

REYNOLDS METALS COMPANY
Metallurgical Research Division
Finishing & Composites Section
Fourth and Canal Streets
Richmond, Virginia 23219

FACILITY FORM 602

N66 32434
(ACCESSION NUMBER) (THRU)

58
(PAGES) (CODE)

CR-76458
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

15

A SPRAY OR BRUSH ANODIZING
PROCESS FOR ALUMINUM ALLOYS

Six-Month Progress Report
Phase I
Contract No. NAS 8-20157
MRD No. 35-170-820

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 2.50

Microfiche (MF) .50

June 20, 1966

ff 653 July 65

HJC:jcw

Harold J. Coates
Harold J. Coates
Senior Electrochemist

Approved by: Erik F. Barkman
Erik F. Barkman
Assistant General Director

J. H. Jackson
J. H. Jackson
General Director

TABLE OF CONTENTS

	<u>Page</u>
Summary	1
Introduction	2
Objectives	3
Conclusions	3
General Conclusions	5
Recommendation	6
Methods of Investigation	6
A. Alloys	6
B. Chemicals	7
C. Equipment	7
D. Other Materials	8
Experiments, Results, Discussion	9
A. Pretreatment	9
1. Pretreatment by Electropolishing	9
2. Electrolytic Desmutting	10
3. Effect of Pretreatment on Abraded, Anodized Welded Plate of 2219	10
B. Anodic Coating Studies	11
1. Discussion of Anodizing	11
2. High Current Density Coating Defects	15
3. Selection of Electrolyte	17
4. Weight Change During Anodizing of 2219 and 2014 Alloys	17
5. The Relationship of Abrasion Resistance and Electrolyte Concentration	18

TABLE OF CONTENTS

	<u>Page</u>
C. Flow Rate Studies	18
1. Description of Agitation Apparatus	20
2. Relationship of Anodizing Variables to Electrolyte Flow Rate	21
3. Abrasion Resistance as Affected by Coating Thickness and Electrolyte Flow Rate	21
4. Some Relationships of Anodic Coating Forming Conditions and Coating Properties	22
D. Post Anodic Treatments	24
1. Hot Water Sealing	24
2. Steam Sealing of Anodized 2219-T87	24
3. Chemical Conversion Sealing	25
Acknowledgments	27
Appendix	28
Tables	
Graphs	
Illustrations	

LIST OF TABLES

Table No.

- | | |
|------|--|
| I | Data on Pretreatment of 2219-T87, 0.050 inch, by Electropolishing in 50% by Weight Sulfuric Acid |
| II | Change in Weight as a Result of Anodizing in 26% Sulfuric Acid; Flow Rate ~ 300 ft/min. |
| III | Results of Anodizing 2219-T87 and 2014-T6 Alloys in Varying Concentrations of Sulfuric Acid at 20°C and 15 amps/ft ² for 30 Minutes |
| IV | Apparent Densities of Anodic Coating Formed on 2219-T87 Alloy at Varying Current Density in 26 wt.% Sulfuric Acid at 30°C |
| V | Materials Being Used or Tested |
| VI | Data on Current Density-Flow Rate Relationships |
| VII | Abrasion Resistance as Affected by Flow Rate and Coating Thickness |
| VIII | Abrasion Resistance and Coating Thickness |
| IX | Salt Spray Corrosion of Steam Sealed 2219-T87 at Various Steam Pressures |
| X | Results of Exposure of 2219-T87 to 240 Hours Salt Spray after Various Surface Treatments |

LIST OF GRAPHS

Figure No.

- 1 Etch Rates of 2219 and 2024 Alloys in 4% 30R at 150°F
- 2 Weight Change During Anodizing Versus Current Density Employed
- 3 Abrasion Resistance of 2219 and 2014 Anodized in Varying Concentrations of Sulfuric Acid for 30 Minutes at 20°C and 15 amps/ft²
- 4 Current Density Versus Apparent Density of Coating and Theoretical Cell Wall Thickness
- 5 Anodizing Voltage of 2219-T87 Alloy at Varying Current Density in 26% by Weight Sulfuric Acid and 30°C; Flow Rate = 140 Feet Per Minute
- 6 Flow Rate Versus Electrolyte Temperature and Current Density with Visual Evaluation
- 7 Abrasion Resistance of 2219-T87 Alloy (0.050") as a Function of Flow Rate and Coating Thickness
- 8 Abrasion Resistance of 2219-T87 Alloy as a Function of Coating Thickness

LIST OF ILLUSTRATIONS

Photo. No.

- | | |
|----------|---|
| A | Salt spray exposure samples with and without Pretreatment |
| B | Agitation device (page 20) |
| C1,2,3,4 | Anodizing 2219 illustrating defects encountered during high current density anodizing |
| D | Salt spray exposure samples of anodized 2219 sealed in steam |
| E | Salt spray exposure samples with chemical conversion treatment with and without anodizing |

SUMMARY:

32434

The initial research, or Phase I, of Contract No. NAS 8-20157 entitled "A Spray or Brush Anodizing Process for Aluminum Alloys" has been completed. The principal objectives in this phase were centered around the investigation of anodizing parameters of the aluminum alloy 2219 and the evaluation of coating quality on the samples produced. This information was gathered and used to formulate a spray anodizing process.

Phase I has covered anodic coating studies, electrolyte flow rate relationships with other anodizing variables, pretreatment and post treatment effects, and materials.

It has been found that 2219 can be anodized at current densities of 800 amps/ft² or more under the proper conditions of the electrolyte type, concentration, temperature, and flow rate.

The concept of spray anodizing 2219 has been proven feasible by the establishment of the proper anodizing conditions.

It is recommended that approval be given for continuation of this contract into Phase II, or the engineering, design, and testing phase.

Author

INTRODUCTION:

NASA needs better corrosion protection for the aluminum parts on their S-1C components and propellants tanks. The parts are assembled and then must be protected from corrosion for periods up to three years prior to their use. Engineers at NASA believe that anodic coatings would be an improvement over the presently used chemical conversion coatings. Since the components in question could not be conveniently brought to an anodizing tank, a portable brush or spray anodizing system was proposed. A "cost-plus-fixed-fee" type contract was awarded to Reynolds Metals Company.

The system in question requires portability to the extent that the system can be brought to the part to be anodized. The system involved must produce a coating of sufficient quality to meet the requirements of Specification MIL-A-8625. The anodizing system should be versatile enough to anodize curvilinear or flat parts in the horizontal or vertical position. The electrolytes used in this operation must not contaminate surrounding equipment.

The approach taken to meet the above requirements has been one which uses a sliding spray head with an electrolyte being flushed across the surface being anodized. For this reason much of the effort in Phase I has been concentrated on original work in the study of the effects of electrolyte flow rates on the several anodizing variables. For this study a special piece of equipment was constructed which would control flow rate during anodizing. Very high current densities were obtained using this technique.

Another point of concern was the sealing of anodized parts which could not be sealed using conventional techniques (hot water or steam). Our approach was to use chemical conversion treatments at room temperature after anodizing. Some of the test results using this technique are very promising.

A pretreatment was needed in this system which would remove a small amount of metal prior to anodizing and insure a uniform response to the anodizing treatment. One method was evolved using 50% sulfuric acid at a temperature above ambient and which electropolishes the surface. This system has the advantage of not needing a rinse step and utilizes the power equipment already available.

OBJECTIVES:

1. To generate the technical data necessary to develop a spray anodizing process for 2219 alloy.
2. To determine the feasibility of such a process.

CONCLUSIONS:

1. Anodic Coating Studies

- a. Uniform anodic coatings can be formed on 2219-T87 within the ranges of the following anodizing conditions:

Current Density Range: 15-800 amps/ft²

Voltage Range: 14-50 volts DC

Electrolyte Temperature Range: 20-40°C

Sulfuric Acid Electrolyte Concentration Range: 17-40 wt.%

Electrolyte Agitation Rates: 0-540 ft/min

- b. The density of the coating on 2219 alloy increased with increasing current density.
- c. During anodizing, forming voltage decreases with increasing electrolyte concentration.
- d. Forming voltage decreases with increasing temperature.
- e. The anodic coating dissolution rate increases with increasing electrolyte temperature and concentration.

2. Flow Rate Studies

- a. A device was designed and built which allowed an aluminum sample to be moved through the electrolyte at controlled rates of speed while the sample was being anodized.
- b. Burning can be controlled through increasing the flow rate of the electrolyte.
- c. Coatings become powdery if the flow rates are too low.
- d. If the temperatures are held too low, say 20°C, then high current densities could not be obtained without running into certain types of high current density coating defects.
- e. The coating defects appeared if the electrolyte concentration was too low. For example, 2219 alloy anodized at 200 amps/ft² in 17% sulfuric acid at 30°C would almost invariably develop a defect which could be called "selective anodizing on a moving front."¹

3. Electrolyte Studies

- a. Anodizing in proprietary mixtures of oxalic acid, sulfuric acid, and ferric oxalate produced coatings on 2219 which were spotty or barrier type. The samples showed a tendency to burn at voltages exceeding 100 volts.
- b. Sulfuric acid in concentrations of 26% and 30% by weight produce a uniform anodic coating on 2219 alloy.

4. Acid-resistant construction materials, coatings, and adhesives were tested and are reported in Table V.

5. Pretreatment

- a. Pretreated and anodized 2219 samples showed superior corrosion resistance to unpretreated, abraded 2219 when tested in the 5% salt spray for 240 hours.
- b. Alloy 2219 or 2014 can be electrolytically desmutted in dilute sulfuric acid by applying a potential of 15 volts prior to anodizing.

¹ These defects are discussed in detail on page 15.

- c. 2219 can be electropolished in 50 wt.% sulfuric acid at 40°C and at current densities of 450 amps/ft² or more.

6. Post Treatments

The following post anodic treatments are satisfactory when tested for 240 hours in 5% neutral salt spray.²

- a. Boiling water sealing - samples of 2219 anodized to a coating thickness of 0.25-0.30 mil, sealed for 15 minutes in boiling water at pH range 5.5 to 7.0.
- b. Steam sealing - samples of 2219 anodized to a coating thickness of .35 to .40 mil, sealed for 3 minutes at pressures of 10 psi of steam above atmospheric.
- c. Chemical conversion sealing - samples of 2219 anodized to a coating thickness of .35 to .40 mil, immersed in a chemical conversion solution of Alodine 600, 1200, or 1200S for 2 minutes at 74°F.

GENERAL CONCLUSIONS:

1. 2219-T87 can be given an anodizing treatment which meets the requirements of Specification MIL-A-8625 as to coating quality and weight.
2. The coating can be applied at rates which would meet or exceed the contract requirement of 1/4 ft/min.
3. It is feasible to anodize 2219-T87 by a spray anodizing technique by applying the technology developed in the first phase of this contract.

RECOMMENDATION:

Based on data and techniques originated thus far in the performance of the contract, it is recommended that approval of Phase II of this contract be given.

² Satisfactory in this case is a 4" x 6" panel which shows no more than three pits on the exposed surface.

RECOMMENDED PROCESS STEPS:

1. Degrease.
2. Rinse in tap water.
3. Pre-etch-10 second dip in 3% hydrofluoric, 10% nitric acid aqueous solution. This step may be omitted if surface is freshly machined. Recommended where there is an excessive heat treat scale or corrosion on the surface.
4. Etch in caustic for 5 minutes at 30°F; 4 to 6 oz/gal (30 to 45 gms/liter). Diversey Aluminux, Clepo 30R, or equivalent proprietary etchants may be used.
5. Rinse in tap water.
6. Desmut for 1 minute at room temperature in 1:1 nitric acid. An alternative electrolytic desmutting step was developed in which the sample is immersed in the sulfuric acid and a 15 volt potential is applied.
7. If 1:1 nitric acid is used as a desmut, then rinse in tap water. If electrolytic desmutting is used, the rinse step may be omitted. Alternative to the etching steps is electropolishing in 50% sulfuric acid. If this is used, the part may be anodized immediately after the electropolish without a rinse.
8. Anodize in 26% sulfuric acid at 30°C for a time and current density necessary to achieve a coating of the desired quality and thickness.
9. Tap water rinse.
10. Seal for 2 to 3 minutes in Alodine 600, 1200, or 1200S at room temperature (over 70°F).

METHODS OF INVESTIGATION:

A. Alloys

2219-T87	0.050"
2219-T87	0.50" welded plate
2014-T6	0.109"

B. Chemicals

<u>Reagent or Chemical</u>	<u>Manufacturer</u>
Sulfuric Acid 96% Reagent	B & A
Oxalic Acid Tech.	Pfizer
Ferric Oxalate Tech.	Pfizer
Nitric Acid 70% Reagent	B & A
Caustic Etchant (30R)	F. R. Gumm Co.
Desmut (514)	Diversey Corp.
Hydrofluoric Acid	B & A

C. Equipment

1. AR Constant Current Regulator

Purpose: For maintaining constant current with varying voltage.

Manufacturer: Hevi-Duty Electric Company
Milwaukee, Wisconsin

Maximum Voltage: 250 VDC
Maximum Current: 25 Amps
Maximum Wattage: 1.2 KW

2. Type SK - DC Generator

Purpose: To provide anodizing power source with constant voltage.

Manufacturer: Westinghouse Electric Company

Maximum Voltage: 154 DCV
Maximum Current: 267 Amps
Wattage: 40 KW
RPM: 1750

3. Agitation Device (Controller and Motor)

Purpose: To move a sample through a solution in one plane at varying rates of speed.

547 DC Motor Controller

Manufacturer: Gerald K. Heller Company
Las Vegas, Nevada

Input 115 VAC, Single Phase, 50-60 Cycle, 500 Watts

DC Motor - "Master" Gearmotor

Manufacturer: Master Electric Division
Reliance Electric & Engineering Co.
Columbus, Indiana

Horsepower: 1/3

Type: 115 V Shunt

RPM: 1725

Amps: 2.85

4. Taber Abraser

Purpose: For weighted abrasion wheel abrasion tests.

Manufacturer: Taber Instrument Corporation
North Tonawanda, New York

CS17 abrasion wheels used.

5. Analytical Balance Sartorius Selecta

Purpose: For various analytical weight measurements.

0-200 Grams, Sensitivity ± 0.1 Milligram

6. Dermatron

Purpose: An eddy current device for measuring thickness
of anodic coatings.

Manufacturer: Unit Process Assemblies
Woodside, New York

D. Other Materials

Table V shows a list of materials investigated,
their manufacturer, their intended use, and other features.

EXPERIMENTS, RESULTS, DISCUSSION:

A. Pretreatment

Pretreatment of aluminum surfaces prior to anodizing may have several purposes. If a specular surface is desired, the aluminum in question must be given a buff and a bright dip prior to anodizing. If a uniform appearance is needed, a caustic etch will usually suffice as a pretreatment. If a coating with good corrosion protection to the base metal is needed, any surface imperfection which would tend to give a nonuniform response to anodizing and thus weaken the protective value of the coating must be removed.

The preparation of panels during Phase I of this work has involved the immersion of the panels in dilute hot caustic. The caustic treatment usually removes about 1 mil of aluminum from the surface. (See Figure 1.) The engineers at NASA have said that this much metal removal could not be tolerated.

1. Pretreatment by Electropolishing

Electropolishing in a sulfuric acid electrolyte may be feasible because of the controlled metal removal and the use of sulfuric acid which would eliminate a rinse step between the pretreatment and anodizing steps.

Individual samples of 2219-T87 were anodized in a solution of 50% by weight sulfuric acid in current density increments of 50 amps/ft² between 50 and 600 amps/ft². The experiment was performed between 20 and 40°C. Data and results are given in Table I. This experiment shows that the surface can be pretreated by this method, but more research work may be necessary to have it become a standard treatment.

2. Electrolytic Desmutting

A sample of 2219-T87 was etched for several minutes in caustic to form a heavy smut. Then it was made the anode in a 26% sulfuric acid solution at a potential of 15 volts. The smut was removed in a matter of several seconds. The significance of this may be that the steps between the etch pretreatment and anodizing may be eliminated. These steps would be rinse, desmut, rinse followed by the anodizing step. The effect of copper contamination on the anodizing electrolyte has not been determined at this time.

Although this practice may not have direct application to the spray anodizing process, it could save considerable time in the removal of heavy smut from a chemical milling operation.

3. Effect of Pretreatment on Abraded, Anodized Welded Plate of 2219

The effect on corrosion resistance of an anodized aluminum surface which has not been pretreated will depend upon the type of contamination or surface imperfection which is present. If an aluminum surface has been buffed but not cleaned and then anodized, there is a good chance that some buffing compound will be entrapped in the anodic coating. Often sand blasted surfaces will show particles of sand entrapped after anodizing. In the case of the weldment on the 2219 plate, the problem involves a grinding operation which removes the weld bead. When aluminum is ground or sanded, sometimes particles of aluminum are picked up during one revolution of the grinding disk and are redeposited through friction welding or stick-slip phenomena onto the surface of the metal on the next

revolution. During anodizing, the particles are bypassed when the slight contact joint to the base metal is anodized through.

To illustrate these effects, the following experiment was performed. The weld bead of two groups of welded plate samples of 2219-T87, 0.5", was ground even with the surface. One group was given a standard pretreatment consisting of an alkaline degrease, an acid pre-etch dip, a 5 minute caustic etch, and a desmut in 1:1 nitric acid. The second group of samples was only degreased as a pretreatment to anodizing. Both groups were anodized to 0.4 mil and sealed in boiling water for 15 minutes. ASTM ratings on the samples after 240 hours exposure to salt spray were as follows.

	<u>Rating</u>
Normal Pretreatment	8.0
Unpretreated	4.3

Photographs of these exposed samples are shown in Photo. A.

B. Anodic Coating Studies

The purpose of this study is to determine the physical properties of the oxide coating on 2219 and 2014 alloys. The measurement of the density of the oxides on the two alloys will be necessary to later estimate the weight added to the launch vehicle by the oxide coating. The abrasion resistance will be used as a method to determine the coating quality, and salt spray corrosion tests will be used to establish minimum or optimum film thickness. The effect of several anodizing variables will be shown by abrasion and thickness measurements.

1. Discussion of Anodizing

The operation of anodizing aluminum is performed in a suitable electrolyte by setting a potential and passing

current or passing current at a given ratio of $\frac{\text{amperes}}{\text{unit area}}$ until the desired coating thickness is reached.

Electrolytes used in aluminum anodizing are divided into two groups, depending upon their solvent action on the coating.

Anodizing in nondissolving electrolytes is characterized by high voltages and low current densities. The thickness of the barrier type coatings is voltage dependent; that is, the higher the voltage, the thicker the coating. Such coatings are usually formed on high purity aluminum and are used in capacitors.

Anodizing in dissolving type electrolytes is characterized by higher current densities to form much thicker coatings. The voltages used are relatively lower.

When current is passed through the surface of the aluminum anode in a sulfuric acid solution, the reaction which takes place in the first few seconds is the formation of a barrier film, similar to that formed in nondissolving electrolyte. At some potential sufficient to cause current to flow through the barrier film, the coating starts to grow thicker. The current flowing through discrete points in the barrier film causes point-heat build-up. The sulfuric acid, being a dissolving type electrolyte, attacks the oxide coating in these regions of greatest heat build-up. The attack and subsequent dissolution of the oxide starts a pore.

Once anodizing has begun, a rather complicated equilibrium is achieved. The equilibrium is between current density, voltage, barrier film thickness, electrolyte temperature, concentration and agitation or flow rate. If any of the anodizing conditions or parameters are changed, then the others may be affected. For example.

raising the electrolyte temperature would increase the solubility of the electrolyte, lower the barrier film thickness, lower the voltage (if power source is constant current), or raise the current (if power source is constant voltage).

The equilibrium is also affected if differences in electrolyte flow rate cause localized temperature differences which result in variations in the thickness of the barrier film. Localized differences in barrier film thickness may result in a number of coating defects, which include burning and associated nonuniformities. The barrier film can be considered as a variable resistor in an electrical circuit. However, when the temperature increases, the conductivity of the barrier film increases.

A number of workers have studied the phenomena of anodic coating formation on aluminum. Hunter and Fowle³ have done basic work in the field of anodic oxide formation. Of particular interest was the section of their paper dealing with factors affecting the barrier film thickness. They found the unit barrier thickness (measured in angstroms per volt) changed with bath temperature, electrolyte type, and electrolyte concentration. Total barrier film thickness was found to be a function of the voltage drop across the coating. They found that the unit barrier thickness reaches a minimum and does not change appreciably in the concentration range of 25-60 wt.% sulfuric acid. (See Figure 1A on page 14.)

³ "Factors Affecting the Formation of Anodic Oxide Coatings," M. S. Hunter and P. Fowle, Journal of the Electrochemical Society, October, 1954.

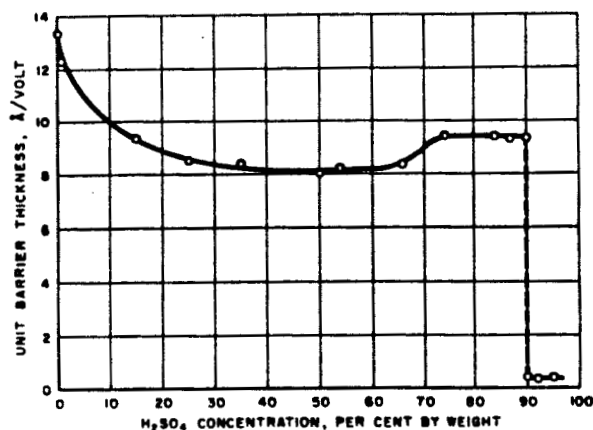


Figure 1A
Relation between sulfuric acid concentration and unit barrier thickness of coating formed on 99.99% aluminum at 70°F and 15 volts.

The effect of bath temperature on unit barrier thickness is shown in Figure 1B below. Notice that a minimum value is reached at about 80°F and remains relatively constant through about 160°F.

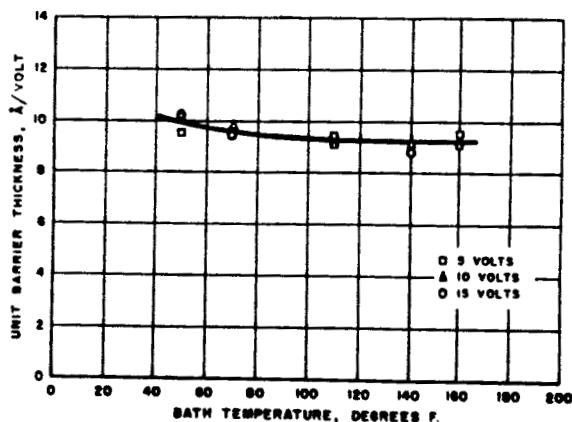


Figure 1B
Effect of voltage and temperature on unit barrier thickness for coatings on 99.99% aluminum formed in 15% sulfuric acid.

Figures 1A and 1B were taken from the article, "Factors Affecting the Formation of Anodic Oxide Coatings," by M. S. Hunter and P. Fowle, Journal of the Electrochemical Society, October, 1954.

2. High Current Density Coating Defects

Coating thickness variations encountered during anodizing will ultimately depend upon several interacting variables. Where current flows through the barrier film, anodic oxide is formed. A high temperature at the interface between the electrolyte and barrier film causes a lowering of resistance and a passage of current. There are a number of defects which one will encounter during high current density anodizing. These defects should be defined and discussed. In common terms, the defects would all be classified as burning. For the purposes of describing samples produced under these experiments, it is necessary to further differentiate the term "burning."

A burn on an anodized part is defined as the total disintegration of oxide in metal at an area or point on the surface of the sample. The aluminum surface at the burn site seems to be polished. The burned area is usually surrounded by powdered oxide as a result of hot electrolyte attack. Outside the area surrounding the burn, however, there is usually a heavy build-up of oxide thicker than that on the remainder of the sample. The oxide build-up is a result of high electrochemical activity in that area.

An "arrested burn," as shown in Photo. C3, is a burn which started but later in the same anodizing cycle was caused to recover. It is recognized on a panel when the powdered oxide is present around the edges of the burn site, but the burn itself is covered with good quality anodic coating. There is also a reduction in the thickness in the aluminum where the aluminum was dissolved. A burn can be corrected during the anodizing cycle if the operator recognizes the indications of the burn starting. This can be observed by changes in the current and voltage during

anodizing. The burn manifests itself by a sudden drop in voltage of 3 to 5 volts and a simultaneous surge in the amperage. The correction is made by lowering the power input or by increasing the agitation rate of the electrolyte.

"Thermochemical attack" on the anodic coating (shown in Photo. C1) is an area of loosely adhering powdery oxide which is soft enough to be scratched off with the fingernail or wiped off with a rag. This condition is caused by imbalance in the heat input-heat removal rates in a localized area. In the case of thermochemical attack, the nonequilibrium condition has not reached the catastrophic proportions of a burn. The temperature of the interface at the electrolyte-outer oxide coating in the affected area has reached a point where the anodic coating is readily soluble. The resulting attack on the coating by the hot electrolyte leaves the oxide with virtually no mechanical strength.

Photo. C2 also shows a variation in the high current density anodizing which we have termed "selective anodizing on a moving front." In this situation, the initial electrochemical attack is confined on a corner or an outside edge. The energy induced by the attack heats the surrounding area. The initiation point will then either burn or, if the heat has been removed rapidly enough, merely anodize at a higher rate. The increase in coating thickness causes an increase in electrical resistance and the anodizing is transferred to a less resistive area. In this case it is the warm area adjacent to the area of highest activity. This phenomena continues and traverses the panel in an irregular manner following the path of least resistance. The coating on the dark areas in Photo. C2 may be as much as 5 to 10 times as thick as the coating in the adjacent lighter areas.

Another phenomena which we describe as "light coating around the edges of the panel" and shown in Photo. C4 is a result of heat being extracted from the edges of the panel more rapidly than in the center--the cooler edges having a more resistive barrier film than the center. This brings about a relative increase in the electrochemical activity in the center of the panel yielding a thicker coating there.

3. Selection of Electrolyte

From literature and experimentation, it was decided that the proper concentration and temperature of the electrolyte would be in a range where localized temperature variations would not result in variations in the barrier film thickness. The data from the literature indicate that a sulfuric acid concentration of about 25% or greater and a temperature of about 30°C is in the range of minimum unit barrier film thickness formation during anodizing.

Other criteria are the maximizing conductivity and the minimizing rate of coating solubility. Hunter and Fowle indicate that conductivity of sulfuric acid is at a maximum at 30 wt.% and that coating solubility rate is at a maximum between 10 and 30 wt.%.

4. Weight Change During Anodizing of 2219 and 2014 Alloys

A series of 2219-T87, 0.05", and 2014-T6, 0.109", samples was anodized in 26 wt.% sulfuric acid at 30°C at varying current densities. The samples were weighed after pretreatment, after anodizing, and after stripping. The principal results were that after anodizing at a low current density (or long exposure to electrolyte), there was a net loss in weight after anodizing; but as current

densities increased to 50, 100, and 200 amps/ft², there was a net gain in weight as a result of anodizing. The results are shown in Table II and Figure 2.

5. The Relationship of Abrasion Resistance and Electrolyte Concentration

In order to determine the effects of electrolyte concentration on the abrasion resistance of anodic coatings on 2014-T6 and 2219-T87 alloys, samples were prepared in the following manner:

- a. Degreased in Diversey 17 at 140°F, tap water rinse.
- b. Pre-etched in a very dilute solution of hydrofluoric and nitric acid at room temperature, tap water rinse.
- c. Etched in 30R caustic solution at 150°F for 5 minutes.
- d. Desmuted in 1:1 nitric acid, tap water rinse.
- e. Anodized at 15 amps/ft² at 20°C for 30 minutes in solutions of 10, 20, 30 and 40% by weight sulfuric acid.
- f. The samples were not sealed.

The samples were evaluated by measuring weight loss after 1000 revolutions on the Taber Abrasion Tester using CS-17 wheels and 1000 grams load. Both sides of the sample were abraded with the average weight loss recorded. The results of this experiment are given in Table III and Figure 3. The differences shown are on the order of 0.5 mg and are not considered as significant in this particular experiment.

C. Flow Rate Studies

The purpose of this study is to find critical electrolyte flow rate-current density-temperature relationships and relate this study to the main program by optimizing these operating variables.

The rate at which the electrolyte moves across the surface of the anodizing aluminum governs the rate at which heat can be removed from the surface. The temperature of the electrolyte controls the dissolution rate of the oxide coating in the sulfuric acid. The temperature of the electrolyte in the oxide film varies with the current density applied. When the current density is too high in relation to the rate at which the heat is removed, then burning disintegration of the coating and aluminum occurs.

The measurement of the flow rate of electrolyte past a point and its effect on heat dissipation will be performed by equipment described herein.

To produce a good quality anodic coating and meet the technical demands of this contract, it was felt that the anodizing head should flush the electrolyte across the surface being anodized. To build an anodizing head capable of doing this job, certain data had to be generated as to the effect of flow rate of the electrolyte on various anodizing variables.

To produce such data, it was required that we design an apparatus which would move an aluminum sample through the electrolyte at various rates of speed, flushing the surface uniformly with electrolyte. An aluminum sample attached to the end of the shaft of an electric stirrer had been tried, and it was found that the coating quality varied from the edge of the sample to the middle where the sample was mounted. The coating grew softer as the rate of agitation decreased toward the center of the sample. From this work a sample holder was designed which reciprocated from an eccentrically mounted shaft on a revolving disk attached to the shaft of an electric motor. When the sample moved to the top or bottom of a cycle, there was a momentary stop. During this moment of zero or near zero movement, the sample tended to burn. This experiment pointed out the need for an apparatus which would move the sample at uniform speeds.

1. Description of Agitation Apparatus

Photo. B shows the agitation device which was designed to produce the data we required. Here, two disks, each with a $4\frac{1}{2}$ " radius, are connected by contact bar, synchronized with an idling gear, and driven by a belt from a variable speed DC motor. The contact bar holds the square titanium rack which is rigidly connected to the contact bar. The sample is connected to the titanium rack and describes a circle nine inches in diameter in a single plane through the electrolyte. The connection to the contact bar is held rigidly to prevent flexing of the wire during operation.

The variables under investigation in these experiments are the effects of flow rate on other anodizing variables. The methods of evaluating the effects of the change in variables are (1) simple visual observation, (2) coating thickness measurement, (3) abrasion resistance measurement, and (4) coating weight measurements.

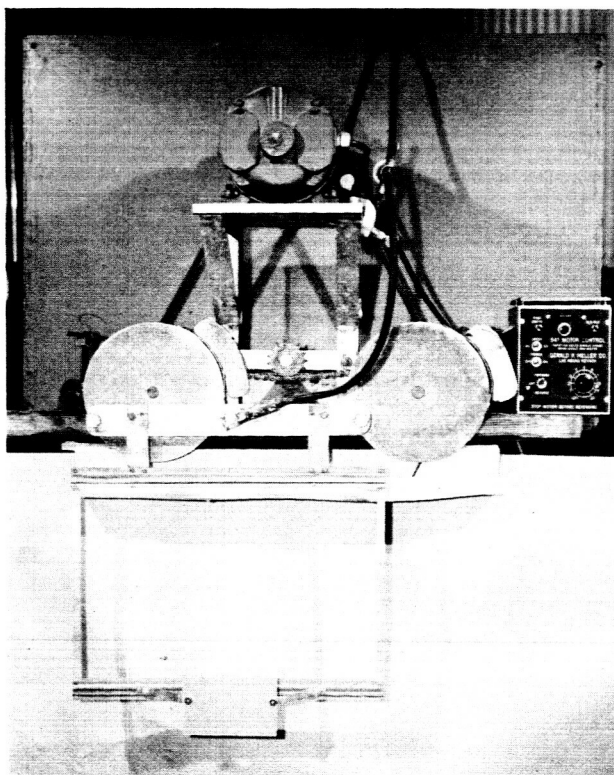


Photo. B

2. Relationship of Anodizing Variables to Electrolyte Flow Rate

The work on this sub-phase was completed on 2219-T87 alloy. The results and data are listed in Table I of this report. Figure 6 is a graphic plot of the electrolyte temperature versus the electrolyte flow rate and current density as related to the resulting anodic coating. This work points to the variables which must be controlled in order to achieve a good quality anodic coating. Good quality here means a coating which is uniform in appearance and not obviously soft. In a simple visual evaluation technique, if a sample is easily scored when handled or rubbed one against the other, then the coating is adjudged to be obviously soft.

From Figure 6 and Table VI it can be seen that a good coating can be formed in the 30-40°C electrolyte temperature range at a flow rate greater than 100 feet per minute and at current densities of at least 200 amps/ft².

3. Abrasion Resistance as Affected by Coating Thickness and Electrolyte Flow Rate

Figure 7 and Table VII show the effect of the flow rate of the electrolyte on the abrasion resistance of 2219 anodized to several coating thicknesses. The samples were anodized at 100 amps/ft² because this is the approximate current density to be used in the process itself. In the anodizing head now under design, 100 amps/ft² will produce a 0.3 mil (desired thickness) coating at an anodizing rate of approximately 6 linear inches per minute.

In Figure 7 no special notice is taken of the abrasion resistance of the 0.3 and 0.5 mil thicknesses, except that they are approximately the same. However, the 1.0 mil

coatings show a marked increase in abrasion resistance as the electrolyte flow rate is increased. This data would support the contention that if heat is removed rapidly enough from the reaction site, there is less solution action on the coating by the hot electrolyte and, therefore, a more abrasion resistant oxide is produced.

The reduction in abrasion resistance in coatings formed in an electrolyte with a flow rate of less than 150 feet per minute is probably due to an insulating effect of the thicker oxide coating. The additional insulation allows the hot electrolyte more time to attack the thicker coatings.

Figure 8 and Table VIII show a decrease in abrasion resistance as the thickness of the coating increases. It is interesting to compare the results of the abrasion tests on the panels anodized at 15 amps/ft² with those of comparable thicknesses anodized at 100 amps/ft². Where heat removal is a factor (less than 150 feet per minute flow rate at 100 amps/ft²), the quality of thicker coatings suffers.

4. Some Relationships of Anodic Coating Forming Conditions and Coating Properties

A very important aspect of the work to date is the calculation of the weight of an anodic coating of a given thickness formed under a given set of anodizing conditions. Previously, it has been shown that the density of the coating would vary with the thickness;⁴ that is, the thicker the coating, the lower the density due to electrolyte attack; the time of exposure; the concentration; and the bulk electrolyte temperature.

⁴ Kissin, G. H., et al., Finishing of Aluminum, Reinhold Publishing Corporation, New York, 1963, pp. 13-31.

From the data presented in this report, it was concluded that the density of the coating also varied with current density. This is probably the result of the greater cell wall thickness brought about by the higher forming voltage required at the higher current densities. (See Figures 4 and 5.) Another variable which affects the density of the coating is the electrolyte flow rate. Flow rate of the electrolyte affects the temperature near the surface of the coating being formed, thus affecting the dissolution rate of the coating in the electrolyte.

A series of 2219-T87, 0.050", 4" x 6" panels was anodized at various current densities including 15, 50, 100, and 200 amps/ft² at 30°C in 26% wt. sulfuric acid and an electrolyte flow rate of 140 feet per minute. A rate of 140 feet per minute flow rate was chosen because this was shown to be a minimum flow rate at which 2219-T87 could be anodized at 200 amps/ft² without adversely affecting the coating. (See Figure 6.) Two more samples were anodized at 800 amps/ft² in the same bath and temperature, but the variables of flow rate had to be changed to accommodate the gross increase in current density. (See Table IV.) After anodizing and weighing (coatings were not sealed), the coating thicknesses were measured on the Dermatron and the Ultrasonoscope.⁵ Ten measurements were made on each sample on both sides and with each instrument. Two samples 2" x 4" (5 x 10 cm) were cut from each 4" x 6" panel. These samples were stripped and weighed in accordance with MIL-A-8625A 4.4.3.2.

⁵ Both the Dermatron and the Ultrasonoscope are based on the eddy current principle.

D. Post Anodic Treatments

An aluminum surface which has been freshly anodized in sulfuric acid has the property of being highly porous and absorptive. This property allows a number of treatments. Various post anodic treatments can render the article functional according to the particular needs dictated by the end use. The open-pore anodic coatings may be printed, impregnated with photographic emulsion or lubricants, electroplated, dyed, and/or sealed.

1. Hot Water Sealing

Sealing is, ordinarily, a 15 minute immersion of the freshly anodized article in boiling water. The mechanism of the sealing process is commonly believed to be a reaction between water and the anodic oxide to form the mono- and the tri-hydrated forms of aluminum oxide. The reaction products cling to the pore walls and the oxide surface and physically block the entry of foreign or corrosive ions or molecules. A sealed surface is sometimes tested with a drop of dye. A sample is not considered adequately sealed if it accepts the dye.

To provide additional protection from corrosion, particularly from the chloride ion, chromates are sometimes introduced in low concentrations into the seal baths. It is believed that the chromium forms a complex oxide with the aluminum which does not readily hydrolyze in the presence of the chloride ion and water.

2. Steam Sealing of Anodized 2219-T87

Previous experiments in our laboratories have shown steam sealing to be approximately comparable to a good distilled or deionized water seal when tested by accelerated

corrosion tests (CASS). Since boiling water sealing is not applicable in this problem, it was felt that steam sealing should be investigated as an alternative approach to the problem. The following experiment was performed to determine the steam pressure needed to produce a good seal over a 3 minute exposure. A series of 18 panels of 2219-T87, 0.05", was anodized at 15 amps/ft² in 26 wt.% sulfuric acid for 20 minutes. They were then steam sealed for 3 minutes at varying pressures starting at atmospheric; 5, 10, 15, and 20 psi above atmospheric. A group of samples which had been sealed in boiling water accompanied these as controls. The samples were then exposed for 240 hours in 5% salt spray and evaluated by the ASTM rating technique. The results are shown in Table IX and Photo. D. These results indicate that in order to provide adequate steam sealing on anodized panels of 2219, it will be necessary to expose them for 3 minutes at pressures of 10 psi or greater to pass this corrosion test.

3. Chemical Conversion Sealing

The main objective in this work is to provide corrosion protection. The approach of sealing with steam or boiling water is not considered feasible in this particular application. A method of post anodic treatment which appears to meet the needs is a chemical conversion treatment following anodizing. This treatment would substitute for the impractical hot water or steam treatments. It is applied at room temperature and treatment time is about two minutes.

An experiment was performed to test the effectiveness of chemical conversion post anodic treatments.

Three types of Alodine were used to treat 0.35-0.40 mil anodic coatings on 2219-T87, 0.050". These were Alodine

1200, Alodine 1200S, and Alodine 600. The concentration used was 15 grams/liter at 74°F for two minutes. The samples were then rinsed in a 0.05% by weight solution of phosphoric acid and dried. Also included in the experiment for comparison were samples of 2219 anodized and water sealed, anodized and left unsealed, bare metal and panels given the Alodine treatment without anodizing. Following preparation, the samples were exposed for 240 hours in 5% neutral salt spray and rated by the ASTM rating system. The results are shown in Table X and Photo. E.

The results indicate that the chemical conversion coatings provide an adequate substitute for a sealing treatment on the anodized aluminum at this particular thickness.

ACKNOWLEDGMENTS:

The writer wishes to acknowledge the assistance of Mr. Erik F. Barkman for his part in the initiation of this project; Mr. Charles E. Garbett, who performed most of the experiments outlined in this report; and Miss Jean Whitt who has typed and edited this and previous monthly reports.

APPENDIX

TABLE I

Data on Pretreatment of 2219-T87, 0.050 inch,
by Electropolishing in 50% wt./wt. Sulfuric Acid

Current Density (amps/ft ²)	Voltage		Sample Appearance	
	20°C	40°C	20°C	40°C
50	19.8	9.3	Anodized	Slight anodic coating formed
100	23.5	15.0	Anodized	Slight anodic coating formed
150	28.5	17.5	Anodized	Slight anodic coating formed
200	24.0	17.5	Anodized	Slight anodic coating formed
250	25.0	16.5	Anodized	Slight anodic coating formed
300	23.1	16.5	Poorly anodized	Slight anodic coating formed
350	21.3	16.5	Poorly anodized	
400	21.0	14.0	Poorly anodized	
450	19.3	13.5	Poorly anodized	Electropolished - no coating
500	18.3	13.5	Poorly anodized	Electropolished - no coating
550	19.0	13.5	Poorly anodized	Electropolished - no coating
600	15.2	13.0	Poorly anodized	Electropolished - no coating
1000		14.0		Electropolished - no coating

TABLE II

CHANGE IN WEIGHT AS A RESULT OF ANODIZING
IN 26% H₂SO₄; FLOW RATE ~ 300 FPM

<u>Sample No.</u>	<u>Alloy</u>	<u>Anodizing Current Density</u>	<u>Volts</u>	<u>Anodizing Time (min.)</u>	<u>Thick-ness (mils)</u>	<u>Wt. Change During Anodizing (grams)</u>
L285	2014	15	12-14	48	.65	-.7916
L286	2014	50	19-20	14	.88	.0629
L287	2014	100	22-25	7	1.04	.3174
L288	2014	200	27-28	3	.90	.2268
L289	2219	15	14-15	48	.21	-.7822
L290	2219	50	11-22	48	.84	-.7167
L291	2219	150	25-27	7	1.00	.2083
L292	2219	200	27-30	3	1.13	.3482
L293	2219	15	12-15	14	.24	-.0044
L294	2219	50	21-23	4	.29	.1059
L295	2219	100	25-26	2	.32	.1607
L296	2219	200	27-28	1	.68	.2863
L297	2014	15	11-13	14	.22	-.0210
L298	2014	50	19-20	4	.23	.1267
L299	2014	100	22-23	2	.27	.1770
L300	2014	200	25-26	1	.32	.2106
L301	2219	15	14-15	48	.67	-.7831

TABLE III

Results of Anodizing 2219-T87 and 2014-T6 Alloys in Varying Concentrations of H₂SO₄ at 20°C and 15 amps/ft² for 30 minutes

Sample No.	Alloy	H ₂ SO ₄ wt. %	After 15 Min.	Voltage Range 0-30 Min.	Average (watt/ft ²)	Coating Thickness (mils)	Weight Loss Per 1000 Revolutions on the Taber Abrasion Tester (mg)	Total Reflectance	Remarks
L-264	2219	9	34	15.0-35	510	-	-	-	Spotty coating
L-263	2014	9	32	31.0-32.5	480	-	-	-	Spotty coating
L-262	2014	9	Other attempts to anodize in the 9% solution also resulted in spotty or preferential nonuniform anodizing.						
L-265	2219								
L-266	2219	20	27	20.0-28.8	405	0.43	3.5	54.4	Uniform
L-266-1	2219	20	28.1	15.0-29.5	422	0.41	3.5	54.6	Uniform
L-266-2	2219	20	28.0	16.0-28	420	0.40	3.5	54.3	Uniform
L-267	2014	20	24	16.0-24.9	360	0.37	3.6	60.0	Uniform
L-267-1	2014	20	24	16.0-24.5	360	0.40	4.3	58.7	Uniform
L-267-2	2014	20	24	16.0-24.8	360	0.42	4.1	59.1	Uniform
L-268	2219	30	17.2	16.5-17.5	258	0.48	3.3	55.1	Uniform
L-268-1	2219	30	17.0	16.5-17.5	255	0.44	3.3	56.0	Uniform
L-268-2	2219	30	17.0	16.8-17.5	255	0.44	3.5	56.0	Uniform
L-269	2014	30	14.5	14.5-14.8	218	0.41	4.3	63.8	Uniform
L-269-1	2014	30	14.5	14.4-14.8	218	0.42	4.3	64.5	Uniform
L-269-2	2014	30	14.5	14.4-14.8	218	0.43	3.5	63.5	Uniform
L-270	2219	40	10.4	10.2-10.6	156	0.50	4.6	56.7	Uniform
L-270-1	2219	40	10.5	10.1-10.6	157	0.48	4.3	56.0	Uniform
L-270-2	2219	40	10.2	10.0-10.4	153	0.47	4.3	57.5	Uniform
L-271	2014	40	9.9	9.9	148	0.49	4.1	60.0	Uniform
L-271-1	2014	40	9.8	9.5-9.9	147	0.50	4.2	59.6	Uniform
L-271-2	2014	40	9.5	9.4-9.7	142	0.48	3.9	59.8	Uniform

TABLE IV

The Apparent Density of the Anodic Coating Formed on 2219-T87 Alloy at Varying Current Density in 26 wt.% H₂SO₄ at 30°C - Strip and Weigh Technique

Sample No.	Electrolyte Flow Rate (ft./min.)	Current Density (amps/ft ²)	Voltage Range	Sample Length (cm)	Size Width (cm)	Oxide Thickness (mils)	Oxide Weight (gm)	Apparent Density (gm/cc)
L-272	140	15	10-13	10.155	5.072	0.49	0.1634	1.28
L-272A	140	15	10-13	10.147	5.131	0.50	0.1651	1.25
L-272B	140	50	20-21	10.173	5.128	1.03	0.4165	1.52
L-272C	140	50	20-21	10.175	5.083	0.97	0.4136	1.63
L-273A	140	50	20-21	10.163	5.131	0.98	0.3646	1.40
L-273	140	50	20-21	10.168	5.098	0.98	0.3637	1.41
L-274	140	100	23-24.5	10.163	5.075	1.21	0.5147	1.62
L-274A	140	100	23-24.5	10.163	4.996	1.08	0.5072	1.82
L-274B	140	100	23-24	10.168	5.105	0.99	0.4726	1.81
L-274C	140	100	23-24	10.163	5.095	1.02	0.4815	1.80
L-275	140	200	25-27	10.163	5.116	1.17	0.5328	1.73
L-275A	140	200	25-27	10.155	5.095	1.19	0.5240	1.68
L-275B	140	200	28-31	10.124	5.055	1.16	0.6196	2.05
L-275C	140	200	28-31	10.124	5.080	1.16	0.6218	2.05
L-276A	330	800	33-42	10.200	5.072	1.15	0.5405	1.82
L-276B	330	800	33-42	10.196	5.062	1.19	0.5382	1.73

Table V

Material Being Used or Tested

<u>Material</u>	<u>Manufacturer</u>	<u>Use</u>	<u>Feature</u>	<u>Description</u>
Plexiglas	Rhom & Haas Chemical Co.	Construction of prototype anodizing head	Acid resistance, transparency	Clear acrylic plastic sheet
Plexiglas Cement M18	Masco Chemical Company	Bonding Plexiglas joints	Forms thick, strong joints -- 30-minute set	Three-part adhesive
Teflon felt "Armalon"	DuPont	Sliding gasket on anodizing head	Low coefficient of friction, acid resistance	0.25" thick brown mat
One-side etched teflon sheet	Cadillac Plastic Company	Reinforcement of teflon gasket	Low coefficient of friction, acid resistance	0.010" sheet -- white on one side, brown on etched side
Silastic RTV 891	Dow Corning Corporation	General adhesive where flexible joints are wanted	Very elastic, chemical resist- ance, room temp. vulcanization, adhesion to almost any surface	White rubbery elastic packaged in a collapsible tube

Table VI

DATA ON CURRENT DENSITY-FLOW RATE RELATIONSHIPS

Alloy 2219-T87, 0.050" gauge, anodized in 26% wt. H₂SO₄

<u>Sample No.</u>	<u>Flow Rate (FPM)</u>	<u>Current Density (ASF)</u>	<u>Temperature (°C)</u>	<u>D.C. Volts</u>	<u>Anodizing Time (Min.)</u>	<u>Remarks</u>
L141	348	100	20.6	30	2.5	Uniform
L142	352	200	20.6	29-35	2.5	Moving anodizing front
L143	352	200	20.6	30-35	1.5	Moving anodizing front; lost contact at 90 seconds
L144	352	50	20.6	25-27	2.5	Uniform
L145	348	15	20.6	11-15	2.5	Iridescent, not uniform
L149	207	200	20.6	28-30	2.5	Lighter coating around bolt holes
L150	207	100	20.6	27-28	2.5	Lighter coating around edges
L151	207	50	20.6	25	2.5	Uniform
L152	207	15	20.6	14-16	2.5	Uniform
L153	94	200	21	28	2.5	Burned on corner then burn was arrested
L154	94	100	21	25	2.5	Burned on corner then burn was arrested
L155	103	50	21	24-25	2.5	Uniform
L156	94	15	21	15-16	2.5	Uniform
L157	70	200	21	27-25	2.5	Light coating around edges; thermo-chemical attack on oxide in 5 in. sq. area in center
L158	75	100	21	25-24	2.5	Light coating around edges

Table VI (Continued)

<u>Sample No.</u>	<u>Flow Rate (FPM)</u>	<u>Current Density (ASF)</u>	<u>Temperature (°C)</u>	<u>D.C. Volts</u>	<u>Anodizing Time (Min.)</u>	<u>Remarks</u>
L159	75	50	21	23-24	2.5	Uniform
L160	70	15	21	14-16	2.5	Uniform
L161	354	200	30	29	2.5	Uniform
L162	354	100	30	26-27	2.5	Uniform
L163	354	50	30	20-22	2.5	Uniform
L164	354	15	29	12-14	2.5	Uniform
L165	215	200	29	27-29	2.5	Uniform
L166	206	50	29	20-22	2.5	Uniform
L167	215	100	29	25-26	2.5	Uniform
L168	206	15	28	12-14	2.5	Uniform
L169	94	200	30	23-25-24	2.5	Thermo-chemical attack on about 2 sq. in. in center of panel
L170	89	100	30	20-21	2.5	Uniform
L171	94	50	30	18	2.5	Uniform
L172	94	15	29	11-12	2.5	Uniform
L173	70	200	30	22-23-22	2.5	Thermo-chemical attack on about 8 sq. in. in center of panel
L174	75	100	30	21-22	2.5	Uniform
L175	70	50	30	18-19	2.5	Uniform
L176	70	15	30	10-11	2.5	Uniform
L177	73	200-400	30	22-24	2.5	Thermo-chemical attack on 18 sq. in. area in center of panel

Table VI (Continued)

<u>Sample No.</u>	<u>Flow Rate (FPM)</u>	<u>Current Density (ASF)</u>	<u>Temperature (°C)</u>	<u>D.C. Volts</u>	<u>Anodizing Time (Min.)</u>	<u>Remarks</u>
L178	470	400	30	32-50	2.5	Dark gold color; very uniform
L179	348	200	40	23-24	2.5	Uniform
L180	215	100	40	17-19	2.5	Uniform
L181	348	100	40	19	2.5	Uniform
L182	354	50	40	13-14	3.0	Uniform
L183	354	15	40	7-8	3.0	Uniform
L184	215	200	40	22-23	3.0	Uniform
L185	215	50	40	14-15	3.0	Uniform
L186	206	15	40	7-8	3.0	Uniform
L187	94	200	40	20	3.0	Thermo-chemical attack on oxide, 12 sq. in. area in center of panel
L188	94	100	40	17-18	3.0	Uniform
L189	94	50	40	13-15	3.0	Uniform
L190	98	15	40	7-8	3.0	Uniform
L191	42	200	40	17-18	3.0	Thermochemical attack on ~ 95% of surface
L192	47	200	40	18-16	3.0	Thermochemical attack on ~ 90% of surface
L193	47	100	40	17-18	3.0	Uniform
L194	52	50	40	13-14	3.0	Uniform
L195	42	15	40	7-8	3.0	Uniform
L196	0	15	40	7-9	3.0	Uniform

Table VI (Continued)

<u>Sample No.</u>	<u>Flow Rate (FPM)</u>	<u>Current Density (ASF)</u>	<u>Temperature (°C)</u>	<u>D.C. Volts</u>	<u>Anodizing Time (Min.)</u>	<u>Remarks</u>
L197	47	200	10	32-36	2.6	Wide current fluctuation-- apparent burning, coating is uniform
L198	60	100	10	29-32	3.0	Nonuniform anodizing on a moving front
L199	60	50	10	28-29	3.0	Nonuniform anodizing on a moving front
L200	60	15	10	27-23	3.0	Uniform
L201	85	200	10	30-41	3.0	Uniform
L202	90	100	10	29-32	3.0	Nonuniform anodizing on a moving front
L203	94	50	10	28-31	3.0	Nonuniform anodizing on a moving front
L204	104	15	10	26-28	3.0	Uniform
L205	178	200	10	31-49	3.0	Initially moving front anodizing but later became a uniform coating
L206	178	100	10	30-34	3.0	Nonuniform anodizing on a moving front
L207	188	50	10	30-31	2.0	Nonuniform anodizing on a moving front
L208	188	15	10	23-30	3.0	Uniform
L209	310	200	10	34-60	3.0	Uniform; small area around bolt hole where anodizing on a moving front occurred initially
L210	305	100	10	33-42	3.0	Nonuniform anodizing on a moving front

Table VI (Continued)

<u>Sample No.</u>	<u>Flow Rate (FPM)</u>	<u>Current Density (ASF)</u>	<u>Temperature (°C)</u>	<u>D.C. Volts</u>	<u>Anodizing Time (Min.)</u>	<u>Remarks</u>
L211	305	50	10	32-35	2.0	Nonuniform anodizing on a moving front
L212	310	15	10	26-30	3.0	Uniform

Table VII

Abrasion Resistance as Affected by Flow Rate and Coating Thickness

Taber Abrasion Tester used with CS-17 wheels and 1000 gram load.
Alloy 2219-F87, 0.050 gauge, anodized in 28% H₂SO₄ at 100 ASF and 30 °C.

<u>L#</u>	<u>Coating Thickness, mils</u>	<u>Flow Rate, FPM</u>	<u>Weight Loss After First 1000 Rev., mg</u>	<u>Weight Loss After Second 1000 Rev., mg</u>
213	0.3	75	2.3	
214	0.3	75	4.2	3.6
215	0.3	75	4.2	
216	0.5	153	4.4	
217	0.5	153	4.0	2.6
218	0.5	153	3.9	
219	0.3	153	3.3	
220	0.3	153	4.1	3.5
221	0.3	153	3.4	
222	0.3	334	4.2	
223	0.3	334	3.6	3.9
224	0.3	334	4.2	
225	0.3	400	4.1	
226	0.3	398	4.1	3.2
227	0.3	398	4.2	
228	0.5	70	6.6	
229	0.5	75	4.4	4.7
230	0.5	75	4.6	
231	0.5	304	3.1	
232	0.5	310	3.6	3.6
233	0.5	304	3.2	
234	0.5	398	2.4	
235	0.5	405	2.9	3.7
236	0.5	405	3.5	
237	1.0	405	4.8	
238	1.0	405	6.4	3.8
239	1.0	414	5.5	

Table VII (Continued)

<u>L#</u>	<u>Coating Thickness, mils</u>	<u>Flow Rate, FPM</u>	<u>Weight Loss After First 1000 Rev., mg</u>	<u>Weight Loss After Second 1000 Rev., mg</u>
240	1.0	320	5.4	
241	1.0	310	5.7	4.7
242	1.0	310	4.5	
243	1.0	150	7.6	
244	1.0	150	9.2	3.1
245	1.0	150	11.1	
246	1.0	75	25.4	
247	1.0	75	26.2	5.2
248	1.0	66	25.6	

Table VIII

Abrasion Resistance and Coating Thickness

Taber Abrasion Tester used with CS-17 wheels and 1000 gram load.
Alloy 2219 anodized to various thicknesses
at 15 ASF, 19°C, 17% wt. H₂SO₄.

<u>I.#</u>	<u>Coating Thickness, mils</u>	<u>Weight Loss After 1000 Revolutions, mg</u>
249	0.19	3.0
250	0.20	3.4
251	0.40	3.6
252	0.40	4.6
253	0.80	4.8
254	0.82	6.1

Table IX

This table shows the effect of sealing anodized 2219-T87 in steam at varying pressures on the corrosion resistance in salt spray. Exposure time at steam pressure was 3 minutes. The samples were anodized in 26 wt.% H₂SO₄ to the coating thicknesses shown.

<u>Sample No.</u>	<u>Steam Pressure</u>	<u>Average* Coating Thickness (mils)</u>	<u>Average* ASTM Rating</u>
L259	0 psi (Atmospheric)	0.38	4
L260	5 psi	0.39	7
L261	10 psi	0.38	8.7
L262	15 psi	0.37	9
L263	20 psi	0.35	9
L264	Control-sealed 20 min. in boiling water	0.24	9

* Average of three panels.

Table X

THE RESULTS OF EXPOSURE OF 2219-T87 TO 240 HOURS 5% NEUTRAL
SALT SPRAY AFTER VARIOUS SURFACE TREATMENTS

(Photographs on Opposite Page)

<u>Sample No.</u>	<u>Surface Treatment</u>	<u>Average** Coating Thickness (mils)</u>	<u>Average** ASTM Rating</u>
L277-1	Normal Pretreat* + Alodine 600	Conversion Coating	2
L277-2	Pretreat + Anodize + Alodine 600	0.39	8.9
L278-1	Normal Pretreat + Alodine 1200	Conversion Coating	2
L278-2	Pretreat + Anodize + Alodine 1200	0.40	9
L279-1	Normal Pretreat + Alodine 1200S	Conversion Coating	2
L279-2	Pretreat + Anodize + Alodine 1200S	0.41	9
L282	Control Samples; Boiling Water Seal	0.43	9
L281	Pretreat + Anodize; Unsealed	0.43	5
L280	Pretreat Only	0.0	0

* Normal Pretreatment:

1. Nonetch alkaline degrease
2. Acid pre-etch dip
3. Caustic etch (30R) for 5 minutes
4. Desmut

** Average of three panels.

Figure 1

ETCH RATES OF 2219 AND 2014 ALLOYS IN 4%
30R (PROPRIETARY CAUSTIC ETCH) AT 150°F

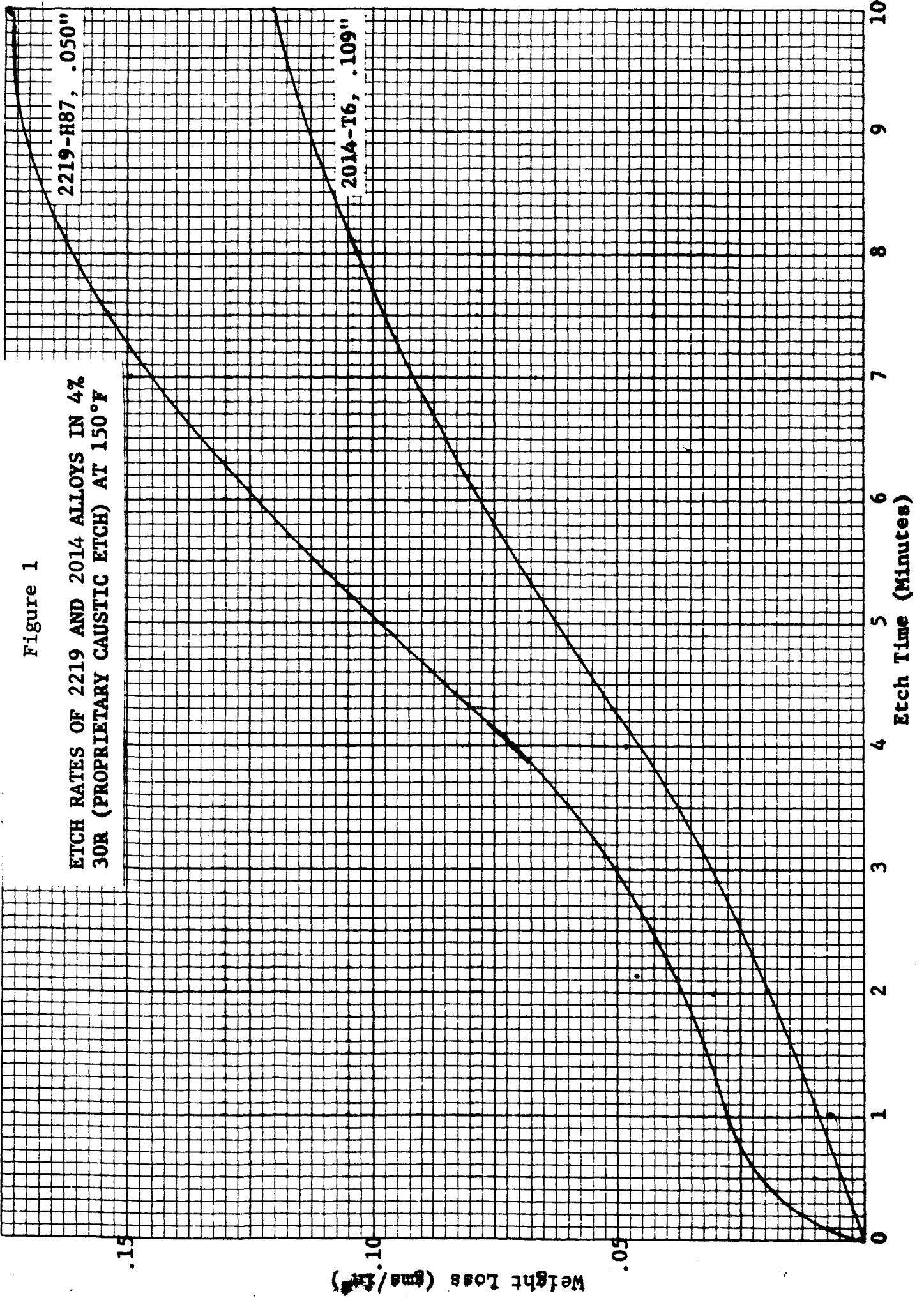


Figure 2

WEIGHT CHANGE DURING ANODIZING
VERSUS CURRENT DENSITY EMPLOYED

26% H₂SO₄, 30°C
Alloys, 2219 and 2014
Flow Rate, 300 FPM
Sample Area, 48 sq. in.

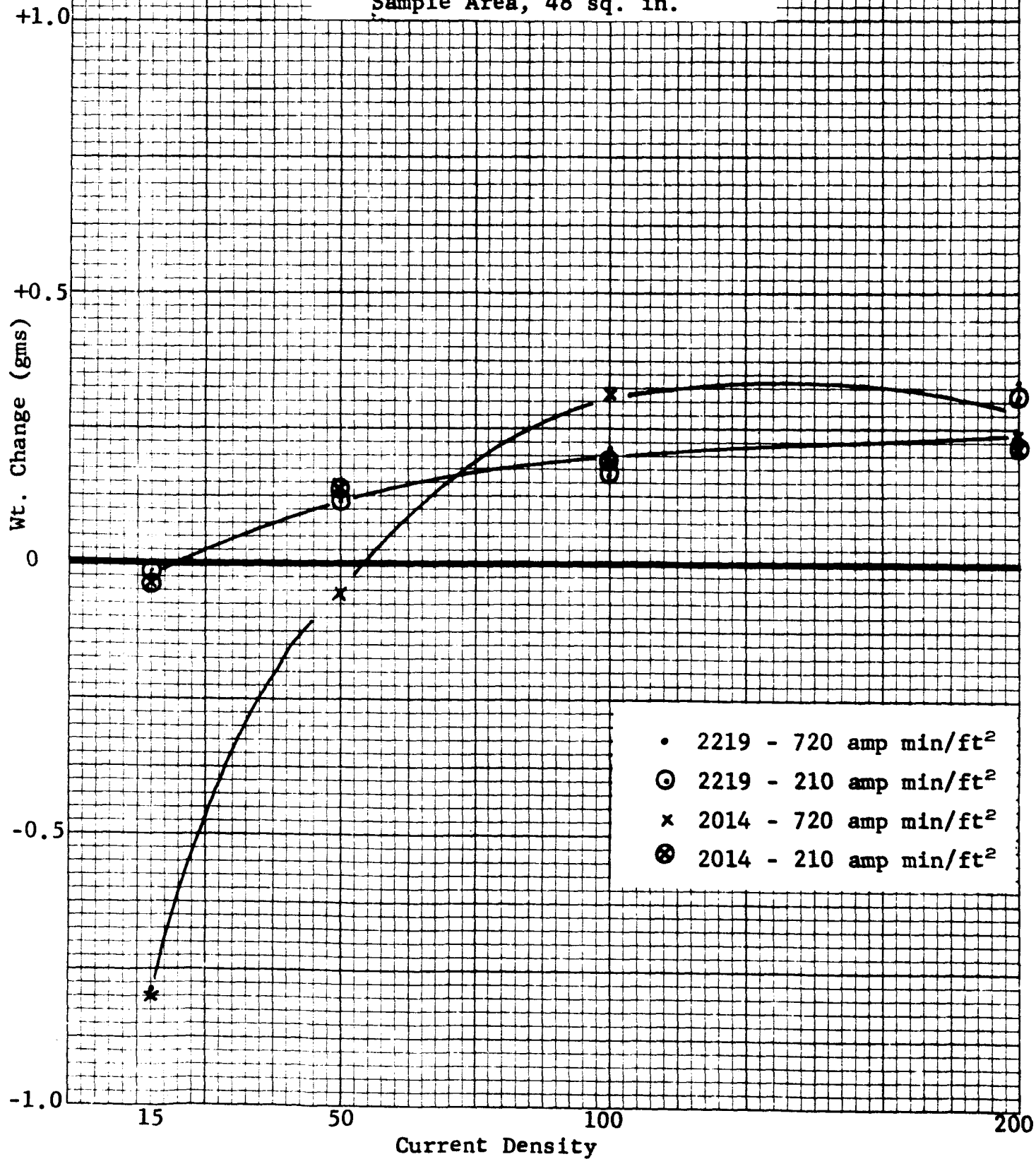


Figure 3

Abrasion Resistance of 2219-T87 and 2014-T6 Anodized in Varying Concentrations of H_2SO_4 for 30 Minutes at $20^\circ C$ and 15 amps/ft²

Weight loss was measured after 1000 revolutions on the Taber Abrasion Tester using CS-17 wheels and 1000 grams load.

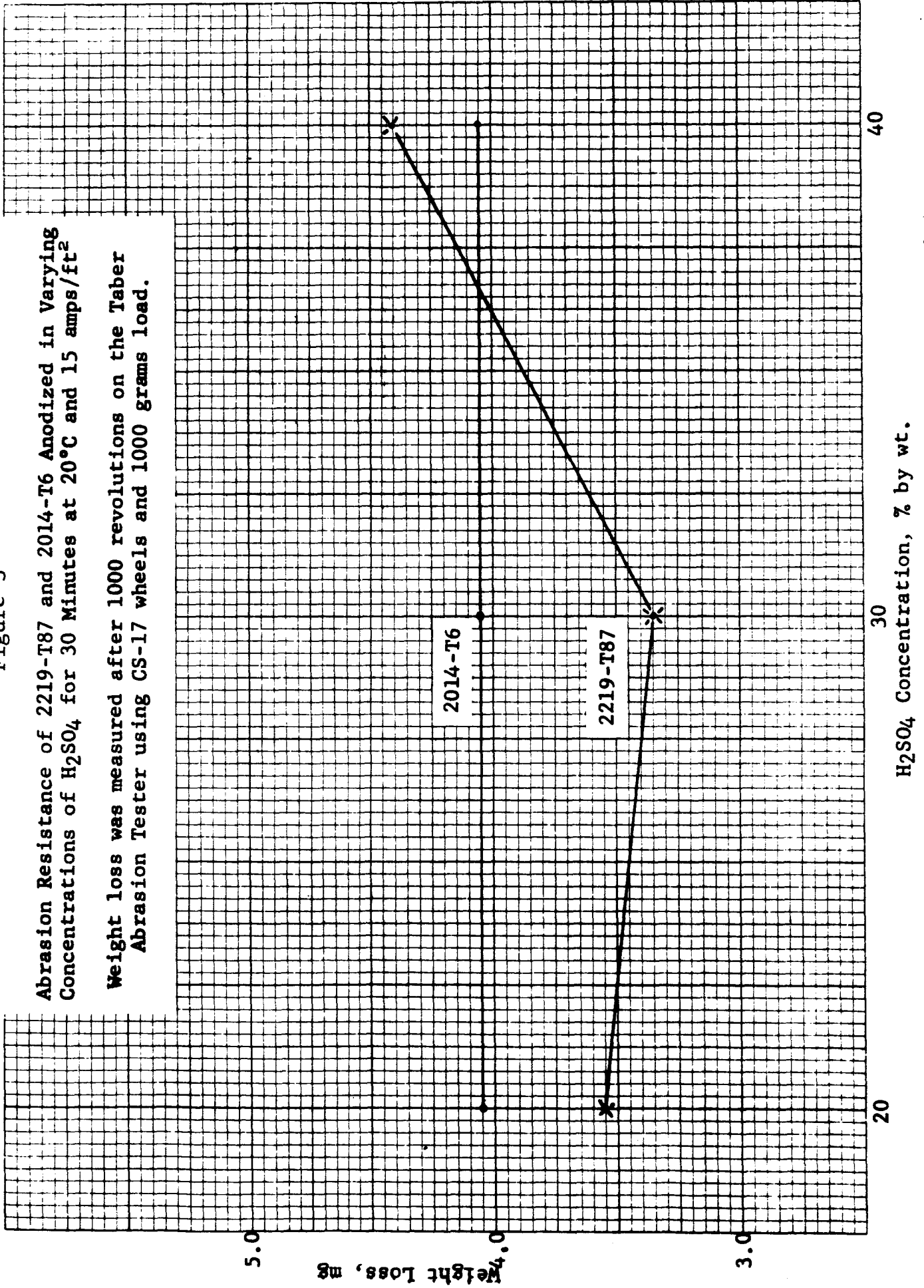


Figure 4

Current Density Vs. Apparent Density of Anodic Coating and Cell Wall Thickness (8.5 A/volt)

Electrolyte, 26% wt. H_2SO_4 , 30°C
Flow Rate, 140 feet per minute

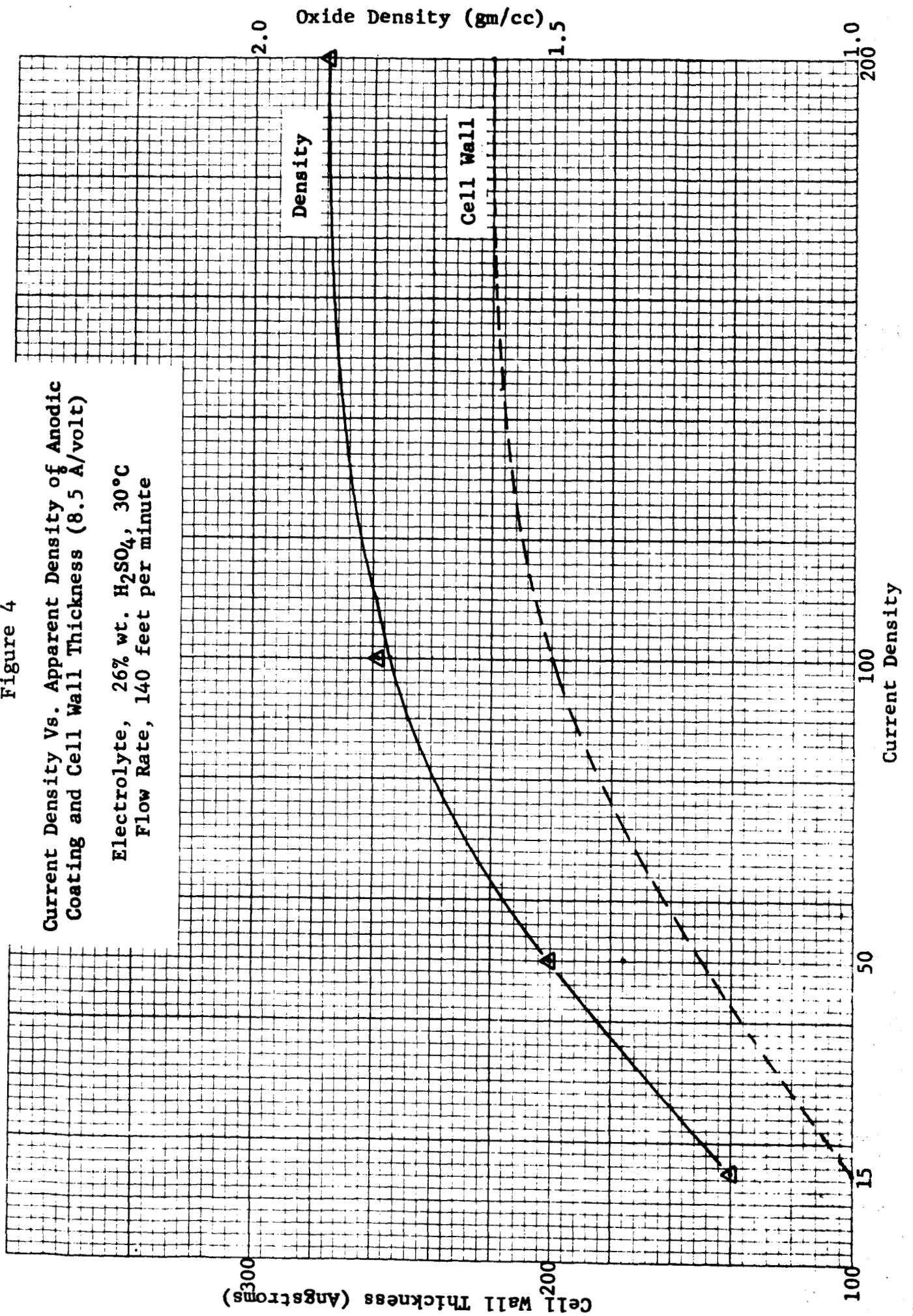


Figure 5

Anodizing Voltage of 2219-T87 Alloy at Varying
Current Density in 26% by Wt. H_2SO_4 and 30°C

Electrolyte Flow Rate, 140 Feet Per Minute

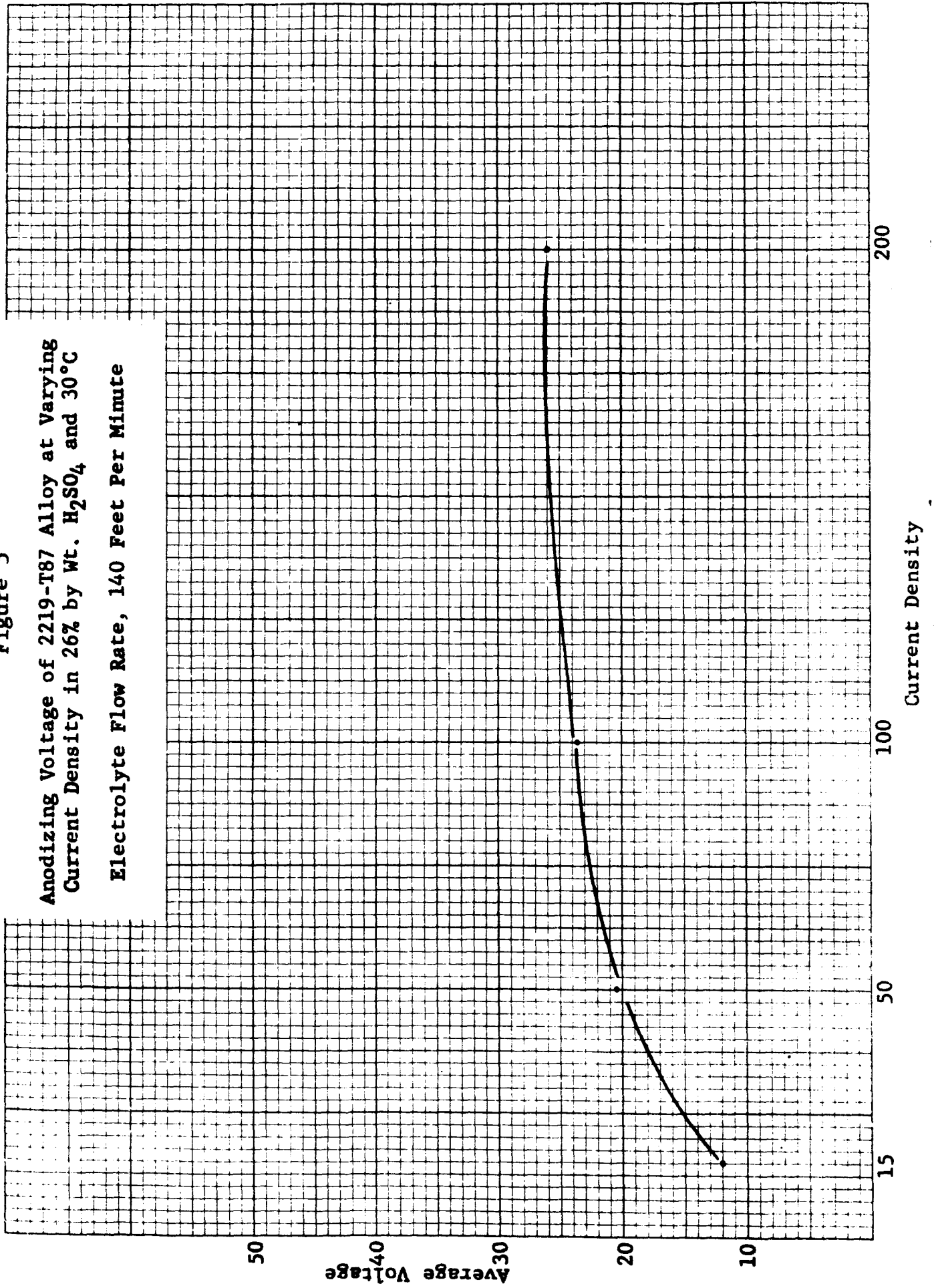
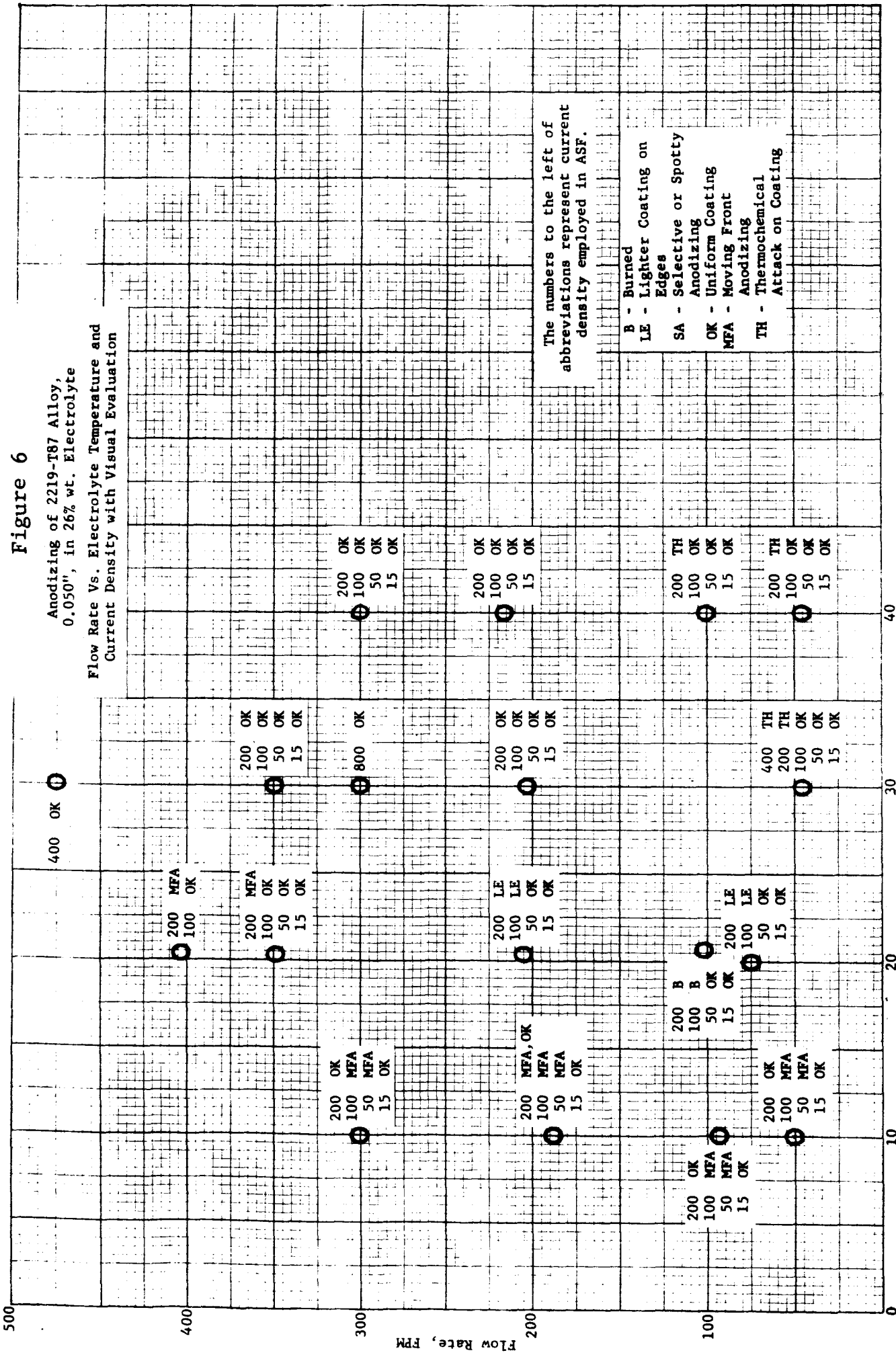


Figure 6

Anodizing of 2219-T87 Alloy,
0.050", in 26% wt. Electrolyte

Flow Rate Vs. Electrolyte Temperature and
Current Density with Visual Evaluation



The numbers to the left of
abbreviations represent current
density employed in ASF.

- B - Burned
- LE - Lighter Coating on Edges
- SA - Selective or Spotty Anodizing
- OK - Uniform Coating
- MFA - Moving Front Anodizing
- TH - Thermochemical Attack on Coating

Bulk Electrolyte Temperature, °C

Figure 7

Abrasion Resistance of 2219-T87 Alloy (0.050")
Anodized in 26% wt. H₂SO₄ at 100 ASF and 30°C
as a Function of Coating Thickness and Flow
Rate of the Electrolyte

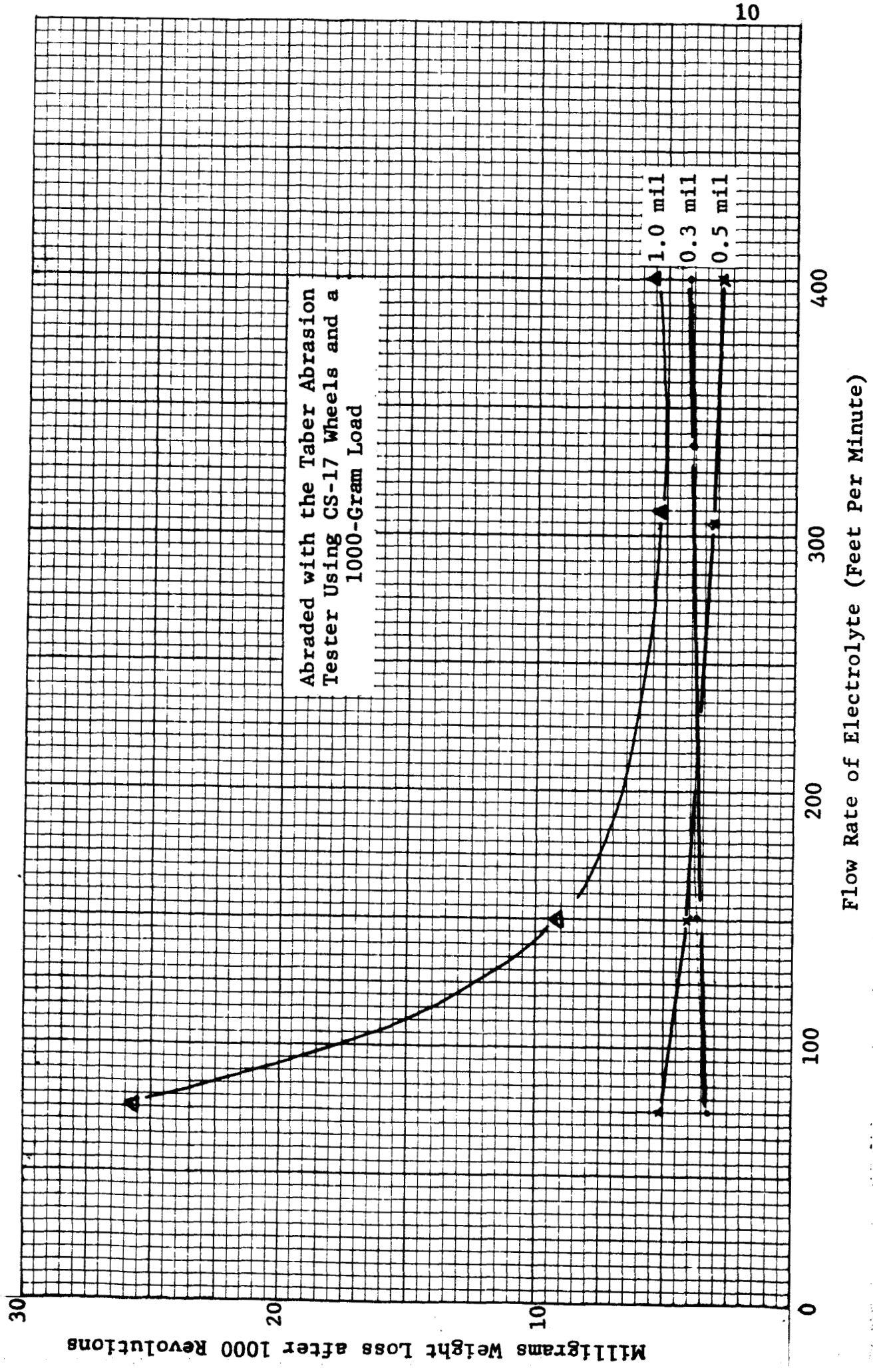


Figure 8

Abrasion Resistance of 2219-T87 Alloy
as a Function of Coating Thickness
Anodized in 17% wt. H₂SO₄ at 19°C and 15 ASF

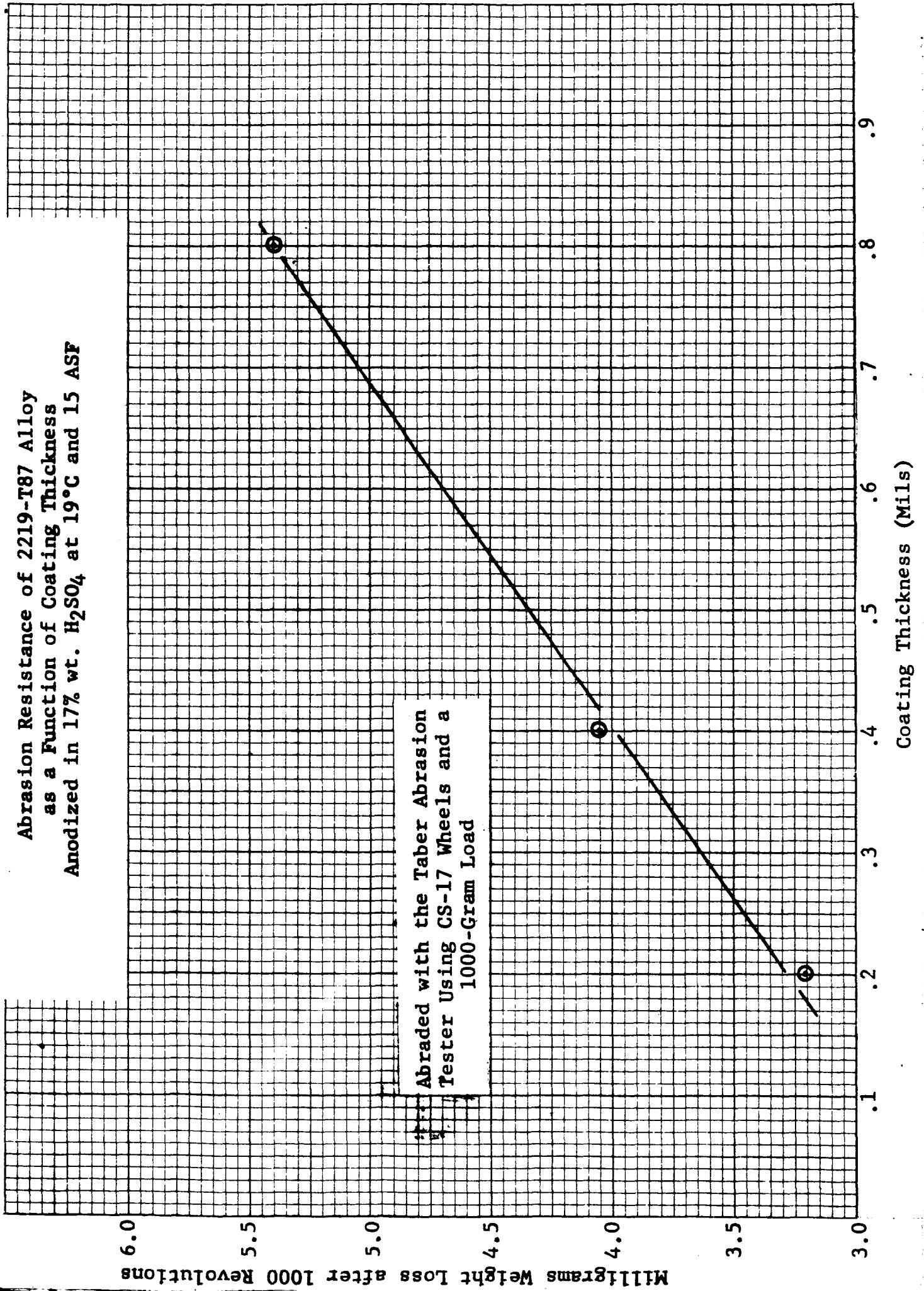
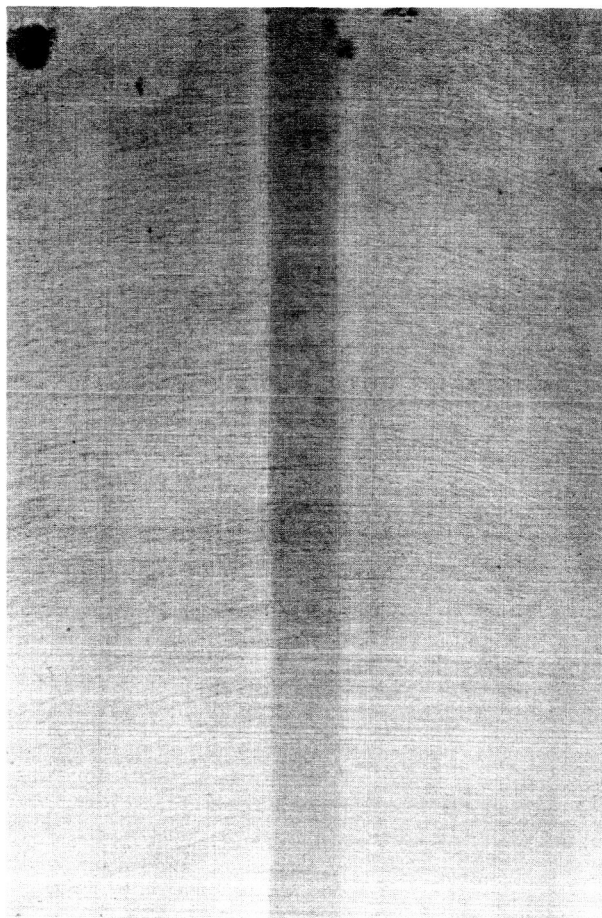
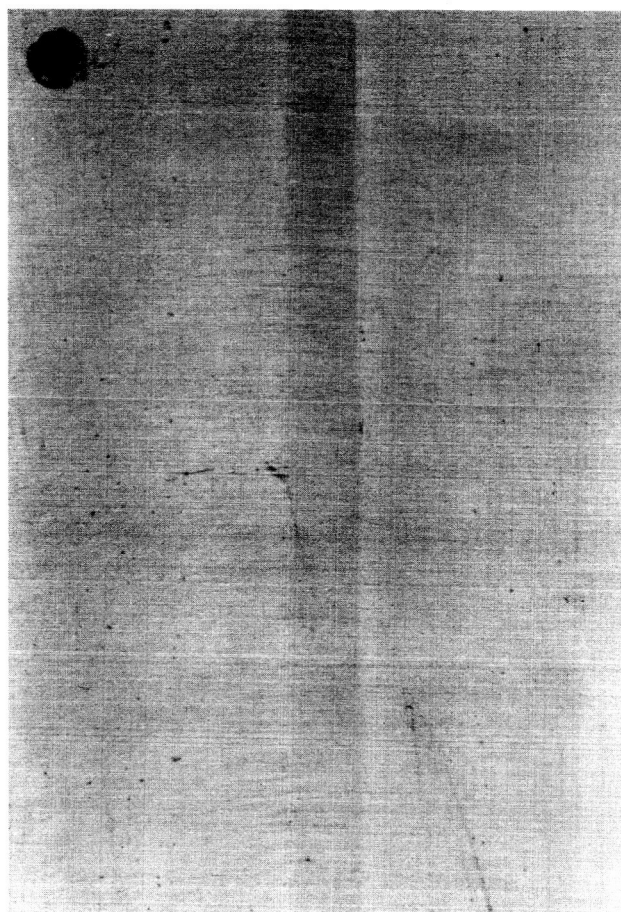


FIGURE 3 A

PRETREATMENT VERSUS NONPRETREATMENT PRIOR TO ANODIZING



Normal Pretreatment

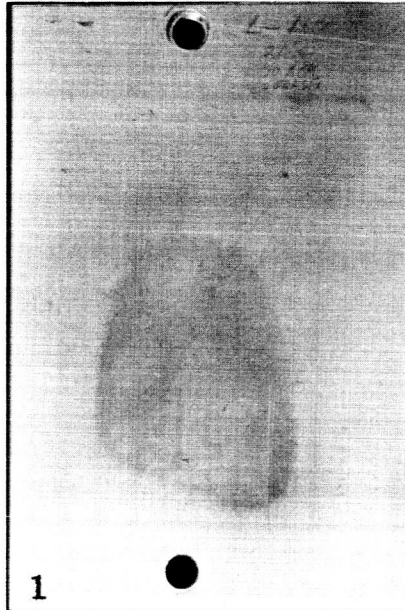


No Pretreatment

The sample on the left was given a normal pretreatment whereas the sample on the right was only degreased prior to anodizing. After being exposed to 240 hours of salt spray, the untreated sample had a rating of about 4 while the normally pretreated sample had a rating of 8. (A rating of 9 is perfect.)

Figure C

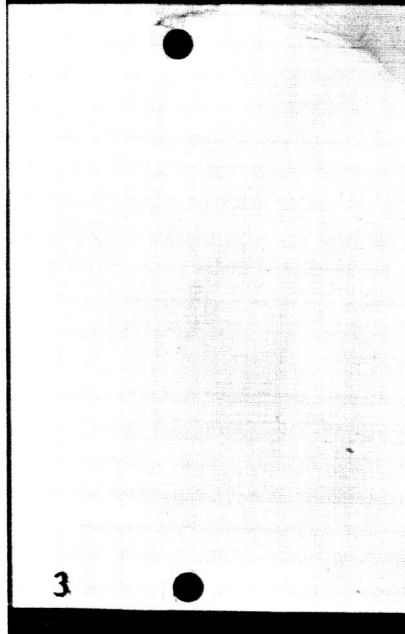
C1 • This sample shows "thermo-chemical" attack on the anodic coating. Part of the affected area has been abraded with a dry paper towel.



C2 • This panel illustrates "burning" in the left corner and variation in coating thickness from a "moving anodizing front."



C3 • An "arrested burn" is shown in the upper right hand corner.



C4 • This sample has a light edge and heavier center coating. The photo does not show this well.

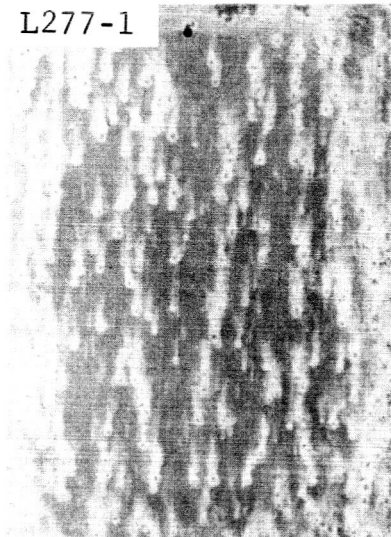


Shown above are four samples of 2219-T86 alloy (0.050", 4" x 6") which illustrate defects encountered in high current density anodizing.

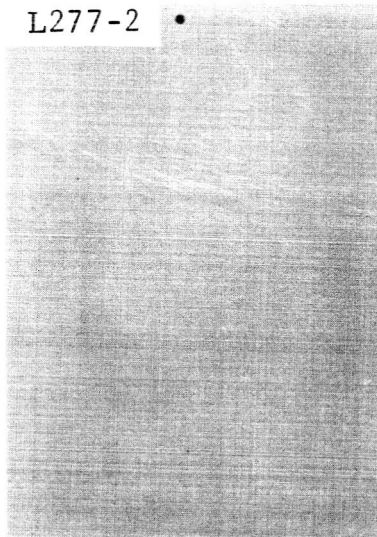
FIGURE 2 D

VARIOUSLY TREATED 2219-T87 AFTER 240 HOURS EXPOSURE TO SALT SPRAY

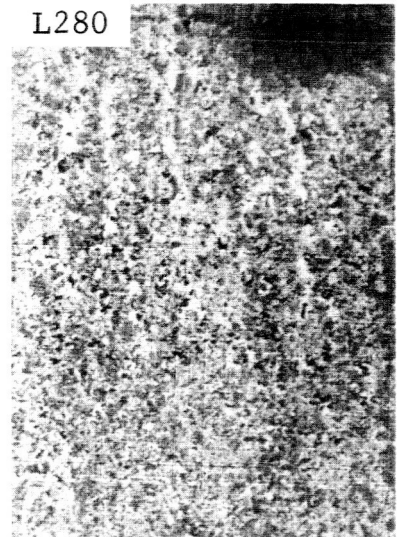
L277-1



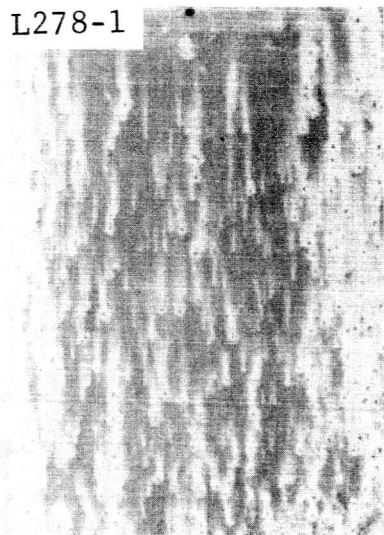
L277-2



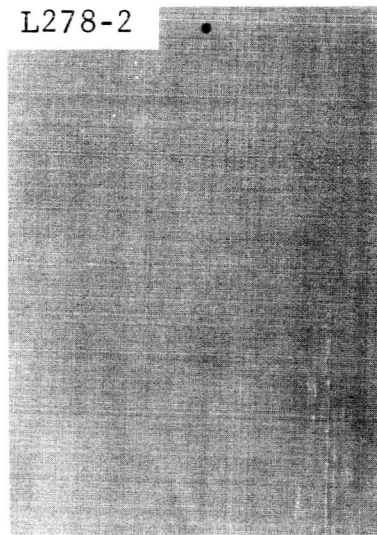
L280



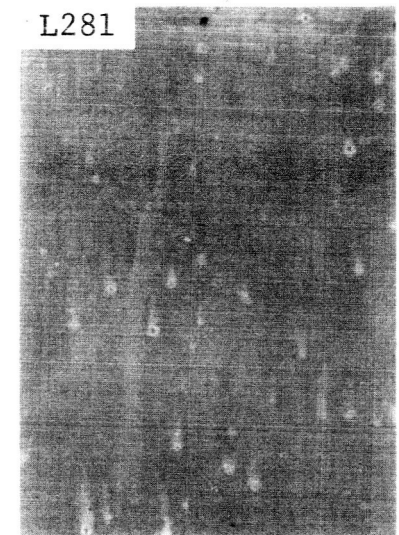
L278-1



L278-2



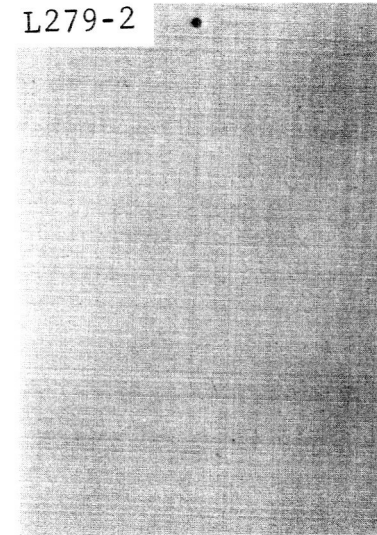
L281



L279-1



L279-2



L282

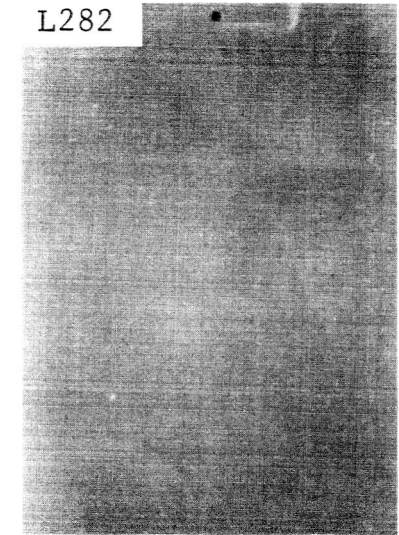


FIGURE X E

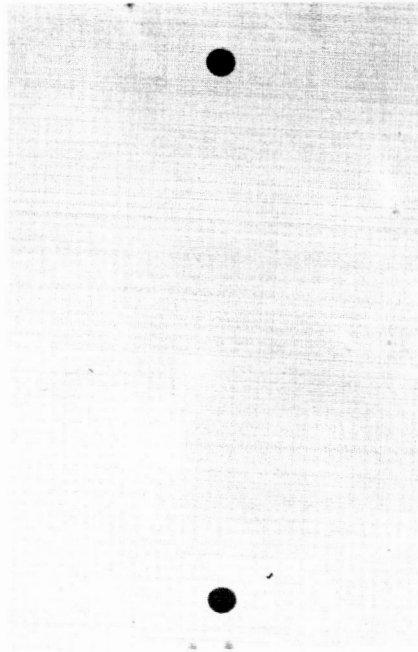
STEAM SEALING

The samples shown below are 4" x 6", anodized to approximately 0.4 mil and sealed in steam at various pressures for 3 minutes, then exposed to salt spray for 240 hours.

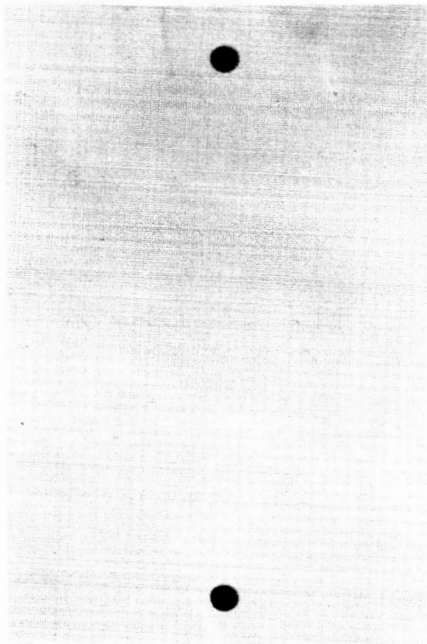
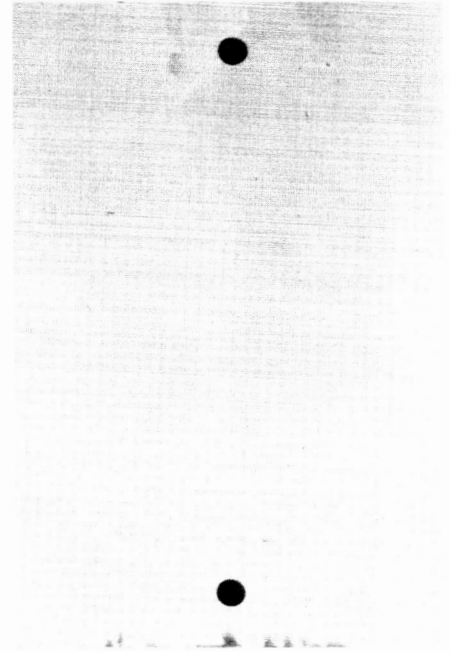
Rating 4
0 psi



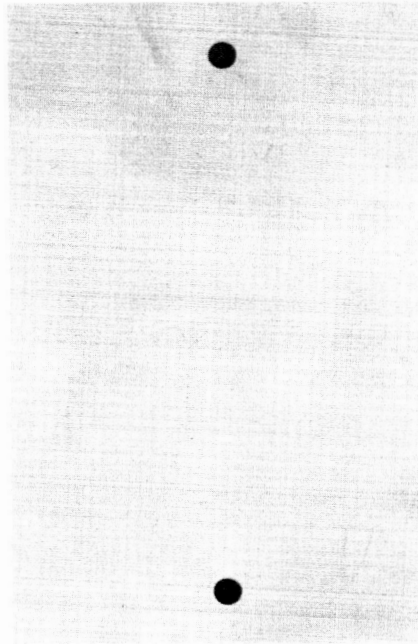
Rating 7
5 psi



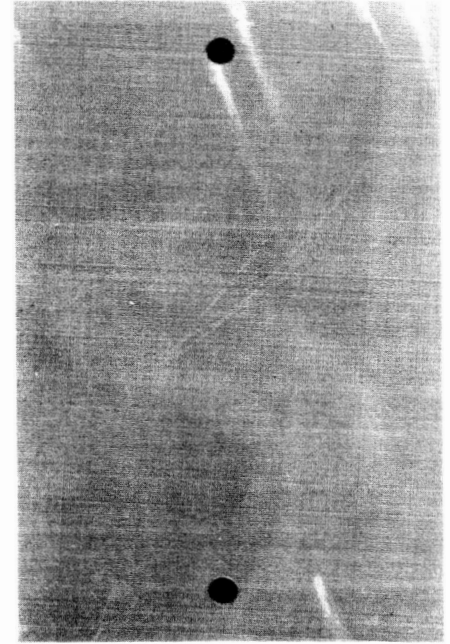
Rating 8.7
10 psi



Rating 9
15 psi



Rating 9
20 psi



Rating 7
Boiling Water Seal

DISTRIBUTION LIST

R. W. Clatworthy (10 copies)
Contracting Officer
George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Huntsville, Alabama

Research & Development

W. G. Reynolds - EXO
J. H. Jackson - MRD
G. R. Shockley - PDD
S. J. Sansonetti - MRD
E. F. Barkman - MRD
C. W. Golgart - MRD
T. I. C. - MRD
Library - MRD

Legal

A. I. Palmer - EXO