

Corrosion testing (references 9, 16, 17, 21, 23, 24, 29, 30, 43, 44) continued to develop with better physical testing procedures and advances in instrumentation. Today more reliance is placed on instrumental procedures in which absolute control and reproducibility of environment are possible. More emphasis is being placed on the electrochemical nature of corrosion due to the accuracy with which electrical measurements can be made and confirmation of theory by test results (37-39).

The interpretation of test results must be made with caution, as results obtained are only specific for the particular conditions of the test and do not necessarily reflect service conditions. It should be possible, however, to evaluate the protective value of surface treatments under a number of specific environments and, consequently, to judge their respective values in the field.

Magnesium alloys have been formulated for maximum corrosion resistance and for specified mechanical properties. Controlled purity alloys have markedly reduced the inherent corrosion of the base metal (8, 56, 57). Particularly effective has been the reduction of the iron and nickel content below critical limits. However, each alloy is specific in its corrosion response in a given environment, and considerable variation is possible between similar specimens (6, 7, 35).

The mechanism of corrosion (10, 12, 13, 18, 25, 26, 31, 35, 40, 46, 56, 57) is electrochemical in nature (10, 20, 59) when occurring in a liquid environment. Many investigators believe corrosion in all environments is so governed.

Since the products of magnesium alloy corrosion are for the most part hydroxides and oxides of magnesium and are loosely held to the surface, other chemical pretreatments (3, 11, 14, 15, 19, 28, 34, 41, 47, 50, 51, 62) have been developed which form adherent protective films.

Fluorides, chromates, and anodic ceramic films make up the bulk of these chemical and electrochemical treatments. There are other less pertinent methods of corrosion control (42) which have not been discussed here.

With regard to the specific phases of this project, the following information is of interest.

A. Corrosion Resistance

1. Protection Against Corrosion

Magnesium alloy surfaces are generally protected against corrosion by a combination of process treatments such as:

(1) Manufacture of controlled composition alloys having inherent corrosion resistance. These are intended to minimize the amount of cathodic impurities.

(2) Special cleaning procedures which include grinding, buffing, alkali, solvent, and acid processing. These remove surface impurities such as oils, dirt, and mill scale. Mill scale is especially undesirable as it forms local corrosion cells. The alloy surface is also made more receptive to successive treatments.

(3) Chemical and electrochemical treatments following cleaning. Oxidizing acids form protective salt films which function as surface passivators. Soluble chromate ions block anodic reaction in solution corrosion. The following processes are used:

(a) Treatment with oxidizing acids such as chromates. Acid salts formed with nonoxidizing acids act as adherent barriers to the corroding medium.

(b) Treatment with nonoxidizing acids which form adherent, insoluble salt films; i.e., hydrofluoric acid.

(c) Application of ceramic anodic coatings, using an external current, to the metal as cathode in an alkaline solution.

(4) Application of zinc chromate primers. This treatment further retards penetration of the surface by water or air. Soluble chromate ion is again involved in protecting against anodic attack.

(5) Application of aluminized lacquers greatly inhibits corrosion and forms the final barrier to corroding environments. Synthetic resins are selected with desirable film properties. The presence of metallic aluminum further reduces penetration because of its plate-like structure.

2. Corrosion Resistance Evaluation

The literature available in the corrosion field is voluminous. However, information specifically relevant to magnesium is limited. A generalized but thorough study of the factors involved in corrosion has been made by Uhlig (1) and Champion (2). Many test procedures are cited without any specificity to given conditions or materials.

The following accelerated laboratory tests for corrosion resistance testing are presented in the literature and were considered for this project:

(1) Salt spray tests (6, 7, 9, 16, 23, 27); both intermittent and continous and with 3% and 20% sodium chloride solutions. These tests are used extensively. However, they exhibit poor correlation and reproducibility and little dependence can be placed on them. Intermittent sprays are considered best for aluminum-magnesium corrosion. The weight loss/area/time is determined.

(2) Immersion tests (1, 2, 30):

(1) Complete immersion.
(2) Alternate immersion.

This test as well as the salt spray is time consuming and results are often questionable. Variation between specimens of the same species makes interpretation difficult. Weight loss/area/time is determined.

(3) Humidity cabinets, weatherometers, outdoor exposure.

These tests more nearly simulate service conditions than most tests. However, they are time consuming; i.e., often months are required for determinable corrosion rates. Again, they represent corrosion specific to a given set of conditions.

(4) Potential measurements and electrochemical tests (4, 10, 48, 52, 53, 58, 60, 61). These tests represent a newer and very promising approach to the study of corrosion. Considerable information can be obtained from the determination of relative potentials of treated metals in an electrolyte and the potential change with time. These data are especially indicative of film failure and/or repair. Several methods of this type are useful.

a. Direct and Indirect Methods

These are based on voltage and current measurements of corroding cells. Measurements are usually made with equipment designed not to interfere with the corrosion process. An example is potentiometric determinations of voltage in which no current is drawn from the cell. Current determinations can also be made by short circuiting the cell through a one ohm resistance and measuring the IR drop with the same potentiometer.

b. Polarography (48-52, 53-60)

Methods have been developed for the measurement of minute quantities of dissolved metal salts in solution; or determination of the change in concentration of a corrosive constituent as it reacts with the metal and is removed from solution. For example, the concentration of the aluminum, zinc, and magnesium may be determined in a given electrolyte after immersion of the specimens for a given time. Also, changes in concentration of oxygen and carbon dioxide may be measured.

c. Potential-Time Curves

Open circuit potentials of a corroding specimen against a reference electrode are recorded with time. The determination of whether the metal is active or passive and how the protective film functions is possible. Film failures are easily detected by this method.

d. Resistance and/or Conductance Measurements

Changes in electrolytic conduction with contamination by corrosion products are determined. The evaluation of resistance changes of dilute electrolytes or surface resistance changes due to accumulation of corrosion products is feasible.

e. Current-Density Curves

The current density varies with the application of a constant current with the sample first as anode, then as cathode. The variation of current with time is recorded. Leakage current after anodization is a measure of soluble film constituents as well as of film porosity.

f. Boiling Nitric Acid Test (Huey Test)

This test has been standardized (ASTM) for testing stainless steels. However, it does not appear to be useful for magnesium alloys.

g. Oxidation at Elevated Temperatures (21)

Tests are made in a controlled atmosphere at appropriate temperatures. Weight changes with time are recorded. This method is not well adapted to magnesium alloys or to painted surfaces.

h. Microscopic Examination (45)

This method is not an accurate quantitative evaluation of corrosion, but is useful in the examination of the corrosive products and the type of corrosion.

i. Gravimetric Methods (22, 33, 38)

The determination of loss or gain in weight is convenient if bare metal is considered. Where protective coatings are involved other factors must be considered. Gravimetric methods can be used to determine corrosion products formed, but these are sometimes tedious, especially in the presence of interfering substances.

j. Spectrographic Methods (27)

Spectrographic analysis is a useful tool, although lacking in sensitivity for this purpose.

k. Radiographic Methods (X-Rays)

A beam of penetrating radiation is passed into the metal. Radiographs of transmitted radiation are compared before and after corrosion. At present this method is useful only for qualitative examinations.

l. Loss in Mechanical Properties

Types of measurements made after exposure to the corroding environment are:

(1) Loss in tensile strength.
(2) Flexural strength.
(3) Change in elastic modulus.
(4) Percent elongation.

These methods are not conveniently adapted to the problem at hand. Sample preparations after corrosion exposure are time consuming.

m. Changes in Optical Properties (36)

(1) Measurement of specular reflection.
(2) Measurement of the change in reflectivity with an optical smoothness meter.

These methods are not applicable to coated specimens.

n. Absorption of Fluorescent Liquids (2)

A fluorescent solution is applied to the surface under study. Absorption into cracks in films is rated under ultraviolet exposure. This method is not sufficiently sensitive for our purposes.

o. Ultrasonic Vibrating Methods (32)

These permit measurement of the thickness of metal; however, they are not sensitive to pit type corrosion.

p. Gamma Rays

Inspection of metal parts is possible with these rays. Corrosion assessment is determined by the uniformity of transmission through the specimen. This method is not sensitive enough for our purposes.

q. Gasometric Measurements (1, 2)

Under wet conditions the evolution of hydrogen or absorption of oxygen or both may be measured as a specimen corrodes. Magnesium corrosion liberates hydrogen in a solution free of oxidizing agents. It is possible to calculate the amount of magnesium solubilized from the hydrogen data with resultant checks by polarographic methods.

r. pH Measurements

The pH of sea water and other electrolytes is increased by the corrosion of magnesium and its alloys. Observation of the rate increase with time would indicate the corrosion rate. An increase in pH would indicate the breakdown of protective films on metals. An important advantage is the possibility of measurement with standardized readily available laboratory equipment.

s. Indicator Methods (5, 54)

Color changes produced in a liquid environment on introduction of metal ions or indicator reactions at anodic areas have been used. Magnesium, however, does not lend itself to color reactions, and these methods also lack sensitivity.

The preceding methods represent the principal attacks used by the other investigators. Many other refinements have been developed, but the modified methods generally have not been accepted as standard tests. The most promising procedures selected for investigation in this project included:

(1) Electrochemical measurements.
(2) Change in hydrogen ion concentration.
(3) Gasometric analysis.

B. Suitability as a Paint Base

Accepted adhesion testing methods are listed by Gardner (49). These consist essentially of adhesively binding a cloth or metal with the material in question and removing it under standard conditions. The force per unit area to remove the material is determined and is a measure of the adhesive forces existing at the interfaces.

Tests fall into three general categories, being dependent on:

(1) Direct tensile pull.
(2) A cutting or scratching action.
(3) Deformation of the base.

Impact and abrasion tests have also been used to determine the degree to which a coating maintains continuity of coverage, hence also its adhesion.

Since most investigators have developed test methods particularly applicable to their needs (32, 63), a similar approach was contemplated for this project. Initially, modifications of the above tests were used.

BIBLIOGRAPHY

1. H. H. Uhlig (Mass. Inst. of Tech., Cambridge), "The Corrosion Handbook," John Wiley & Sons, Inc., 1948, 1188 pp.

2. F. A. Champion, "Corrosion Testing Procedures," John Wiley & Sons, Inc., 1952, 369 pp.

3. W. F. Higgens, "The Protection of Magnesium Alloys," Electroplating 3, No. 8, 287-91 (1950).

4. W. Jellinghaus, "Magnetic and Electrical Processes for Nondestructive Testing of Metallic Pieces," Metaux Corrosion, Inds. 27, 34-43 (1952).

5. S. Tanimoto and K. Morita (Asahi Glass Ind. Co., Makiyama, Yahata), "Microcolorimetric Determination of Magnesium with Titan Yellow," Chem. Analysis and Reagents 3, 153-8 (1950).

6. E. R. W. Jones and M. K. Petch (Selected Gov't. Reports, London), "Variations in Corrosion Properties on Different Parts of Magnesium Alloy Sheets," Protection and Electro-Deposition of Metals 3, 171-84 (1951).

7. L. F. LeBrocq and T. L. Williams, "Tropical Corrosion Tests on Magnesium Alloy Sheet in Contact with Other Metals," ibid, 3,224-6 (1951).

8. F. A. Fox, "Magnesium Alloys Research" (London), 5, 77-81 (1952).

9. F. L. LaQue (Internat. Nickel Co., New York) "Corrosion Testing," Proc. ASTM 51, 89 pp. (1951).

10. R. Audubert, "Theory of Overpotential and the Mechanism of Corrosion," J. Chim. Phys. 49, No. 7-8, C97-104 (1952).

11. M. Froger and H. A. Evanbelides, "Getting the Most from HAE Coatings," Metal Progress 62 (Sept. 1952), 81-4.

12. R. C. L. Bosworth, "The Five Properties Concerned in the Transport of the Active Corrodant Agent," J. Proc. Roy. Soc., M. S. Wales 85, Pt. 1, 53-8 (1950).

13. I. M. Parker, "The Literature on Corrosion," Corrosion 7, 450-4 (1951).

14. V. F. Henley, "The Surface Treatment of Aluminum and Magnesium," Light Metals 14, 378-88 (1951).

15. Tukasa Kawamura (Furakawa Elec. Co.), "Anticorrosive Treatments for Magnesium," Proc. First World Met. Congr., Am. Soc. Metals 1951, 645-50.

16. J. Hudson, et al., "Second Report of the Methods of Testing Corrosion," J. Iron Steel Inst. (London) 171, 255-72 (1952).

17. E. C. Holmberg, "Corrosion Testing. A Tool of Conservation," Chem. Eng. Progress 48, 377-80.

18. G. Schikorr, "Inverse Dependence of the Corrosion of Metals upon a Few Factors," Metal 6, 356-60 (1952).

19. L. W. Haase, "The Formation of Covering and Protective Films," Werkstoffe u. Korrosion 3, 198-205 (1952).

20. F. Todt, "The Limits of the Electrochemical Investigation of Corrosion Processes and Oxygen Contents," Werkstoffe u. Korrosion 3, 205-9 (1952).

21. I. A. Makolkin, "The Oxidation of Magnesium and its Alloys at High Temperatures," J. Applied Chem. USSR 24, 505-13 (1951) (Engl. translation).

22. E. C. Pigott (West Hartlepool Engl.), "Metallurgical Microanalysis," Metal Treatment 19, 147-54 (1952).

23. T. P. May and A. L. Alexander (Internat. Nickel Co.), "Spray Testing with Natural and Synthetic Sea Water," Proc. ASTM 50, 1131-41; also II, "A Study of Organic Coatings," ibid. 1144-50

24. E. Gasior (Prace Glownego Inst.), "Methods and Apparatus Used in Testing of Resistance of Metals to Stress Corrosion," Metal 3, 241-50 (1951).

25. U. R. Evans (Cambridge Univ., Engl.), "Corrosion of Metals -A Historical Treatment," Chem and Ind. 986-93 (1952).

26. H. Sawamura and S. Yamaguchi (Sci. Res. Inst., Tokyo), "Metallic Corrosion and Thixotropy," Repts. Sci. Res. Inst. (Japan) 28, 85 (1952).

27. E. C. Mills and S. E. Herman (Heavy Duty Alloys, Ltd., Slough, Engl.), "Comparison of Some Simple Condensed Spark Circuits in the Spectrographic Analysis of Aluminum and Magnesium Alloys and Pure Magnesium," Metallurgia 46, 213-15 (1952).

28. H. G. Cole, "Tests on Some Special Base Paints for the Protection of Magnesium Alloys, "Selected Govt. Res. Repts. (London), Paints 2, 35-48 (1949).

29. R. F. Hanstock, "The Nondestructive Testing of Metals," 1951, 163 pp.

30. Chuk, Ching Ma (Tulane Univ., New Orleans), "Alternate Immersion-Corrosion Test Equipment," Ind. Eng. Chem. 44, 583-5 (1952).

31. A. Marsden, "Corrosion, Its Causes and Prevention," Ind. Finishing (London) 4, 697-9 (1952).

32. H. Drainer and E. Krainer (Gebr. Bohler & Co., Kapfenberg, Austria), "Nondestructive Testing of Materials with Ultrasonics," Radex Rundschau (1951), 323-9, cf. Felix, Radex Rundshau (1951), 167-77.

33. J. Davidson (Rowett Res. Inst.), "Microdetermination of Magnesium in Plant Materials with 8-Quinolinol," Analyst 77, 263-8 (1952).

34. M. K. Petch (Selected Govt. Res. Repts.) (London), "Protection of Magnesium Alloys against Corrosion by Electrolytic Chromate Films," Protection and Electro-Deposition of Metals 3, 216-23 (1951).

35. L. Rakowski, "The Influence of Surface Contamination on the Corrosion of Magnesium Sheet to Specification DTD 118," ibid. 3, 187, 215 (1951).

36. H. Thielsch (Welding Res. Council, New York), "Visual and Optical Evaluation of Metal Surfaces," Metal Finishing 49, No. 5, 54-61 (1952).

37. F. L. LaQue, "Critical Look at Salt Spray Tests," Materials and Methods 35, Feb. 1952, 77-81.

38. A. J. Carwardive, "The Analytical Chemistry of Magnesium," The Chemical Age 67, No. 1722, 47-52 (1952).

39. F. L. LaQue and B. B. Knopp, "Planning and Interpreting Corrosion Tests," Corrosion and Metal Protection 2, 17-23 (1945).

40. J. D. Hanawalt, et al., "Corrosion Studies of Magnesium and Its Alloys," Metals Technology 8, No. 6 (1941).

41. J. G. Jewell (Gulf Res. & Revel. Co., Harmarville, Pa.), "Chemical Treatment to Mitigate Corrosion," Corrosion 8, 100-8 (1952).

42. H. H. Uhlig (Mass. Inst. of Tech., Cambridge), "Trends in Corrosion Control," Metal Progress 61, No. 3, 82-8 (1952).

43. C. A. Lobry de Bruyn (Centraal Inst. voor Materia alonderzoek, Delft, Holland), "Present State of Investigation on Corrosion and of Protective Methods in Holland," Ossature Metal 15, 581-8 (1950).

44. K. Matthaes, "Experience with Nondestructive Material Testing," Metal 5, 544-6 (1951).

45. A. Portevin, "Methods of Metallographic Analysis and Their Extension to Inorganic Chemistry," Ind. Chim. Belge 15, 157-66 (1951).

46. U. R. Evans, "Metallic Corrosion, Passivity and Protection," Longman Green and Co., 1948, 747-802 (on testing).

47. J. W. Gailer and E. J. Vaughan, "Protective Coating for Metals," Chas. Griffin & Co., Ltd., 1950, 250 pp., 173-250.

48. P. van Rysselberghe, et al. (Univ. of Oregon), "Polarographic Study of Corrosion Phenomena," Corrosion, Mar. - Apr. 1948, 11-16.

49. H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 6th ed. (1933), 1058 pp., adhesion tests 217-222.

50. F. M. Reinhart, "Anodic Surface Treatments for Magnesium Alloys," NBS Report 1364 (1951).

51. F. M. Reinhart, "Protective Value of Surface Treatments for Magnesium Alloys," NBS Report 2026 (1952).

52. K. G. Stone and H. H. Furman, "Polarographic Use of Organic Reagents - Magnesium with 8-Hydroxyquinoline," Ind. Eng. Chem., Anal. Edit., 16, 596 (1944).

53. J. M. Kolthoff and S. Lingane, "Polarography," Vol. II, 2nd ed., Determination of Magnesium," Interscience Publishers, Inc., 1952, p. 430.

54. M. Kronstein, "Color Effects in Electrographic Printing," Paint & Varnish Production, Sept. 1951, 19-21.

55. J. M. Pearson, "Description of Null Methods Applied to Corrosion Measurements," J. Electochem. Soc. 81, 485 (1942).

56. R. Landau, "Some Mechanisms of Alloy Corrosion," J. Electrochem. Soc. 81, 559 (1942).

57. R. E. McNulty and J. C. Hanawalt, "Some Corrosion Characteristics of High Purity Magnesium Alloys," J. Electrochem. Soc. 81, 423 (1942).

58. R. H. Brown and R. B. Mears, "Application of Electrochemical Measurements to Studies of 18-8 Stainless Steels," Trans. Faraday Soc. 35, 467-474 (1939).

59. R. H. Brown and R. B. Mears, "The Electrochemistry of Corrosion," J. Electrochem. Soc. 74, 495-517 (1938).

60. P. Delahay, "A Polarographic Method for the Indirect Determination of Polarization Curves for Oxygen Reduction on Various Metals," J. Electrochem. Soc. 97, 198-212 (1950).

61. W. J. Schwerdtfeger and O. M. McDorman, "Measurement of the Corrosion Rate of a Metal from its Polarizing Characteristics," J Electrochem. Soc. 99, 407-13 (1952).

62. M. Van Loo, et al. (Sherwin Williams Co., Chicago), "Protective Coatings for Magnesium," AF 33(616)-35 (1952) R 601-298.

63. R. L. Solvange, et al., "Adhesion of Lacquers to Metals," Am. Paint J. 27, 13-18 (Oct. 1942).

APPENDIX B.

GASOMETRIC DATA FOR REPRESENTATIVE SPECIMENS

IN 1.0N KCl

SPECIMEN NO. 0851 (p. 72)

Dow #12 Primed FS-1 Alloy
Area = 9.40 sq. in.
Primer Thickness = 0.7 mil
Closed Cell - No Stirring

Total Time Elapsed (hr.)	Barometric Pressure (mm.)	Temperature of Reaction (°C)	Temperature of Gas Collected (°C)	Burette Reading	Volume of H_2 at SDC* (ml./10 in.^{2})
0	731	25.36	23.1	3.17	2.93
13	729	24.92	22.2	3.37	-
21	727	24.80	22.7	3.45	3.12
42	729	24.83	23.0	3.56	-
85	735	25.11	20.5	3.80	3.52
93	734	25.15	23.0	3.94	-
109	737	25.22	23.0	4.03	3.72
117	735	25.40	24.0	4.16	-
133	740	24.97	22.4	4.22	3.91
141	740	25.34	22.8	4.34	-
157	744	25.04	22.0	4.57	4.27
165	743	25.07	23.4	4.57	-
180	744	25.00	22.0	4.67	4.37
189	741	24.92	23.6	4.87	-

* SDC = Standard dry conditions (see formula on p. 66).

GASOMETRIC DATA FOR REPRESENTATIVE SPECIMENS

IN 1.0N KCl

SPECIMEN NO. 0851 (Cont'd)

Dow #12 Primed FS-1 Alloy
Area = 9.40 sq. in.
Primer Thickness = 0.7 mil
Closed Cell - No Stirring

Total Time Elapsed (hr.)	Barometric Pressure (mm.)	Temperature of Reaction (°C)	Temperature of Gas Collected (°C)	Burette Reading	Volume of H_2 at SDC ($ml./10\ in.^2$)
206	740	24.78	21.8	5.05	4.69
214	735	24.46	23.1	5.20	-
237	739	24.87	23.7	5.50	5.07
264	735	25.25	23.3	6.00	-
277	730	25.05	22.3	6.21	5.68
301	733	25.06	22.8	6.56	-
308	731	24.76	22.9	6.72	6.07

Average Rate at 308 hr. $= \frac{6.07}{308 \times 60} = 3.29 \times 10^{-4}$ ml./min./10 in.^{2}

Final Rate $= \frac{6.07 - 5.68}{(308-277) \times 60} = 2.10 \times 10^{-4}$ ml./min./10 in.^{2} between 277-308 hr.

SPECIMEN NO. 1387 (p. 77)

Light Dow #7 Unprimed FS-1 Alloy
Area = 9.36 sq. in.
Magnetic Stirrer Type Cell

Total Time Elapsed (hr.)	Bath Temperature (°C)	Barometric Pressure (mm.)	Burette Reading (ml.)	Volume Change (ml.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	24.86	729	8.92	0	0
1	24.90	729	8.67	0.25	0.227
2	24.85	729	7.64	1.28	1.165
3	24.75	729	6.17	2.75	2.54
5	24.96	729	3.13	5.79	5.275
6	25.04	731	1.58	7.34	6.70
7	25.00	732	0.25	8.67	7.925

$$\text{Average Rate at 7 hr.} = \frac{7.925}{7 \times 60} = 1.89 \times 10^{-2} \text{ ml./min./10 in.}^2$$

$$\text{Final Rate} = \frac{7.925 - 6.70}{(7-6) \times 60} = 2.04 \times 10^{-2} \text{ ml./min./10 in.}^2 \text{ between 6-7 hr.}$$

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 0889 (p. 77)

Specification Dow #7 Unprimed FS-1 Alloy
Area = 9.39 sq. in.
Magnetic Stirrer Type Cell

Total Time Elapsed (hr.)	Bath Temperature (°C)	Barometric Pressure (mm.)	Burette Reading (ml.)	Volume Change (ml.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	24.98	733	9.60	0	0
1	25.00	733	9.24	0.36	0.33
2	25.03	734	8.31	1.29	1.17
3	25.09	734	7.42	2.18	1.99
4	25.06	734	6.40	3.20	2.92
5	25.11	734	5.46	4.14	3.77
6	24.96	734	4.34	5.26	4.79
7	25.09	734	3.23	6.37	5.67
8	25.00	734	2.27	7.33	6.67

Average Rate at 8 hr. $= \frac{6.67}{8 \times 60} = 1.39 \times 10^{-2}$ ml./min./10^2.

Final Rate $= \frac{6.67 - 5.67}{(8-7) \times 60} = 1.67 \times 10^{-2}$ ml./min./10 in.^{2} between 7-8 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1110 (p. 77)

Untreated Unprimed FS-1 Alloy
Area = 9.32 sq. in.
Magnetic Stirrer Type Cell

Total Time Elapsed (hr.)	Bath Temperature (°C)	Barometric Pressure (mm.)	Burette Reading (ml.)	Volume Change (ml.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	24.95	738	8.94	0	0
15	25.10	738	7.44	1.50	1.37
30	25.02	738	5.40	3.54	3.23
45	25.00	738	2.85	6.09	5.56
60	25.04	738	1.44	7.50	6.86

Average Rate at 60 min. $= \frac{6.86}{60} = 11.44 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{6.86 - 5.56}{60 - 45} = 8.67 \times 10^{-2}$ ml./min./ 10 in.^{2} between 45 - 60 min.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. H1209 (p. 81)

Dow #7 Unprimed "H" Cast Alloy
Area= 2.46 sq. in.
Magnetic Stirrer Type Cell

Total Time Elapsed (min.)	Bath Temperature (°C)	Barometric Pressure (mm.)	Burette Reading (ml.)	Volume Change (ml.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	25.40	734	9.10	0	0
60	25.02	734	8.80	0.30	-
120	24.80	734	8.67	0.43	-
240	24.90	734	8.40	0.70	-
300	24.88	734	8.25	0.85	2.97
420	24.86	734	7.95	1.15	-
480	24.81	732	7.78	1.32	-
825	24.80	731	6.52	2.58	8.97
1380	25.20	729	3.72	5.38	18.73

Average Rate at 5 hr. $= \frac{2.97}{300} = 9.9 \times 10^{-3}$ ml./min./10 in.^{2}

Average Rate at 23 hr. $= \frac{18.73}{1380} = 1.36 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{18.73 - 8.97}{1380 - 825} = 1.76 \times 10^{-2}$ ml./min./10 in.^{2} between 14 - 23 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1537 (p. 88)

Specification Dow #12 Unprimed FS-1 Alloy
Area = 9.37 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC* (ml./10 in.^{2})
0	0	30.5	734	0
240	3.74	33.0	734	-
300	4.37	33.0	734	3.83
360	5.51	33.0	734	4.83

Average Rate at 6 hr. $= \frac{4.83}{360} = 1.34 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{4.83-3.83}{360-300} = 1.67 \times 10^{-2}$ ml./min./10 in.^{2} between 5 - 6 hr.

*SDC = Standard dry conditions (see formula on p.66).

SPECIMEN NO. 1538 (p. 88)

Specification Dow #12 Unprimed FS-1 Alloy
Area = 9.36 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * ($ml./10\ in.^2$)
0	0	30.5	734	0
240	3.78	33.0	734	-
300	4.38	33.0	734	3.84
360	5.50	33.0	734	4.83

Average Rate at 6 hr. $= \frac{4.83}{360} = 1.34 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{4.83 - 3.84}{360 - 300} = 1.67 \times 10^{-2}$ ml./min./10 in.^{2} between 5 - 6 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1131 (p. 88)

Heavy Dow #7 Unprimed FS-1 Alloy
Area = 9.40 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * (ml./ 10 in.^{2})
0	0	30.3	737	0
420	3.40	32.7	735	2.98
480	4.24	33.0	735	3.70

Average Rate at 8 hr. $= \frac{3.70}{480} = 7.71 \times 10^{-3}$ ml./min./10 in.^{2}

Final Rate $= \frac{3.70 - 2.98}{480 - 420} = 1.20 \times 10^{-2}$ ml./min./10 in.^{2} between 7 - 8 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1138 (p. 88)

Heavy Dow #7 Unprimed FS-1 Alloy
Area = 9.40 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC* (ml./10 in.^{2})
0	0	30.3	737	0
420	3.59	32.7	735	3.13
480	4.38	33.0	735	3.83

Average Rate at 8 hr. $= \frac{3.83}{480} = 7.98 \times 10^{-3}$ ml./min./10 in.^{2}

Final Rate $= \frac{3.83 - 3.13}{480 - 420} = 1.17 \times 10^{-2}$ ml./min./10 in.^{2} between 7 - 8 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1334 (p. 88)

Light Dow #7 Unprimed FS-1 Alloy
Area = 9.42 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC* (ml./10 in.^{2})
0	0	30.8	736	0
510	7.66	32.0	734	6.68
570	9.26	31.5	734	8.07

Average Rate at 9.5 hr. $= \frac{8.07}{570} = 1.41 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{8.07 - 6.68}{570 - 510} = 2.31 \times 10^{-2}$ ml./min./10 in.^{2} between 8.5 - 9.5 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1710 (p. 88)

Heavy Dow #7 Unprimed FS-1 Alloy
Area = 9.39 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC* (ml./10 in.^{2})
0	0	30.8	736	0
510	5.12	32.0	734	4.47
570	6.24	31.5	734	5.45

Average Rate at 9.5 hr. $= \frac{5.45}{570} = 9.57 \times 10^{-3}$ ml./min./10 in.^{2}

Final Rate $= \frac{5.45 - 4.47}{570 - 510} = 1.63 \times 10^{-2}$ ml./min./10 in.^{2} between 8.5 - 9.5 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1462 (p. 88)

Light Dow #12 Unprimed FS-1 Alloy
Area = 9.35 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	0	31	733	0
315	7.65	32	733	6.70
360	8.75	32	733	7.67

Average Rate at 6 hr. $= \frac{7.67}{360} = 2.13 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{7.67 - 6.70}{360 - 315} = 2.15 \times 10^{-2}$ ml./min./10 in.^{2} between 5 - 6 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1461 (p. 88)

Specification Dow #12 Unprimed FS-1 Alloy
Area = 9.39 sq. in.
Fermentation Shaker Type Cell (25° Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * ($ml./10\ in.^2$)
0	0	31	733	0
315	7.97	32	733	6.96
360	9.31	32	733	8.13

Average Rate at 6 hr. $= \frac{8.13}{360} = 2.25 \times 10^{-2}$ $ml./min./10\ in.^2$

Final Rate $= \frac{8.13 - 6.96}{360 - 315} = 2.60 \times 10^{-2}$ $ml./min./10\ in.^2$ between 5 - 6 hr.

*SDC = Standard dry conditions (see formula on p.66).

SPECIMEN NO. 1933 (p. 88)

Iridite #15 Unprimed FS-1 Alloy
Area = 9.38 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	0	26	738	0
240	5.49	28	738	4.97
300	6.70	28	738	6.07

Average Rate at 5 hr. = $\frac{6.07}{300} = 2.03 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate = $\frac{6.07 - 4.97}{300 - 240} = 1.83 \times 10^{-2}$ ml./min./10 in.^{2} between 4 - 5 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1940 (p.88)

Iridite #15 Unprimed FS-1 Alloy

Area = 9.26 sq. in.

Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	0	26	738	0
240	6.18	28	738	5.67
300	7.20	28	738	6.60

Average Rate at 5 hr. $= \frac{6.60}{300} = 2.20 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{6.60 - 5.67}{300 - 240} = 1.55 \times 10^{-2}$ ml./min./10 in.^{2} between 4 - 5 hr.

*SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1931 (p. 88)

Iridite #15 Unprimed FS-1 Alloy
Area = 9.36 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * ($ml./10\ in.^2$)
0	0	26	737	0
360	4.79	28	738	4.33
420	4.92	29	738	4.42

Average Rate at 7 hr. $= \frac{4.42}{420} = 1.05 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{4.42 - 4.33}{420 - 360} = 1.5 \times 10^{-3}$ ml./min./10 in.^{2} between 6 - 7 hr.

* SDC = Standard dry conditions (see formula on p. 66).

SPECIMEN NO. 1528 (p. 88)

Specification Dow #7 Unprimed FS-1 Alloy
Area = 9.37 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * ($ml./10\ in.^2$)
0	0	29	741	0
120	1.55	29	741	1.42
180	2.43	29	741	2.22
240	3.35	29	741	3.06
300	4.18	30	741	3.82

Average Rate at 2 hr. $= \frac{1.42}{120} = 1.18 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 3 hr. $= \frac{2.22}{180} = 1.23 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 4 hr. $= \frac{3.06}{240} = 1.27 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 5 hr. $= \frac{3.82}{300} = 1.27 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{3.82 - 3.06}{300 - 240} = 1.20 \times 10^{-2}$ ml./min./10 in.^{2} between 4 - 5 hr.

* SDC = Standard dry conditions (see formula on p.66).

SPECIMEN NO. 1967 (p. 66)

Specification Dow #7 Unprimed FS-1 Alloy
Area = 9.38 sq. in.
Fermentation Shaker Type Cell (25°C Bath)

Total Time Elapsed (min.)	Volume of H_2 Collected (ml.)	Temperature of H_2 Collected (°C)	Barometric Pressure (mm.)	Volume of H_2 at SDC * (ml./10 in.^{2})
0	0	29	741	0
120	1.41	29	741	1.21
180	2.20	29	741	2.01
240	2.76	29	741	2.52
300	3.30	30	741	3.02

Average Rate at 2 hr. $= \frac{1.21}{120} = 1.0 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 3 hr. $= \frac{2.01}{180} = 1.11 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 4 hr. $= \frac{2.52}{240} = 1.05 \times 10^{-2}$ ml./min./10 in.^{2}

Average Rate at 5 hr. $= \frac{3.02}{300} = 1.0 \times 10^{-2}$ ml./min./10 in.^{2}

Final Rate $= \frac{3.02 - 2.52}{300 - 240} = 8.3 \times 10^{-3}$ ml./min./10 in.^{2} between 4 - 5 hr.

* SDC = Standard dry conditions (see formula on p. 66).