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VARIATION OF THICKNESS OF HARD ANODIC FILMS

THESIS

Submitted in partial fulfillment

of the requirements for the

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MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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NEWARK COLLEGE OF ENGINEERING

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The experimental work on which this report is based
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Eclipse-Pioneer Division during the year 1954.

ABSTRACT

An investigation was made of the effects of varying processing conditions on the thickness of anodic films produced by the Martin Hard Coat (4) process on commercially pure aluminum and nine aluminum alloys.

This study was conducted to provide sufficient data for designing coating thicknesses on aircraft accessory parts that would conform to the close tolerances maintained in the course of manufacture of precision components. Coating thicknesses up to 0.0051 in. were obtained. Changes in electrolyte strength, temperature of the bath, alloy composition, and current density were made to see their effect on the thickness of the film and growth of the part. The first three aforementioned variables caused slight variations in the film thickness. Current density was the chief determinant of the thickness of the "hard coat" film. Growth of the part was only affected slightly by changes in processing conditions. The growth of the part averaged 0.41 of the over-all film thickness.

Coating ratios increased with time of film formation; higher coating ratios were obtained with low strength electrolytes, low bath temperatures, and high current densities.

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INTRODUCTION

The nation's preparedness program aimed at new and better aerial weapons has renewed the search for materials with improved properties. While aluminum has been the primary material of construction in the fabrication of aircraft and aircraft accessories, there are several properties of the metal that limit its use. Wear resistance is chief among them. Since World War II, several processes for the production of wear-resistant hard-oxide films on aluminum alloys have been presented in the literature (7,28,30). Data consisted of qualitative descriptions of the characteristics of the film and tables listing the alloys in the order of preference to abrasive wear or ease of coating (2,11,20,21). The first compilation of data on the performance of hard-oxide coatings was made by Gillig (7) in a test program directed by the Wright Air Development Center. The design data made available by this addition to the literature makes it possible to select coatings for aircraft applications and to predict their performance.

In the aircraft accessory field, the problem of designing precision parts to be coated with a hard-anodic film requires accurate data on the relation between growth of the part and coating thickness. Finished cams, sheaves, impellers, etc. have dimensional tolerances that are not affected by the thickness of normal anodize but may be exceeded by the greater thicknesses of hard anodize.

Normal-anodic films range in thickness from 0.0001 in. to 0.0008 in.; hard-anodic films range from 0.001 in. to 0.005 in. (29). A coating of 0.002 in. is most generally applied. This investigation was made to provide data applicable to predicting machined dimensions with proper allowance for hard-coating thickness to bring an anodized part within the dimensional tolerances specified for the finished piece.

I Description of Hard Coatings

General Background Hard coating is formed in a similar manner to the more familiar normal-anodic coating. An anodic film is produced electrochemically by forming an oxide film on a piece of metal suspended as an anode in a bath of electrolyte through which a current is passing. The idea of forming an oxide coating on aluminum artificially is about one-hundred years old. A quite formidable number of papers have appeared in the literature describing methods of forming normal-anodic films, theories on film structure and composition, and methods of test and evaluation. The late G. H. Hogaboom compiled a bibliography of thirty-one of the more important articles written on regular-anodic coatings during the period 1904-1945 and forty-three British and American patents issued during the period 1930-1945 (8). Few articles are available on hard-anodic films. The difference between "hard-anodic" films and "normal-anodic" films lies in the

fact that in processing, hard coatings require higher current densities, rapid agitation to prevent burning, and low bath temperatures. Hard coatings are much thicker and harder than normal coatings.

Three processes for producing a hard-anodic coating on aluminum have been developed. The Martin Hard Coat and Alumilite Hard Coat processes are the property of the Aluminum Company of America; the Hardas process is a development of Hard Aluminum Surfaces Ltd., Glasgow, Scotland (7). There are certain basic differences among these processes. The Martin Hard Coat and Alumilite Hard Coat processes employ direct current. In the Hardas process both direct and alternating currents are used; the proportion and actual voltages depending to a great extent upon the alloy and the thickness of film desired.

Processing Requirements Hard anodize as differentiated from the conventional anodize is obtained at low temperature with rapid agitation and high current density. Brace (3) describes the Martin Hard Coat processing conditions as employing a current density of 20-25 amp per sq ft in a 15% sulfuric acid bath, starting voltages of 25-30 v D.C. and finishing voltages of 40-60 v depending on the composition of the anode, and bath temperatures of 0°C. The conditions as described by Brace are similarly stated in Burrow's patent (4). In the patent, no mention is made of saturating the bath with

carbon dioxide. This additive is referred to in the Aluminum Company of America's Bulletin #6 describing conditions for Martin Hard Coat (16). However, although there is not direct mention of carbon dioxide, the possibility of using "additives" in the bath is discussed in the patent.

Bath temperatures on the order of 0°C are employed in all hard-coating processes. The low temperature of the electrolyte serves a double function. Decreased solubility of the coating in the cold electrolyte permits build up of a thick porous coating. The greater temperature gradient between the surface of the piece and the cold electrolyte allows improved heat dissipation. Refrigeration is necessary to keep the bath at operating temperature. The cooling load increases as the film increases (the voltage drop across the film increases). Rapid agitation is required to aid in transferring the heat generated during anodizing. A moving work-rod, mechanical stirrers, and gas sparging lines used in concert are musts if uniform, hard, reproducible films are to be produced.

Literature Survey In some measure, the usefulness of a material is determined by the corrosion and wear resistance of its surface. These properties are a function of more fundamental characteristics, among them is the thickness of the surface coating. Since this is so, the measurement of thickness of aluminum oxide coatings has been the subject of much study. Periodically, articles and

reviews of methods of measurement have appeared in the literature (6,12,29). Destructive and non-destructive tests have been devised and evaluated. Methods vary in accuracy as well as principle employed. Chief among the methods employed are chemical separation, micrometer measurement, microscopic measurement, and voltage breakdown. Chemical separation of the film from the basis metal is frequently used. According to Wernick (29), Treadwell and Obrist are responsible for using dry hydrogen chloride to effect a separation. The anodized sample is heated in a current of hydrogen chloride or chlorine. The aluminum is oxidized to aluminum chloride which volatilizes at the temperature employed and condenses in the cold portion of the reaction tube. The separated film can then be measured with a micrometer. In an early method proposed by Wernick, the oxide is abraded, then treated with mercury, and finally suspended in a solution of mercuric chloride. The oxide coating in the form of flakes is retrieved, washed with distilled water, dried, and measured with a micrometer. Tronstad and Høverstad (27) used an optical method for measuring the thickness of thin-anodic films. By measuring the phase retardation and the ratio of the absorption coefficient before and after treatment along with the refractive index of the solution, the mean thickness was calculated by a method introduced by Tronstad (26). Another non-destructive method of test takes advantage of the electrical characteristics of the film. Within the limits of regular anodize, voltage breakdown is

a linear function of the thickness of the film. Compton and Mendizza (5) correlated thickness of coating with breakdown voltage for normal anodize produced by the Alumilite process on 2S aluminum. The value of 93 v per 0.0001 in. of thickness was reported used in checking production anodized parts. Similar work was reported by Edwards (6). A straight line curve of breakdown voltage versus thickness of coating shows a value of the abscissa of 0.00057 in. corresponding to a value of the ordinate of 950 v. This value differs from that of Compton and Mendizza. Variations of this type are reasonably accurate for routine work. It is necessary to carefully set the condition of test since dielectric strength is not only a function of thickness but also is affected by process variables, among them: the electrolyte used, its temperature, current density, sealing method, and surface preparation. There is doubt that these correlations or this method could be applied to hard coatings. Various sources report values of dielectric strength of 500 to 3700 v for hard-anodic films. These limits are only roughly compatible with the values found for normal anodize by Compton & Mendizza and Edwards. The Filmeter designed by Mason and Cochran (17) is also based on the electrical properties of anodic films. The instrument consists of a portable electronic beat-frequency oscillator. Operation of the Filmeter is dependent on aural tuning of one oscillator circuit to coincide with the reference oscillator circuit. The Filmeter is rapid and non-destructive; however, it is necessary to set the

instrument to zero on a piece of similar composition or temper or chemically strip a portion of the piece before readings on production pieces are made. Good agreement of Filmeter measurements with microscopic and gravimetric methods are reported for normal anodize. It may be possible to adapt this method to the measurement of hard coat.

Although rapid non-destructive tests are available, most studies of anodic films involve destructive tests. The elaborate procedures of gravimetrically determining the thickness of coating or preparing metallographic samples in accordance with the method recommended by the American Society for Testing Materials (24) are accepted as the best means of thickness measurement. Gravimetric determinations of hard-anodize thickness suffer from one drawback. Density of the coating is in doubt. During anodic coating, growth of the coat is opposite to an electroplated coating. The oxide that is formed first is outermost. As the coating increases in thickness, the thickness of the virgin metal decreases while the over-all thickness of the piece increases. The increase in thickness of the piece is a fraction of the total thickness of the coating formed. A "rule of thumb" value of one-half is given in the literature (7,13). Jenny (12) points out that according to Wernick this growth occurs up to a certain limit set by the variables of processing after which the over-all thickness of the piece returns to its unanodized dimension. Still further processing causes a decrease in the over-all thickness of the piece with the attendant risk of physical failure in the

parent metal due to reduced cross-section. Since the first formed layer of anodize has been in contact with the electrolyte the longest time, the surface of the coating has marked porosity (9,10,14); density of the coating is not uniform but increases from the surface of the anodize to the surface of the parent metal. Although this phenomenon exists in the case of normal anodize, the situation is aggravated in the case of hard anodize due to the comparably greater thickness of coating. Several values of the density of anodic aluminum oxide are available in the literature (6,12,17,22). Although processing conditions affect the density obtained, the values reported for normal anodize by several investigators are in fair agreement. A spread of values of apparent density for normal anodize is on the order of 2.00 to 3.25 g/cu cm; an average value might be used in gravimetric calculations on hard coat. An average of the values obtained in this investigation places the apparent density of the hard-coat aluminum-oxide at 2.27 g/cu cm.

The reference procedure for studying coating thickness or investigating a new method for measuring coating thickness is the preparation and examination of metallographic samples. The procedure outlined by Keller and Wilcox (15) is usually followed. Etching of the samples is unnecessary since good contrast between the oxide and the parent metal is obtained. Since the throwing power of the bath is excellent and simple forms such as thin sheet are ordinarily treated, the coatings to be evaluated have good

uniformity of thickness. The thickness of the film can be read on a metallograph with an ordinary micrometer eyepiece, or by measuring the magnified image of the coating with a steel scale.

II Experimental Program

Samples, Equipment, and Procedure Thin sheets of the aluminum alloys selected for test were spectrographically analyzed to conform to the specifications for composition shown in Figure 1. Test pieces 2 in. x 3 in. (5.1 cm x 7.6 cm) were sheared from the sheets. In the case of sand-cast alloys, all the tensile-test bars from which samples were machined were taken from melts whose compositions were analytically determined. The test pieces were turned from the test bars to an outside diameter of approximately 0.45 in. to provide a cylinder with a surface area of six square inches. A hole 1/16 in. in diameter for attaching a hanger wire was drilled through each piece. The test pieces were vapor degreased, immersed in cleaning solution for five minutes (35 cu cm 85% phosphoric acid, 20 g chromic acid diluted to a liter with de-ionized water) at a temperature of 200°F and rinsed with tap water. After drying in an oven for forty minutes at 240°F, the samples were cooled in a desiccator and then weighed on an analytical balance. Sheet thickness and bar diameters were measured with a micrometer. A #15 B&S formvar-covered copper wire was hammered into the hole in the piece and sealed with a drop of an epoxy resin to keep any current from passing through the wire to the electrolyte and by-passing the test piece. The test pieces were hung from the anode bar and clamped to insure contact.

<u>ALLOY</u>	<u>Al</u>	<u>Si</u>	<u>Mn</u>	<u>Cu</u>	<u>Mg</u>	<u>Ni</u>	<u>Zn</u>	<u>Cr</u>	<u>Fe</u>	<u>Ti</u>	<u>V</u>	<u>Weight Per Cent Other</u>
<u>Wrought</u>												
2S-0	99.00 min		0.10 max	0.20 max			0.10 max		Si 1.00 max			Other impurities each 0.05 max; total 0.15 max.
24S-T3	Rem.	0.50 max	0.3- 0.9	3.8- 4.9	1.2- 1.8		0.10 max	0.25 max	0.50 max			Other impurities each 0.05 max; total 0.15 max.
Alclad 24S-T3												
52S-H34	Rem.		0.10 max	0.10	2.2- 2.8		0.10 max	0.15- 0.35	Si 0.45 max			Other impurities each 0.05 max; total 0.15 max.
75S-0	Rem.	0.50 max	0.30 max	1.20- 2.00	2.10- 2.90		5.10- 6.10	.18- .40	0.70 max	0.20 max		Other impurities each 0.05 max; total 0.15 max.
<u>Sand Cast</u>												
Alcoa 142-T77	Rem.	0.50 max		3.75- 4.50	1.25- 1.70	1.80- 2.25			0.75 max			Other impurities each 0.03 max.
Alcoa 195-T4	Rem.	1.2 max	0.30 max	4.0- 5.0	0.03 max		0.30 max		1.0 max	0.20 max		Other impurities each 0.05 max; total 0.15 max.
Alcoa 355-T71	Rem.	4.5- 5.5	0.30 max	1.0- 1.5	0.4- 0.6		0.10 max	Ti 0.08- 0.30	.60 max			Other impurities each 0.05 max.
Alcoa 356	Rem.	6.5- 7.5	0.30 max		0.2- 0.4		0.30 max		0.50 max	0.20 max		Other impurities each 0.05 max; total 0.15 max.
Eclips- alloy 325	Rem.	0.35 max	0.15- 0.45	3.5- 4.5	1.8- 2.25		0.05 max	0.20- 0.40	.40 max	0.06- 0.20	0.02- 0.20	

Figure 1. Chemical Compositions

The bath was prepared by making up six liters of 15 wt% sulfuric acid using reagent-grade concentrated acid. A new bath was made up when a change was made in alloy composition. The acid was titrated to report the acid content correct to 0.1%. Cooling was accomplished by adding lumps of dry ice to the bath; a small laboratory stirrer was used to provide mechanical agitation.

Sufficient samples, usually three, were suspended in the bath to provide thirty-six square inches of anode surface. The apparatus was set up as shown in Figure 2. The agitation of the electrolyte was enhanced by judiciously dropping small pieces of dry ice into the tank during the run. Data was taken as follows: the time was read from a timer and readings of the instruments were recorded at five minute intervals. Temperature was controlled to $\pm 2^{\circ}\text{C}$, current was controlled to ± 0.1 amp, and voltage was controlled to ± 1 volt.

After the run was completed, the pieces were washed in tap water, flooded with acetone, and blown free of solvent with a blast of compressed air. The piece was stripped of the hanger wire, dried for forty minutes in an oven at 240°F , and stored overnight in a desiccator. The following morning the pieces were weighed and measured. In the case of samples of 2S and 52S aluminum, the pieces were stripped in chromic-phosphoric acid at 200°F and rinsed with tap water (6). After drying and cooling, the pieces were weighed and measured. Two metallographic samples of each run

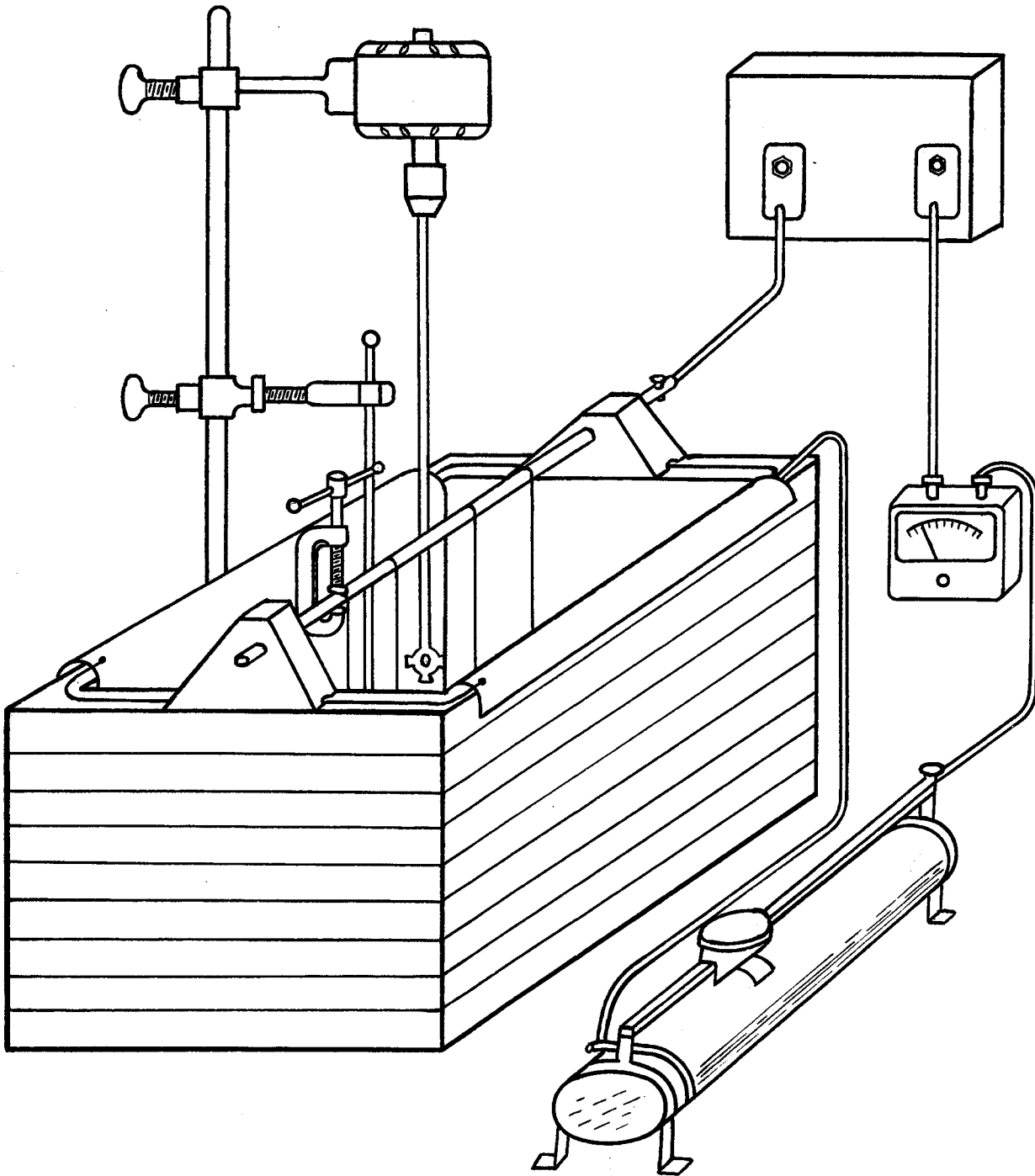


FIGURE 2. Apparatus Set-up

were then made in accordance with the method specified by Keller (15). The thickness of the coat was measured using a micrometer eyepiece in a Bausch & Lomb Research Metallograph.

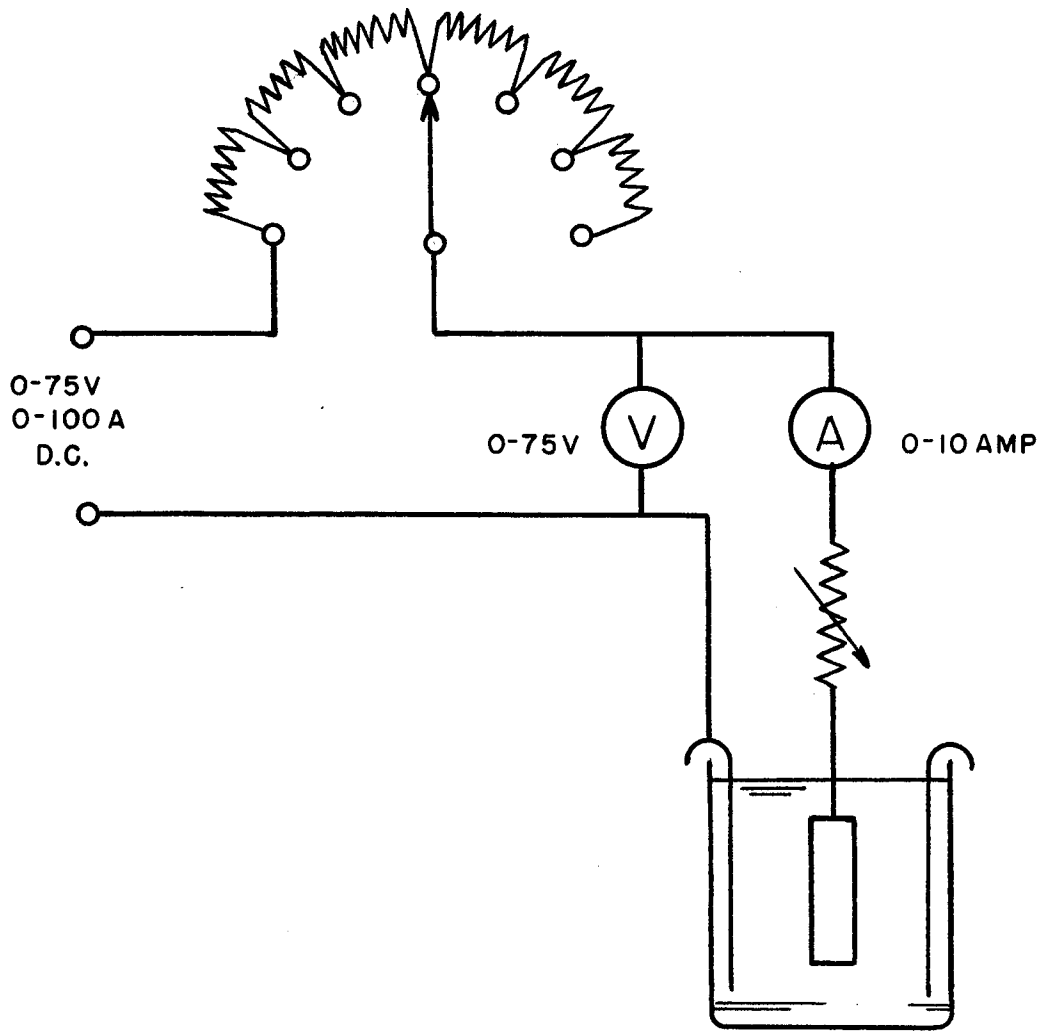


FIGURE 3. Schematic Layout of Apparatus

Chronological Review of Work Accomplished

October, 1953

Prior to starting work in the laboratory, a search of the literature was made. Examination of the Chemical Abstract Indexes for 1948 to 1953 revealed a dearth of articles on hard-anodic films. When this situation became apparent, it was decided that the literature be re-searched not only to uncover papers on hard-anodic films but also to amass a file of references on regular anodic films especially methods of test and evaluation. A review of the Chemical Abstract Indexes for 1948 to 1953 was again made, and a set of cards made up on the references that might be of value. Stress was placed on studying those articles concerned with the measurement of thickness of anodic films. However, references on techniques of producing anodic films, measurement of hardness and porosity and effects of variables on film quality were also noted. Moreover, a copy of Jenny's "The Anodic Oxidation of Aluminum and Its Alloys" was purchased from Griffin & Company, London, England. This textbook was read concomitant with the preliminary work done in the laboratory.

It was decided that the preliminary work in the laboratory would consist of getting the pilot-plant set-up into operation and producing coatings on some of the common aluminum alloys by following the directions given in Alcoa's Bulletin #6 (15). Although the literature contained descriptions of the coating, the author had not seen a hard-anodic coating up to this time. In order to speed

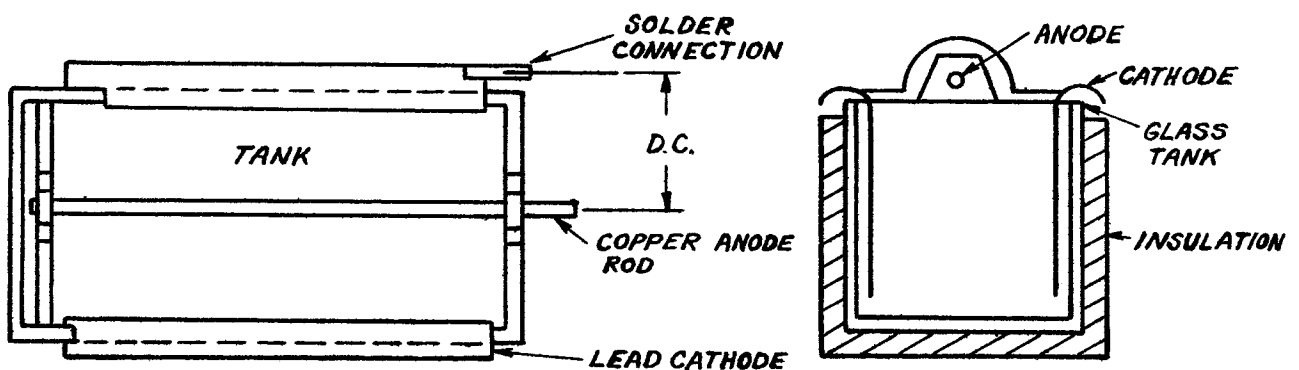
the acquisition of data for the thesis, two lab-bench size experimental tanks were designed. A work order was written to have D.C. stations wired to two laboratory benches to provide current for the projected units.

The pilot-plant size anodizing equipment consisted of two tanks 24" x 18" x 18". One tank was equipped with an over-flow weir and cold water service for washing the samples after anodization. The other tank (23.4 gallon capacity) was lead lined and used for anodizing. The lead lining served as the cathode. Auxiliary equipment for the anodize tank consisted of a lead coil through which a cooled ethylene glycol-water solution was pumped to provide the low temperature necessary for hard anodize, a moving anode rod for racking the work, a gas sparging line for saturating the bath with carbon dioxide, an electric stirrer to enhance the agitation of the bath, and a Partlow temperature controller for regulating the temperature of the bath. Direct current was supplied to the tank by a Rapid Electric rectifier with name plate data as follows:

<u>A.C. Input</u>	<u>D. C. Output</u>
440 volt	0-75 volt
60 cps	7.5 KVA
3 phase	Cont. Duty

For use as lab-bench size plating tanks, two glass tanks approximately 8" wide, 11" long, and 7" deep were purchased. Since the anodizations would be performed around 32°F and heat due to electrical resistance of the film would have to be extracted, it was postulated

that temperature of the bath could be maintained fairly easily by two means: insulating the tank sufficiently - causing poor heat transfer between the surroundings and the tank - and careful additions of dry ice to the bath during the anodization. Subsequent operations proved these premises to be well taken. The sides and bottom of the glass tank were wrapped with layers of crepe paper until a layer one inch thick was obtained. Asbestos board one-quarter inch thick was scored and bent to fit over the crepe paper and secured with paper-backed pressure-sensitive tape. The entire insulating cover was taped to form a unit. The exposed crepe paper around the lip of the tank was covered with asbestos pulp soaked in an epoxy resin (Ciba Co.'s Araldite #504). A one-quarter inch copper rod to be the anode was located midway between the long sides of the tank. Its ends were cast in epoxy resin to anchor the anode along the center line of the tank and insulate it from the rest of the tank. Since commercial practice as well as Mr. Burrow's patent (4) specify lead sheet as the cathode, 8 lb chemical lead was used to make the cathode. Two sheets 10" long by 8" wide were fabricated to lie on either side of the anode bar and be suspended on the tank walls. A $\frac{1}{4}$ " by $\frac{1}{8}$ " copper strip was soldered to form an electrical path between the two lead sheets. The copper connector was insulated with several wraps of Mylar tape.



Auxiliary equipment consisted of a Centigrade thermometer with a -10 to +60°C range with one degree graduations and a variable speed stirrer. The stirrer was placed in the far corner of the tank to cause the electrolyte to move in a counter-clockwise direction around the suspended samples. Thus, the forward part of the tank was free of obstructions so that small pieces of dry ice could be charged intermittingly. Addition of the dry ice during the run was made to maintain the temperature of the bath. The dry ice also aided in agitating the bath and insuring that the bath was completely saturated with carbon dioxide. Direct current lines to the two glass tanks were installed taking current from the pilot-plant rectifier. Six liters of electrolyte were used in the bath. Its strength was determined by the procedure in the Appendix.

Recognizing the need for a good record of the experimental work to be done, the data sheet shown in the Appendix was drawn up.

The sample compositions for test were selected in this manner: recognition was made of the fact that aluminum alloys are classified into alloy numeral ranges; each range reserved for alloys which have the same chief alloying element. A selection was made to try to cover all of the groups of aluminum alloys from available stocks. Ten compositions were taken for test (Figure 1). The basic and starting composition chosen was ordinary

2S aluminum. High copper compositions were represented by 24S, 14S, and 197; high silicon compositions by 355 and 356, high magnesium compositions by 52S, and high zinc compositions by 75S. In addition, Eclipsaloy 325 was selected due to its unusual composition and good physical characteristics. The behavior of "clad" aluminums was demonstrated by a series of runs employing Alclad 24S. Samples were selected from both wrought and sand-cast stocks in order to get a cross-section of alloys that may be hard-coated in actual practice.

This coating is not recommended by its inventor for high copper and high silicon compositions. Nevertheless, the high copper and high silicon compositions were included in this investigation for these alloys are important industrially because of their good physical characteristics. Since attempts to hard coat these alloys would be made, the relationships among time, growth, and thickness would be valuable. Moreover, inasmuch as this paper is concerned chiefly with growth and thickness of the film, the quality of the film was not to be evaluated. Put simply, whether the coating was hard or soft, porous or relatively non-porous was considered secondary to the primary purpose of investigating growth, thickness, and time relationships.

The selection of sample size was based on the following considerations. A set amount of anode area would be used for all runs. The ammeter available for measuring current flow was graduated from zero to ten amperes in one-tenth ampere subdivisions.

When current density would be varied, three values of current density chosen would be 15, 25, and 35 amp per sq ft. If exactly thirty-six square inches of anode area were used, the current flowing at these current densities would be 3.8, 6.3, and 8.8 amp per sq ft respectively. These values of current would be in the range of the ammeter for all runs. Slight variations in anode area would occur in the case of wrought sheet due to the edge and end areas depending on the thickness of sheet used. In the case of cast alloys, the anode area would change slightly since some samples do not contain enough stock to allow a diameter of 0.45 in. Before anodizing each new stock, the anode area would be calculated and the amount of current would have to be adjusted to hold the required current density.

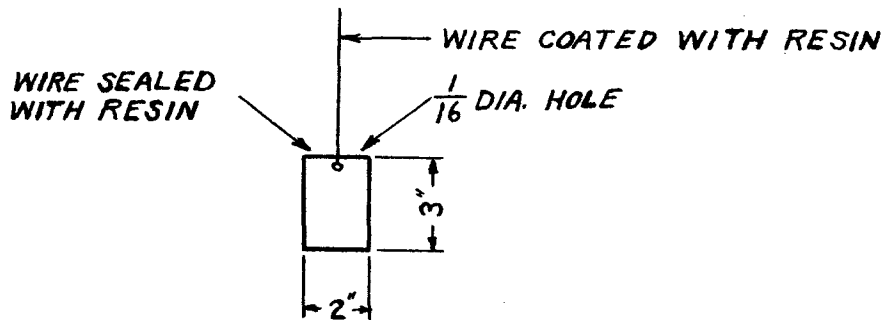
For wrought sheet, a piece nominally six inches by three inches would give the required thirty-six inches of anode area. However, since the samples were to be weighed gravimetrically, a piece this size would not fit on an analytical balance. Moreover, a single sample would not permit cutting a piece for making metallographic samples for thickness measurement and yet remain intact for stripping and weighing to get a weight of coating formed. Three samples 2 in. x 3 in. (5.1 cm x 7.6 cm) would contain the required anode area and allow one piece to be cut for metallographic samples and the other two to be stripped and weighed.

In the case of sand-cast samples, the only stock available were tensile test-bars cast at each melt for physical and chemical testing purposes. A bar lathe-turned to a diameter of 0.45 in. and four inches long would have an over-all surface area of six sq in. Six samples would yield the required thirty-six square inches of anode area.

In order to suspend the samples below the surface of the electrolyte, the holder connecting the sample to the anode bar must be immersed in the electrolyte. The use of bare metal would result in changing the current density to the piece. Also, depending on the alloy used, the hanger would anodize at a different rate than the sample making it impossible to time the anodization of the samples. Using a hanger integral with the sample piece would make calculating the surface area difficult due to the uneven boundary at the surface of the electrolyte. Weighing would be impossible since a portion of the hanger-sample would be unanodized. Use of a stop-off material was indicated to keep the current flowing only from the sample surface to the electrolyte. Although a vinyl tape or lacquer could have been used, an epoxy resin was used to insulate the hanger from the electrolyte because of its excellent adhesion. The epoxy resin served to hold the electrical connection between the hanger and the piece as well as insulate the hanger wire.

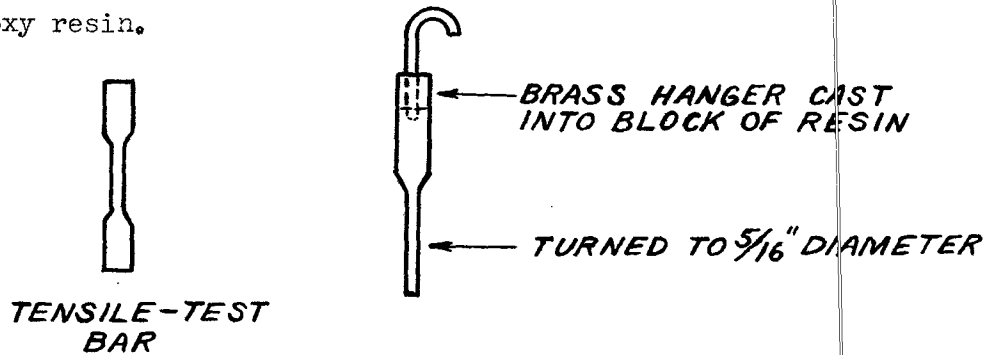
As described in the previous section, all the wrought samples of one alloy were sheared from the same sheet. A sample of each

sheet was spectrographically analyzed to conform with the compositions given in Figure 1. Samples 2 in. x 3 in. were sheared from the sheet. A hole was drilled through the piece with a one-sixteenth diameter drill. The samples were differentiated from one another by stamping letters and numerals on each piece; e.g. 4D, 4DD, 4DDD. (These three pieces were treated as a set differing from all other pieces, but can be recognized as being together by having the combination "4D" in common.) Suspending the wrought samples consisted of inserting the hanger wire, hammering to make good physical contact and sealing the joint with a drop of epoxy resin.

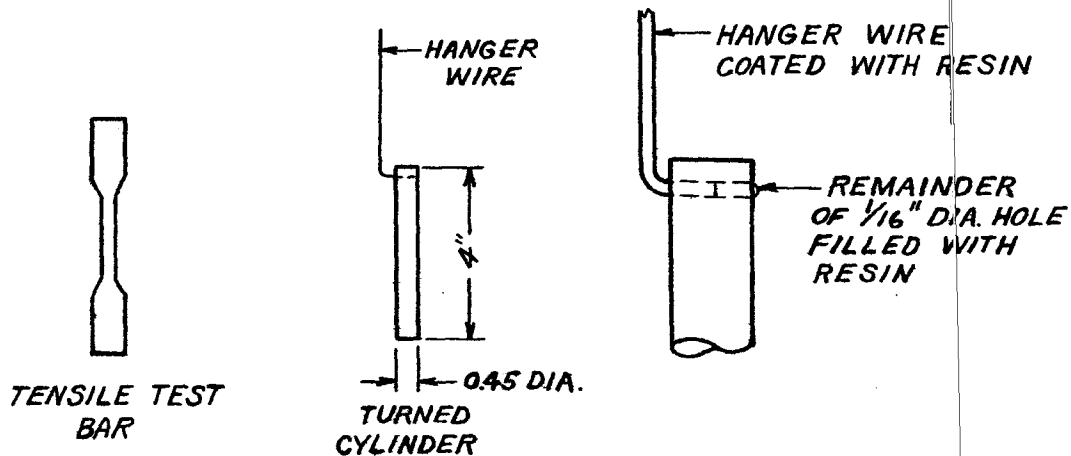


Initially the sand-cast samples consisted of a tensile test-bar lathe-turned to a diameter of $\frac{5}{16}$ in. about 70% of its length. The hanger was a piece of one-quarter inch yellow brass rod. A point was ground on the hanger and inserted in the lathe center hole

and hammered tight. The connection and the part of the brass hanger that was suspended in the electrolyte were cast in a rod of epoxy resin.



The sample was modified finally to a turned cylinder of 0.45 in. in diameter and four inches long. The sample was suspended by drilling a one-sixteenth diameter hole through the piece and cementing a wire in the hole.



The wire was coated with resin to insulate it. As was done with the wrought samples, each sand-cast piece was identified by stamped numbers and letters.

To round out the information considered necessary to designing hard coatings the following points were to be studied:

1. Find to what extent the temperature of the bath, strength of the electrolyte, anode composition, and current density affect the thickness of the film.

2. Obtain sufficient data to arrive at a better value for growth of the part than the "one-half of the film thickness formula".

3. Prepare curves showing the relationship of time of treatment with coating thickness and part growth.

4. Calculate an average density of the hard-anodic film and compare it with the average densities reported for anodic aluminum oxide formed under regular anodic conditions.

5. Compare the values obtained using a micrometer to gauge the thickness of a hard-anodic film with that obtained from examining a metallographic specimen.

6. Calculate "coating ratios" (anode efficiencies) and compare them with the coating ratios obtained on 2S aluminum produced under standard MHC coating conditions.

Variables that would act on the growth of the film and the over-all thickness of a piece of aluminum under anodic treatment were considered. Four variables were chosen for investigation- anode composition, concentration of the electrolyte, temperature

of the bath, and current density. For production control, knowledge of the extent these four variables affect the production of coatings would be valuable. How far may a plater deviate from the accepted values of temperature, acid concentration, and current density and still produce coatings whose thickness would conform to the tolerances on the drawing.

Along with the aim to produce coatings to conform with the specifications on the drawing with regard to thickness, dimensions would have to be calculated to allow for part growth due to anodizing. Gillig (7) and Johnson (13) advise the allowance of one-half the film thickness for growth of the part (Johnson does not make it clear whether his value is based on original work or is based on Gillig's report). As was discussed in the Introduction, the investigation was conducted to verify this value and if possible to report a value more concrete than the "one-half" figure. In aircraft accessory manufacture, the thickness of the coating and the close tolerances on the parts coated require an accurate value for part growth.

It was decided to set the data taken from the runs in the laboratory into two groups of curves. One group of curves would consist of sets of curves showing the relationship between the coating thickness and the time in the bath. Each set of curves would show the effect of varying one variable, e.g. temperature

of the bath, while the other variables chosen - anode composition, strength of the electrolyte, and current density - would be held constant. The second group of curves would consist of sets of curves showing the relationship between the growth of the part and the coating thickness. Each set of curves would be based on data obtained under conditions set up for the corresponding sets of curves in the first group.

An apparent density of the hard-anodic film could be obtained by weighings and metallographic measurements. The following data would be available if the procedure described in the preceding section (Samples, Equipment, and Procedure) were followed:

	<u>Units</u>
W_1 - The weight of the piece before anodizing.	g
W_2 - The weight of the piece after anodizing.	g
W_3 - The weight of the piece after stripping.	g
t - The thickness of the film from a metallographic sample.	in.
A - Total area of the sample anodized. = $(2 \times LW + 2LT + 2WT)$	sq in.
Apparent density $\frac{(W_2 - W_3) (0.061)}{At}$	$\frac{g}{cu\ cm}$

The density calculated in this manner must be considered an apparent density since the films will vary in porosity depending on the conditions of anodization. Also, the apparent density under set conditions will vary with time in the bath.

The data obtained in the preceding paragraph would allow calculation of a coating ratio by performing the following mathematical operation: $\frac{W_2 - W_3}{W_1 - W_3}$ which would give the ratio of the weight of coating formed to the weight of metal lost. These values could be best shown by plotting them versus time and in sets corresponding to the groups of curves of "time in the bath versus coating thickness" and "growth of the part versus coating thickness".

March, 1954

Exploratory runs were started with the pilot-plant bath. Three runs were made with 2S composition samples; sixty, ninety, and one-hundred twenty minutes long. All three sets of samples exhibited hard and thick coatings. Three runs were made on 24ST composition samples; one 60, one 90, and one 120 minutes long. All samples had very thin coatings and burned spots. As indicated in the literature, high copper alloys exhibit poor coating characteristics. Four runs were made on sand-cast stock. One 90 minute run was made on Alcoa 356 test-bars; the coating was a good one. Three runs were made on Alcoa 142-T77; sixty, ninety, and one-hundred twenty minutes long. Satisfactory results were obtained.

Data from these runs were not used in this report. The pieces of 2S aluminum that were coated were the first examples of a hard anodize seen by the author.

Based on these runs, two changes were made:

The use of the pilot-plant set-up was to be abandoned in favor of the laboratory glassware set-up. This decision was made for two

reasons. The pilot-plant rectifier contains a point to point rheostat resulting in discreet jumps in current to the bath. Close control of the current to the sample would be impossible unless the system were modified to allow continuous control of the current. There would be no control on the composition of the electrolyte. The free surface of the electrolyte was open to the air with no means of covering the surface when the bath was not in use. Not only contamination from the surroundings of the bath, but also runs of production parts were being scheduled for anodizing in the bath. In order to have an electrolyte free of any contaminants, the bath would have to be made up fresh before each set of runs. Dumping and recharging 23.4 gallons of 15 wt% sulfuric acid each evening was not feasible.

The sand-cast samples would have to be modified since the overall length was too great for the laboratory glassware tanks. The second design of a sand-cast sample shown above was adopted.

During the early operation of this bath it was found that a good method of suspending samples was absolutely necessary in order to produce good coatings. The rapid movement of the work-rod and electrolyte tend to loosen the electrical connections. Oxidation occurs on the contact surfaces causing loss of coating on the piece; strong heating usually occurs and results in burning at the clamped sections. Also, the high current necessary for building a thick coating may pass through the remaining samples that are tightly suspended resulting in local burning, pitting or parts more heavily

coated than planned. Connections to the anode bar and to the piece should be made with screws or clamps or both. The connection between the rack and the part should be held either by moderately tight screw fittings or tight spring wires. The actual area of contact between the rack and the piece can be very small, but the connection must be very tight. In most cases very small point surfaces are sufficient to carry the necessary current. The small area necessary for conducting the current is advantageous. After anodic coating the unprotected connecting surface is a minimum and may well be so located on the piece that only the anodized area is subjected to abrasion or corrosion.

The laboratory glassware tank was set up as described previously in this section and as shown in Figures 1 and 2. A suitable slide-wire rheostat was placed in the circuit so that the current could be held constant to ± 0.1 ampere by moving the slide. Several tests were performed until reproducible results were obtained.

June, 1954

A chronological sequence of the runs for data used in this report is as follows:

Set No.	No. of Runs	Dates	Conditions	Remarks
		1954		
1	7	June 16-June 23	Std MHC on 2S	25 amp/sq ft 32°F 15 wt% H ₂ SO ₄ sat with CO ₂
2	6	June 29-July 6	Low temp.	22°F
3	6	July 8-July 14	High temp.	42°F

<u>Set No.</u>	<u>No. of Runs</u>	<u>Dates</u>	<u>Conditions</u>	<u>Remarks</u>
4	5	July 15-July 20	High C.D.	35 amp/sq ft
5	6	July 21-July 28	Low C.D.	15 amp/ sq ft
6	6	July 30-Aug.4	High A.S.	25 wt% H ₂ SO ₄ sat with CO ₂
7	6	Aug.5 - Aug. 10	Low A.S.	15 wt% H ₂ SO ₄ sat with CO ₂
8	6	Aug. 11-Aug.16	Change Alloy	52S-H34 Condition as Set No. 1
9	6	Aug.17-Aug.20	Change Alloy High C.D.	52S-H34 Condition as Set No. 4
10	5	Aug.18-Aug.26	Change Alloy Low C.D.	52S-H34 Condition as Set No. 5
11	8	Sept.7-Sept.9	Change Alloy	24S-T3 Condition as Set No. 1
12	6	Sept. 13-Sept.15	Change Alloy	24S-T3 Alclad Condi- tion as Set No. 1
13	3	Sept.29-Sept.30	Change Alloy	142-T77 Condition as Set No. 1
14	3	Oct.4-Oct.5	Change Alloy	Eclipsaloy 325 Condi- tion as Set No. 1
15	3	Oct.11-Oct.12	Change Alloy	195-T4 Condition as Set No. 1
16	3	Oct.14-Oct.18	Change Alloy	355-T71 Condition as Set No. 1
17	3	Oct.19-Oct.21	Change Alloy	75S-0 Condition as Set No. 1
18	3	Oct.26-Oct.27	Change Alloy	356 Condition as Set No. 1

Incomplete data are shown in the Results Data for the following alloys: 24S-T3, 142-T77, Eclipsaloy 325, 195-T4, 355-T71, 75S-0, and 356. The data are incomplete in the sense that these samples were not stripped allowing weight and thickness measurements to be taken. The chromic-phosphoric acid stripper first introduced by Mason would not strip these alloys clean. A smut remained which could be removed by using a hydrofluoric-nitric acid dip. However, there were visible indications that this additional stripping procedure etched the pieces. It seemed advisable to limit the data to the values obtained on alloys that could be stripped in chromic-phosphoric acid stripper.

The Results Data and Curves have few points where the time in the bath was 120 minutes. Although 120 minutes was to be the length of the longest run in a set, the voltage limit of the rectifier (75 v) became the limiting factor on length of time in the bath.

Discussion of Results Data and Curves Two methods for measuring the thickness of anodic films were employed to obtain the values for the films produced in this investigation. Metallographic samples were prepared and evaluated; these values were considered to be the reference measures of the thicknesses produced. Also, the coatings were measured with a micrometer before and after anodization and after chemical stripping. These values were obtained in order to ascertain how closely film thickness could be measured with an ordinary micrometer without recourse to the preparation of metallographic samples. Examination of the Results Data discloses that low values of thickness were consistently obtained based on micrometer readings in reference to the thickness measured metallographically. The average value of all the ratios of micrometer thickness to metallographic thickness measured in this investigation is 0.80; that is, the micrometer thickness averaged roughly eight-tenths of the metallographic thickness. The discrepancy between micrometer thickness and metallographic thickness can be attributed to instrument and manipulative errors. The micrometer was read to four places beyond the decimal point. An error of plus or minus one ten-thousandth of an inch acting in a linear manner, diminishing with increasing film thickness, can be considered affecting each value reported. It appears that this error accounts in a great measure for the larger differences between the micrometer thicknesses and the metallographic thicknesses on the lightly anodized pieces. To a greater

extent than in the value of film thickness obtained metallographically, manipulative errors enter into the value of film thickness obtained by micrometer measurements since it is the difference of two separate measurements and a chemical stripping procedure between measurements. In both cases there is a possibility of getting a non-representative sample; however, the simple section chosen, the excellent throwing power of the bath, and the use of multiple samples, tend to make an error of this nature remote.

A method attributed to Edwards and used by Tarr, Darrin, and Tubbs (25) to express the average thickness of a normal-anodic coating is dependent on an empirical relationship where the average thickness in mils is 1/50th of the weight of the coating thickness expressed in milligrams per square inch. This relationship converted to apparent density yields a value of 3.05 g/cu cm which is in line with values of Edwards who reports densities of 2.79 to 3.25 g/cu cm and Jenny (12) who sets forth values of 2.76 to 3.15 g/cu cm from several sources but is somewhat higher than the density used by Prati (22) of 2.50 g/cu cm and 2.01 to 2.62 g/cu cm mentioned by Mason & Cochran (17). Neither the relationship used by Tarr, Darrin, and Tubbs nor the density in the vicinity of 3 g/cu cm hold well for hard-anodic films. Transposing the equation of Edward's and solving for a new constant using the data obtained in this investigation, an average value of 37 as opposed to 50 is calculated. The

weight of coating was obtained from the weighings on an analytical balance while the average thickness used was that observed on the metallograph. The calculation of density using these values results in an over-all average apparent density of 2.27 g/cu cm for all runs.

The curves plotted in this report can be grouped into two categories; the one consists of ten curves designed to aid in setting controlled conditions for hard anodizing while the last five are plotted to indicate the over-all anode efficiencies realized when certain conditions of processing prevail. Curves 1 to 5 may be employed in predicting the necessary time required to produce a given thickness of coating. In each of these curves a parameter was chosen in order to see the effect of varying the processing conditions on the physical dimensions of the coating. Examining Curves 1 and 3, it is evident that the temperature of the bath or strength of the electrolyte may be varied within wide limits with little effect on the rate of coating formation. It cannot be disputed that these variables may affect other physical characteristics of the coating adversely such as hardness, porosity, corrosion resistance, and adhesion (3,9,13,29). Mistakes in surface area calculations, improper racking, and errors in adjusting the current to the tank - all of which vary the current density - show a marked effect on the rate of coating formation. Hard anodize follows pretty well the precept for normal anodize; the coating thickness is roughly proportional to the quantity of electricity passed (12). On Curve 2, the different rates of film formation on 2S-0 aluminum at 15,

25, and 35 amp per sq ft are indicative of the importance of carefully controlling current density.

Curves 6 to 10 show the relation of coating thickness and growth of the part under different conditions. The machined dimensions of a piece may be calculated by subtracting from the finished piece dimensions the amount the piece will grow due to anodizing. The average of all runs of the ratio of growth to over-all thickness was 0.41.

Curves 11 to 15 show the variation of coating ratio with time for the different conditions used to obtain the relationships shown in Curves 1 to 10. "Coating ratio" is a convenient expression for over-all efficiency with respect to coating formation; the value of the coating ratio is obtained by dividing the weight of coating by the weight of aluminum reacting. No assumption regarding the composition of the coating is required in the calculation of a coating ratio (1,19). Coating ratio may be converted into the practical film efficiency of Tarr, Darrin, and Tubbs by dividing by 1.89. However, the use of the factor 1.89 assumes that pure aluminum anode is reacting electrochemically to form pure aluminum oxide. Mason and Fowle (18) postulate that, "oxide coatings formed on 99.95% aluminum in a 15% (by weight) sulfuric acid electrolyte under certain standard conditions of operation contain about 12-14% SO_3 , some water and the remainder alumina. When the coating contains 14% SO_3 the theoretical ratio would be about 2.2." Pullen (23) also reports that coatings

formed in sulfuric acid contain quantities of sulfate. Since the composition of the hard coat formed is beyond the scope of this paper, coating ratio was considered to be a practical expression for the efficiency of the process. In all the cases considered in this investigation, the values of coating ratio were below the value of 2.2 or 1.89 for that matter, indicating that a small amount of coating dissolved into the electrolyte. The over-all average of coating ratio for all the data taken was 1.73. As was to be expected, the values of coating ratio for 2S-0 aluminum treated at low acid strength, low temperature, and high current density are comparably higher than those obtained at high acid strength, high temperature, and low current density. Changing the composition of the alloy to 52S-H34 and treating at different current densities results in a trend similar to that obtained with 2S-0; that is, higher coating ratios are obtained with increasing current density. Curves 11 to 15 exhibit a slight increase in coating ratio with time. Increase in coating ratio with time was reported in an article by Mason and Fowle (18). Treatment of high purity, 2S-H18, and 61S-T6 aluminum with current densities about 24 amp per sq ft in 15 wt% sulfuric acid resulted in increasing coating ratios with time. The authors suggest that this anomalous phenomenon could be attributed to the reduction of the rate of solution of the coating due to clogging of the pores and to some extent,

to a reduction in the number of pores causing the abnormal voltage increase experienced when pieces are anodically treated for long periods of time at high current densities.

Conclusions Based on the experimental work done in this program, hard-anodic films can be designed to conform to required film thicknesses and dimensional tolerances.

With immersion times ranging up to 120 minutes, the thickness of a hard-anodic film varies almost linearly with the time of formation at a fixed current density. A good estimate of coating thickness would be one mil increase for each twenty-one minutes in the Martin Hard Coat bath. Within the limits of the experimental runs made, variation of temperature of the bath, strength of the electrolyte, and alloy composition have only a small effect on the thickness of the coating. The temperature was varied twenty degrees with data taken at 22, 32, and 42°F. Thickness of coating at respective times for the low and high temperature runs were all within 11% of the corresponding values at 32°F. The strength of the electrolyte was varied 22 wt% with data taken at 5, 16 and 27 wt%. Thickness of the coating at respective times for the low and high strength electrolyte runs were all within 12% of the corresponding value at 16 wt% with the exception of the fifteen minute run at 27 wt% which varied 20%. Nine alloys were coated under similar Martin Hard Coat conditions. Thickness of coating at respective times on all the alloys were within 30% of the corresponding value on 2S aluminum. The current density was varied twenty amp per sq ft with data taken at 15, 25, and 35 amp per sq ft on 2S and 52S samples. Ratios of film thickness to current density at a fixed time show that this type of anodization is roughly coulometric in nature.

Despite the variations in processing conditions, the slopes of the curves of growth of the part versus film thickness are similar. An average of the results of the experiments conducted here fix the ratio of growth to over-all film thickness at 0.41.

Good over-all efficiencies were obtained with Martin Hard Coat. In all cases coating ratio increased with time of treatment. This trend may be indicative of clogging of the pores in the film with solution products. Coating ratios varied slightly with processing conditions; slightly higher values were obtained with low temperature, low strength electrolyte, and high current density. Coating ratios for 2S aluminum coated at 22°F were as much as 3% higher than the values found at the reference 32°F. Coating ratios for 2S aluminum coated in 5 wt% sulfuric acid saturated with carbon dioxide were up to 3% higher than the values found at the reference concentration of 15 wt% sulfuric acid saturated with carbon dioxide. Coating ratios for 2S aluminum coated with a current density of 35 amp per sq ft were as much as 4% higher than the values found at the reference current density of 25 amp per sq ft. An increase of up to 4% in coating ratio is exhibited by treating 52S at 35 amp per sq ft over the coating ratios obtained at the reference 25 amp per sq ft.

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro	Meas				
15	23.9	1.0	0.4	0.40	0.2	2.39	1.694
45	81.1	2.0	1.7	0.85	0.7	2.48	1.714
60	100.1	2.6	2.1	0.81	1.0	2.35	1.732
75	134.4	3.8	3.0	0.79	1.5	2.16	1.781
85	151.1	3.9	3.1	0.79	1.5	2.36	1.788
90	160.4	4.0	3.4	0.85	1.6	2.44	1.793
95	171.8	4.3	3.5	0.81	1.8	2.43	1.803

Conditions:

Temp. of the bath 32°F
 Acid strength 16 wt% H₂SO₄ saturated with CO₂
 Current density 25 amp per sq ft

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio <u>Meas</u> Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro	Meas mil				
15	26.7	0.9	0.6	0.67	0.3	1.81	1.701
30	54.5	1.6	1.3	0.81	0.6	2.08	1.721
45	82.6	2.1	1.8	0.86	0.8	2.40	1.763
60	110.7	2.7	2.4	0.89	1.0	2.50	1.788
75	144.1	3.4	3.2	0.94	1.4	2.59	1.830
82	150.7	3.9	3.2	0.80	1.6	2.36	1.845

Conditions:

Temp. of the bath 22°F
 Acid strength 16 wt% H₂SO₄ saturated with CO₂
 Current density 25 amp per sq ft

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
15	26.9	1.0	0.5	0.50	0.3	1.64	1.642
30	49.6	1.8	1.1	0.61	0.5	1.68	1.638
45	77.0	2.0	1.7	0.85	0.8	2.35	1.649
60	106.7	2.8	2.4	0.86	1.3	2.32	1.677
90	159.9	4.3	3.7	0.86	1.8	2.26	1.717
110	196.9	4.9	4.3	0.88	1.9	2.45	1.763

Conditions:

Temp of the bath 42°F
 Acid strength 17 wt% H₂SO₄ saturated with CO₂
 Current density 25 amp per sq ft

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
30	52.1	1.4	0.9	0.64	0.6	2.26	1.746
45	82.9	2.0	1.6	0.80	0.9	2.53	1.757
60	109.4	3.0	2.3	0.77	1.2	2.22	1.763
75	141.5	3.8	2.8	0.74	1.6	2.26	1.799
90	171.1	4.2	3.5	0.83	1.9	2.48	1.818
110	204.5	5.0	4.2	0.84	2.0	2.48	1.828

Conditions:

Acid strength 5 wt% H_2SO_4 saturated with CO_2
 Temp. of the bath $32^{\circ}F$
 Current density 25 amp per sq ft

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio <u>Meas</u> Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro	Meas				
15	28.0	0.8	0.7	0.88	0.4	2.14	1.669
30	51.5	1.3	1.2	0.92	0.5	1.57	1.660
45	79.0	2.0	1.9	0.95	0.9	1.72	1.700
60	110.4	2.8	2.4	0.86	1.1	2.41	1.723
75	136.1	3.4	3.0	0.88	1.5	2.44	1.764
80	142.8	3.8	3.3	0.87	1.7	2.29	1.776

Conditions:

Acid strength 27 wt% H₂SO₄ saturated with CO₂
 Temp. of the bath 32°F
 Current density 25 amp per sq ft

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
30	27.1	1.0	0.6	0.60	0.2	1.65	1.643
45	41.2	1.2	0.9	0.75	0.4	2.09	1.640
60	54.4	1.5	1.2	0.80	0.7	2.21	1.636
75	70.4	1.9	1.5	0.79	0.7	2.26	1.641
90	80.6	2.1	1.9	0.90	0.9	2.34	1.653
120	111.2	3.0	2.5	0.83	1.1	2.26	1.673

Conditions:

Current density 15 amp per sq ft
Temp. of the bath 32°F
Acid strength 15 wt% H₂SO₄ saturated with CO₂

Results Data

2S-0 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
15	36.1	1.0	0.7	0.70	0.4	2.20	1.698
30	67.8	2.0	1.5	0.75	0.8	2.07	1.712
45	108.5	3.0	2.3	0.77	1.0	2.21	1.756
60	148.5	3.8	3.1	0.82	1.6	2.38	1.807
70	172.2	4.2	3.8	0.90	1.9	2.50	1.821

Conditions:

Current density 35 amp per sq ft

Temp. of the bath 32°F

Acid strength 15 wt% H₂SO₄ saturated with CO₂

Results Data

Alclad 24S-T3 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio <u>Meas</u> <u>Micro</u>	Growth of part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
15	27.6	0.8	0.6	0.75	0.3	2.10	1.655
30	54.4	1.4	1.1	0.79	0.5	2.36	1.682
45	80.1	2.1	1.8	0.86	0.8	2.33	1.703
60	115.4	2.6	2.5	0.96	1.4	2.71	1.764
75	146.1	3.8	3.2	0.84	1.6	2.34	1.792
92	173.4	4.4	4.0	0.91	2.0	2.40	1.803

Conditions:

Temp. of the bath 32°F
 Acid strength 15 wt% H₂SO₄ saturated with CO₂
 Current density 25 amp per sq ft

Results Data

52S-H34 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat Micro Meas mil mil		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
15	23.1	1.0	0.5	0.50	0.3	1.41	1.656
30	51.7	1.5	1.2	0.80	0.6	2.10	1.684
45	77.6	2.0	1.5	0.75	0.9	2.36	1.715
60	109.1	3.0	2.4	0.80	1.3	2.22	1.741
75	138.1	3.5	3.0	0.86	1.5	2.40	1.774
95	175.1	4.8	3.8	0.79	2.1	2.23	1.818

Conditions:

Current density 25 amp per sq ft
 Acid strength 15 wt% H₂SO₄ saturated with CO₂
 Temp. of the bath 32°F

Results Data

52S-H34 Aluminum

Time min	Average Weight of Coat mg/sq in	Thickness of Coat		Ratio <u>Meas</u> <u>Micro</u>	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
		Micro mil	Meas mil				
15	38.3	1.0	0.7	0.70	0.4	2.33	1.687
30	71.9	1.9	1.5	0.79	0.8	2.30	1.718
45	110.1	2.6	1.8	0.69	0.8	2.58	1.766
50	124.8	3.0	2.7	0.90	1.4	2.54	1.777
60	151.0	4.0	3.3	0.83	1.8	2.30	1.814
70	172.5	4.6	4.0	0.87	2.1	2.29	1.841

Conditions:

Current density 35 amp per sq ft

Temp. of the bath 32°F

Acid strength 15 wt% H₂SO₄ saturated with CO₂

Results Data

52S-H34 Aluminum

Time mil	Average Weight of Coat mg/sq in	Thickness of Coat Micro Meas		Ratio Meas Micro	Growth of Part mil	Density of Coat g/cu cm	Coating Ratio
30	29.9	0.9	0.5	0.56	0.3	2.02	1.615
45	45.2	1.2	0.8	0.67	0.4	2.30	1.620
60	63.8	1.4	1.3	0.93	0.6	2.78	1.647
90	92.1	2.2	2.0	0.91	0.9	2.56	1.668
120	126.2	2.7	2.7	1.00	1.3	2.84	1.692

Conditions:

Current density 16 amp per sq ft
 Temp. of the bath 32°F
 Acid strength 15 wt% H₂SO₄ saturated with CO₂

Results Data

24S-T3 Aluminum

Time	Thickness of Coat Micro mil	Growth of Part mil
min		
15	0.8	0.4
30	1.1	0.5
45	2.0	0.7
60	2.5	1.0
72½	2.9	1.3
75	3.0	1.4
90	3.7	1.8
120	5.0	2.3

Conditions:

Temp. of the bath 32°F
Current density 25 amp per sq ft
Acid strength 15 wt% H₂SO₄ saturated with CO₂

Results Data

75S-0 Aluminum
 Alcoa 142-T77 Aluminum
 Alcoa 195-T4 Aluminum

	Time	Thickness of Coat Micro mil	Growth of Part mil
75S-0	15	1.0	0.4
	60	3.0	1.5
	105	4.9	2.3
Alcoa 142-T77	15	0.7	0.4
	60	2.4	1.2
	120	4.6	2.0
Alcoa 195-T4	15	0.8	0.4
	60	2.7	1.4
	120	5.4	2.6

Conditions:

Temp. of the baths 32°F

Current densities 25 amp per sq ft

Acid strength

75S-0	15 wt% H ₂ SO ₄ saturated
Alcoa 142-T77	with CO ₂
Alcoa 195-T4	16 wt% H ₂ SO ₄ saturated
	with CO ₂

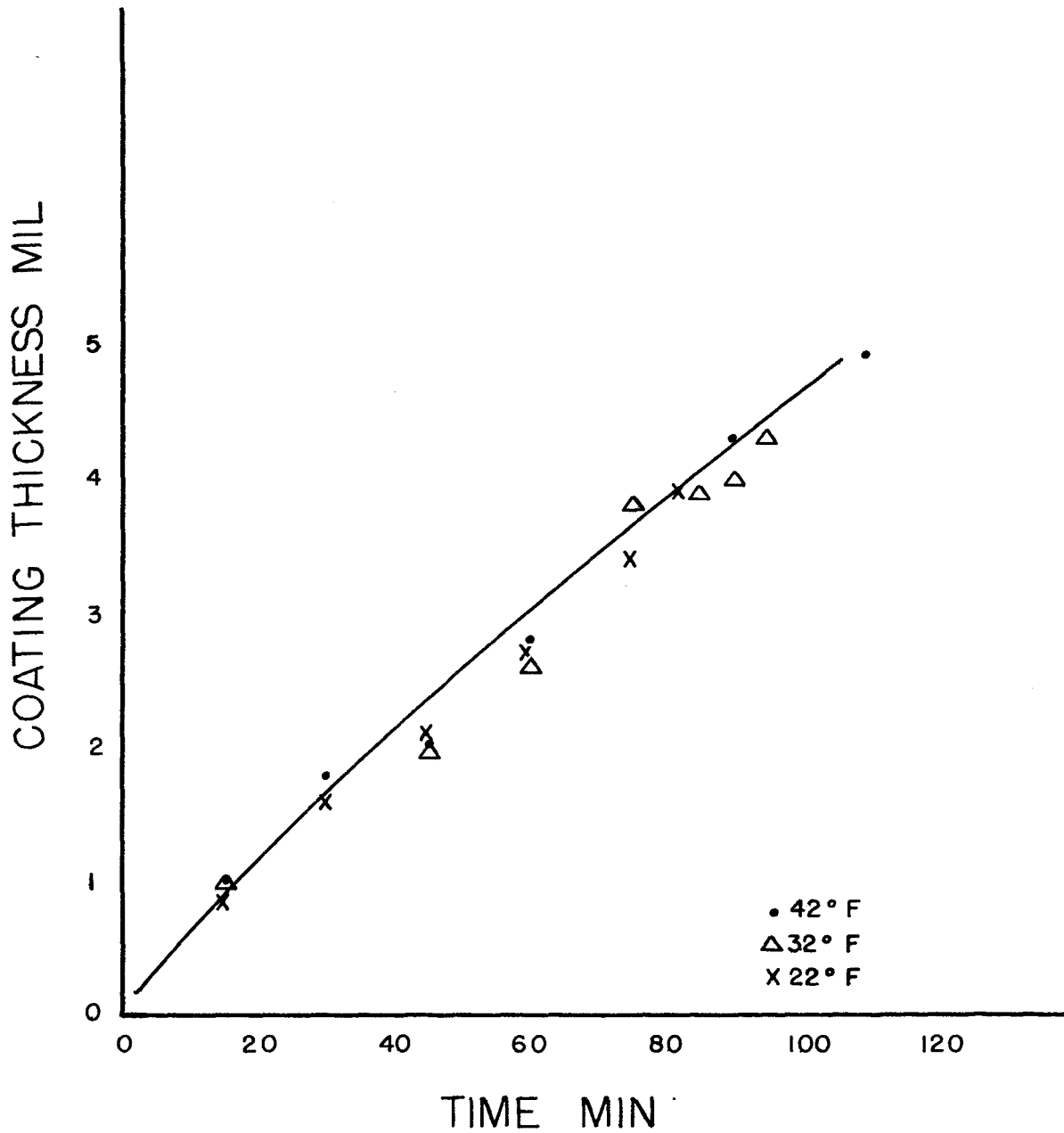
Results Data

Alcoa 355-T71 Aluminum
 Alcoa 356 Aluminum
 Eclipsaloy 325 Aluminum

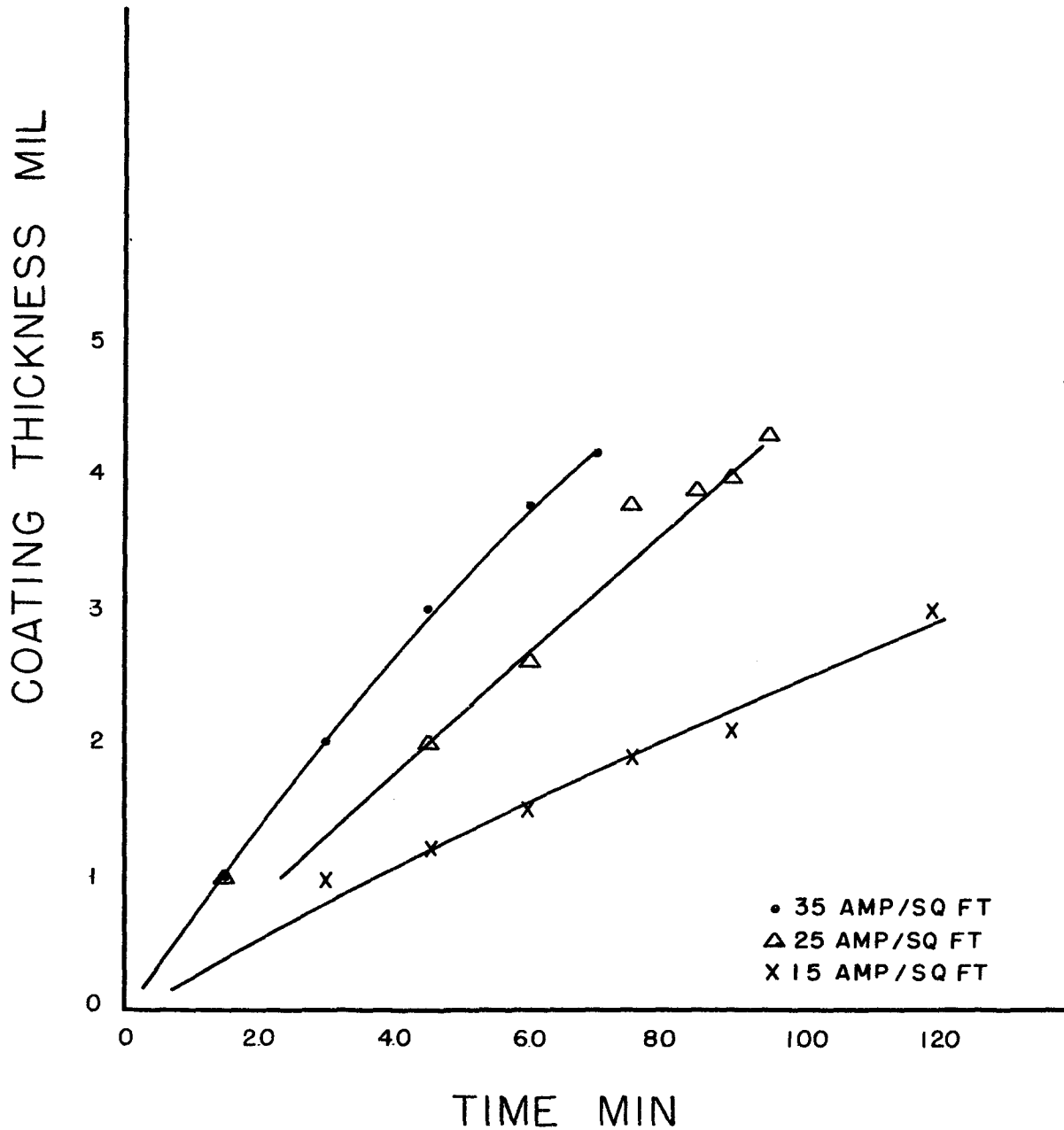
	Time	Thickness of Coat	Growth of Part
	min	Micro mil	mil
Alcoa 355-T71	15	0.9	0.3
	60	2.6	1.0
	90	4.8	2.0
Alcoa 356	15	0.9	0.5
	60	3.4	1.8
	75	4.3	2.4
Eclipsaloy 325	15	0.8	0.3
	60	2.6	0.9
	120	4.9	1.9

Conditions:

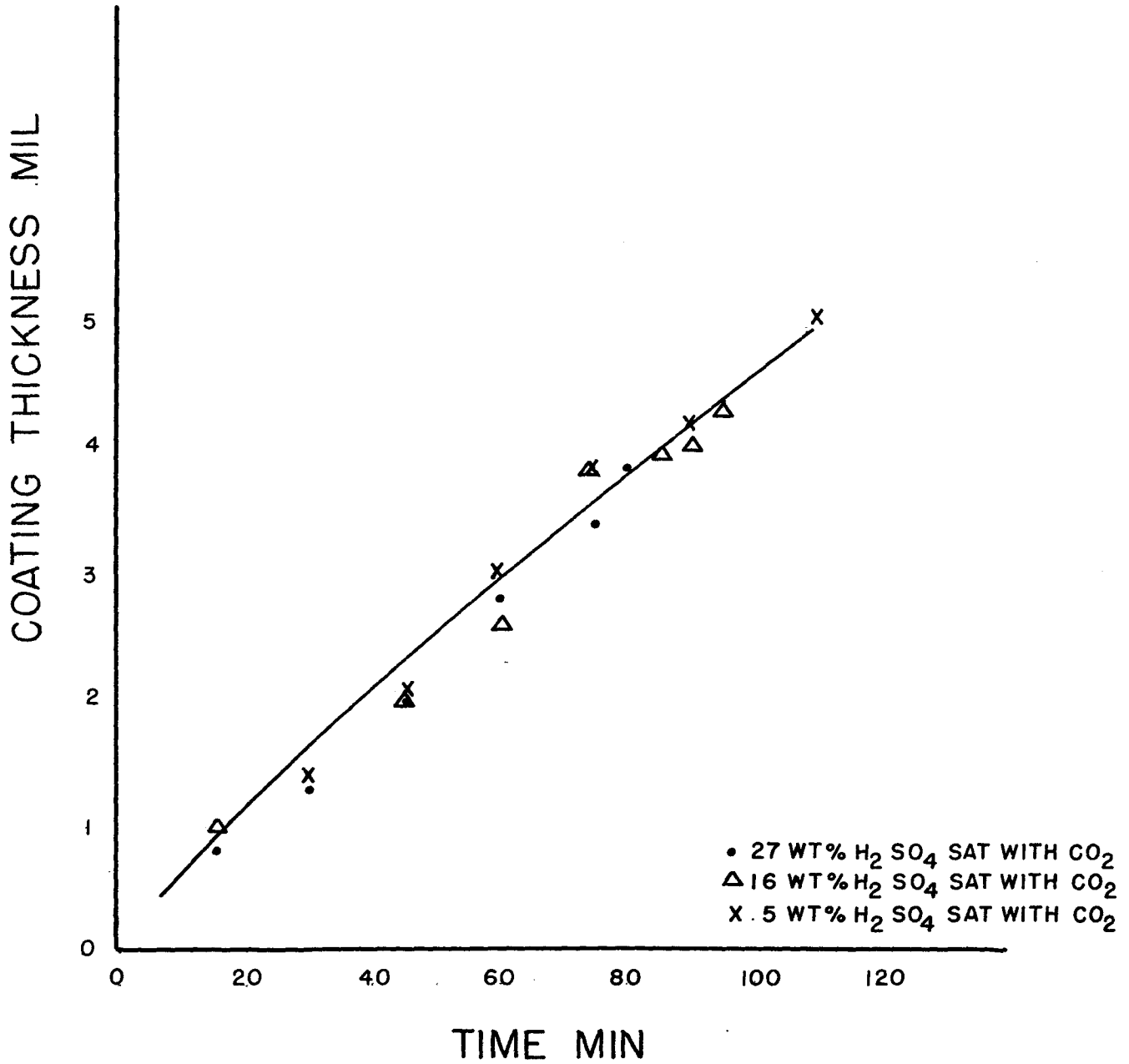
Temp. of the bath 32°F
 Current density 25 amp per sq ft
 Acid strength 15 wt% H₂SO₄ saturated with CO₂



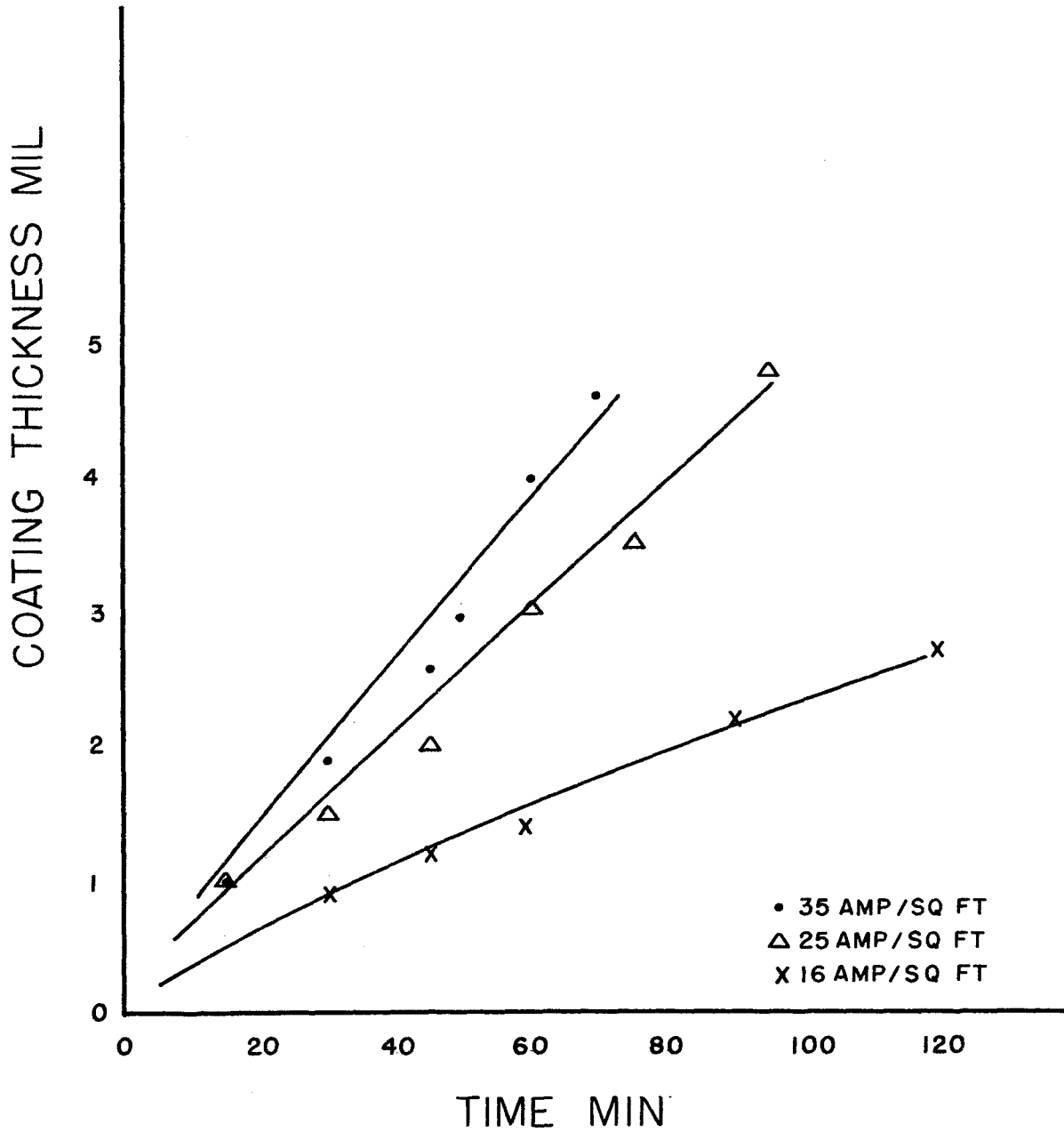
CURVE 1. Relation between Coating Thickness and Time for 2S-0 Aluminum Anodically Treated at Different Temperatures.



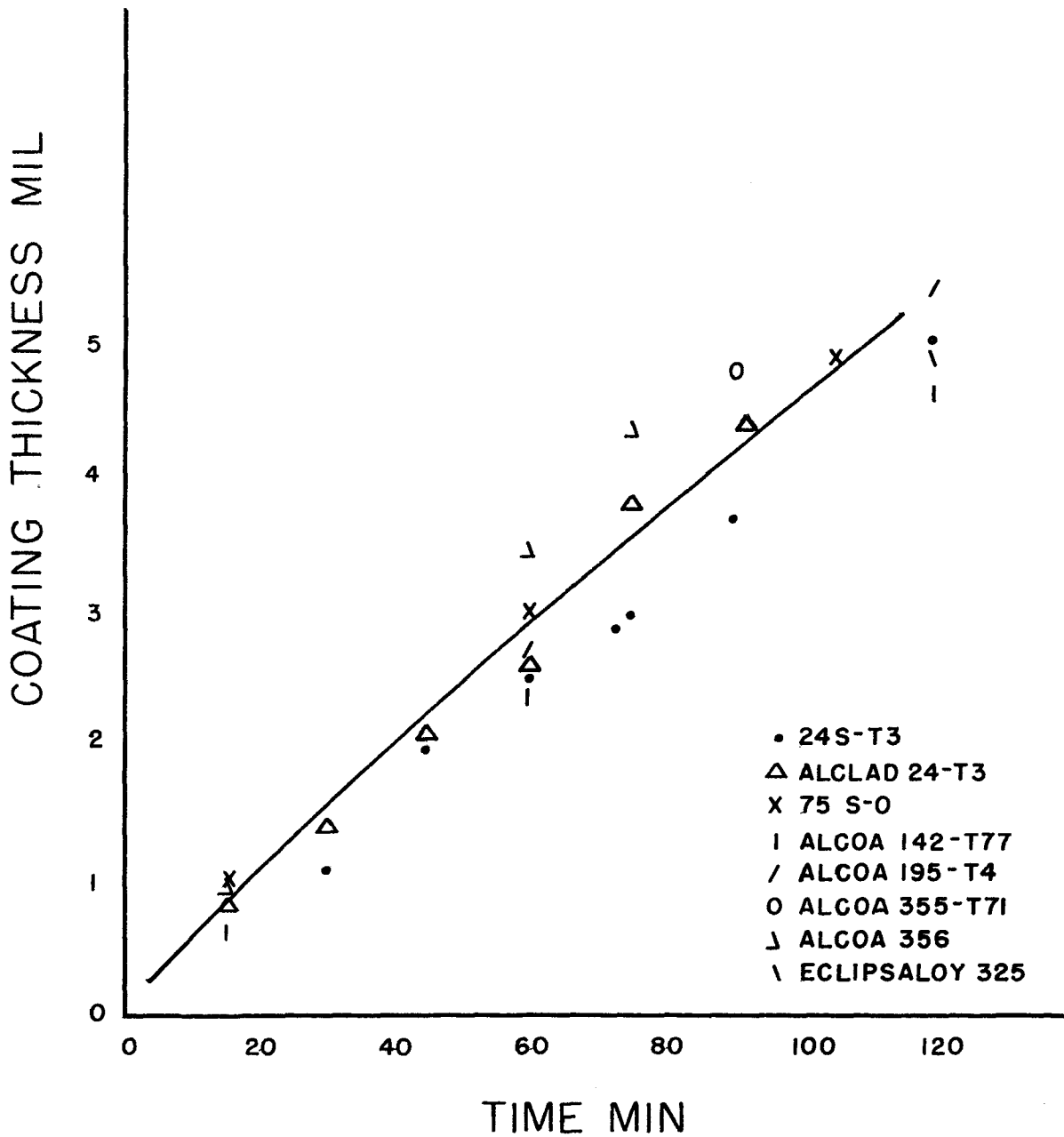
CURVE 2. Relation between Coating Thickness and Time for 2S-0 Aluminum Anodically Treated at Different Current Densities.



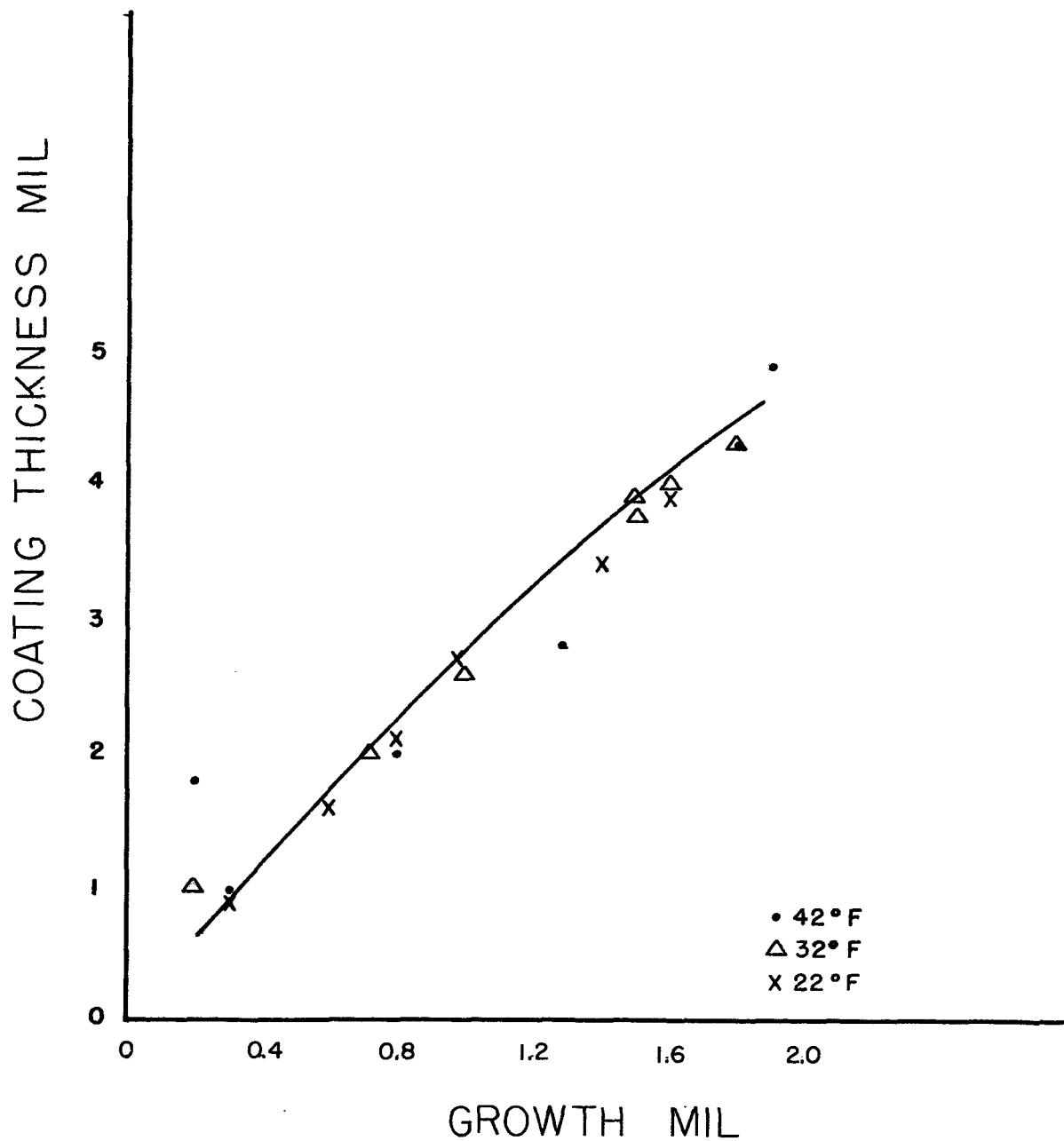
CURVE 3. Relation between Coating Thickness and Time for 2S-0 Aluminum Anodically Treated in Different Strength Electrolytes.



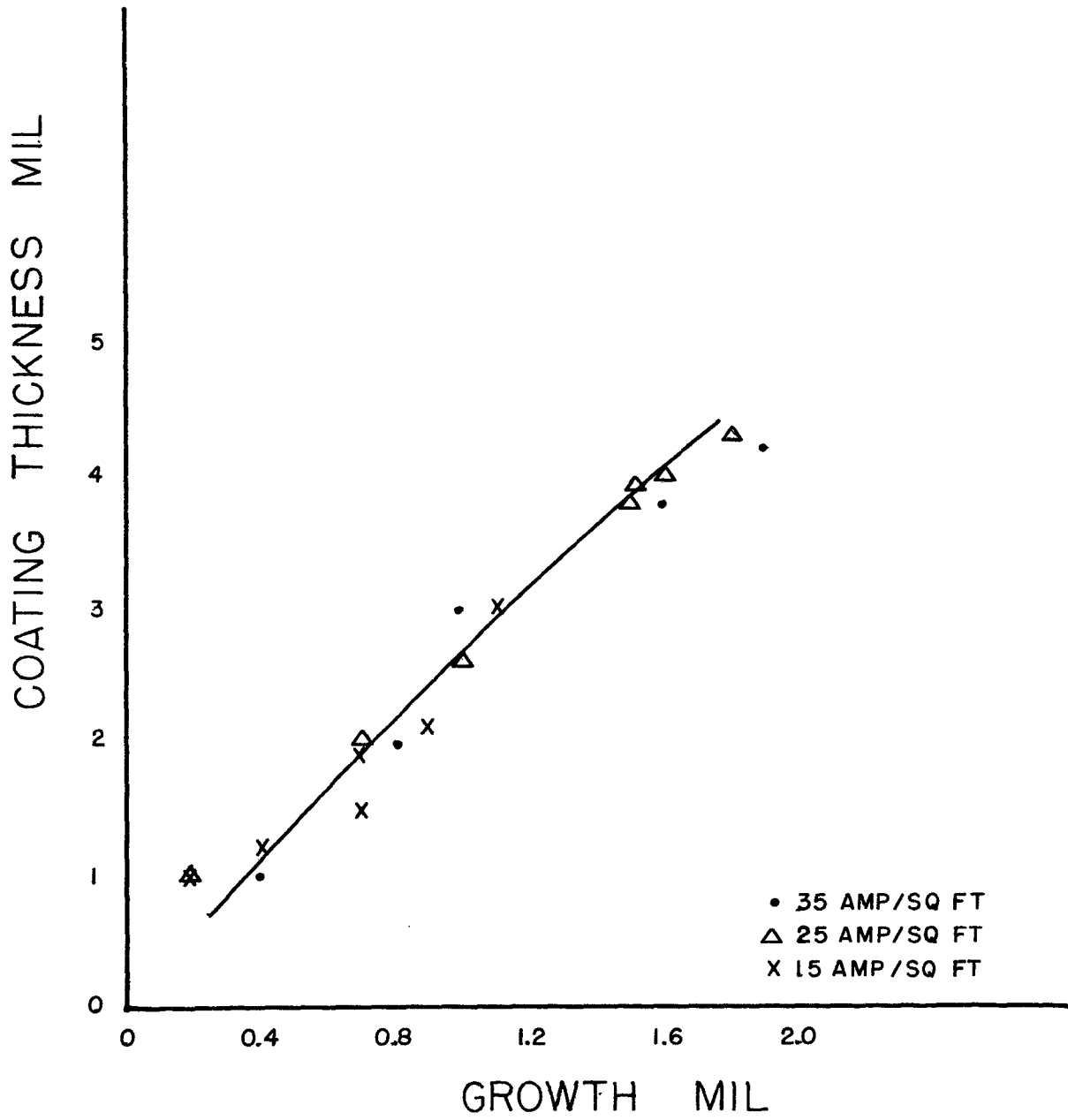
CURVE 4. Relation between Coating Thickness and Time for 52S-H34 Aluminum Anodically Treated at Different Current Densities.



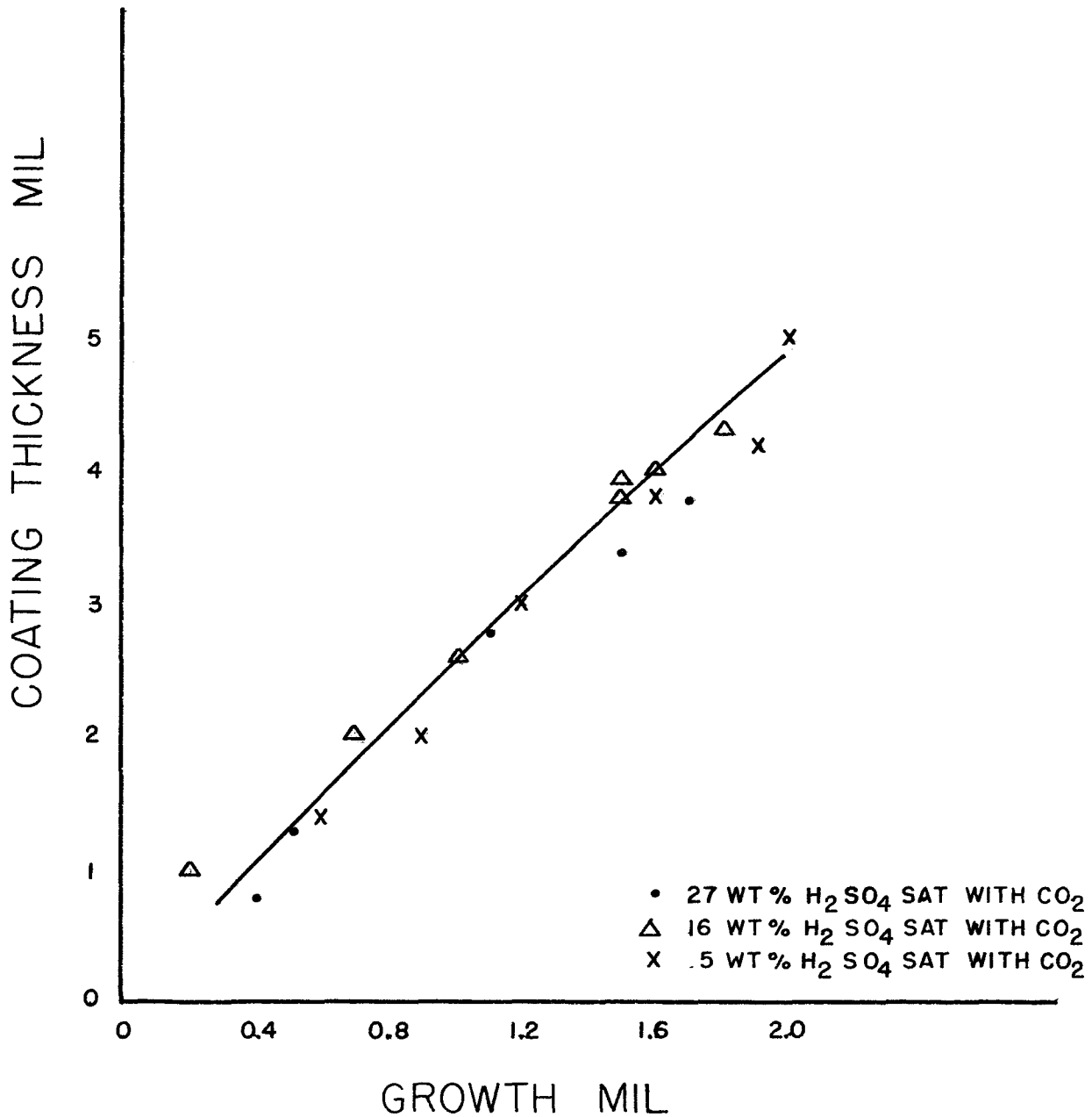
CURVE 5. Relation between Coating Thickness and Time for Different Aluminum Alloys Formed under Similar Conditions of Temperature, Current Density, and Electrolyte Strength.



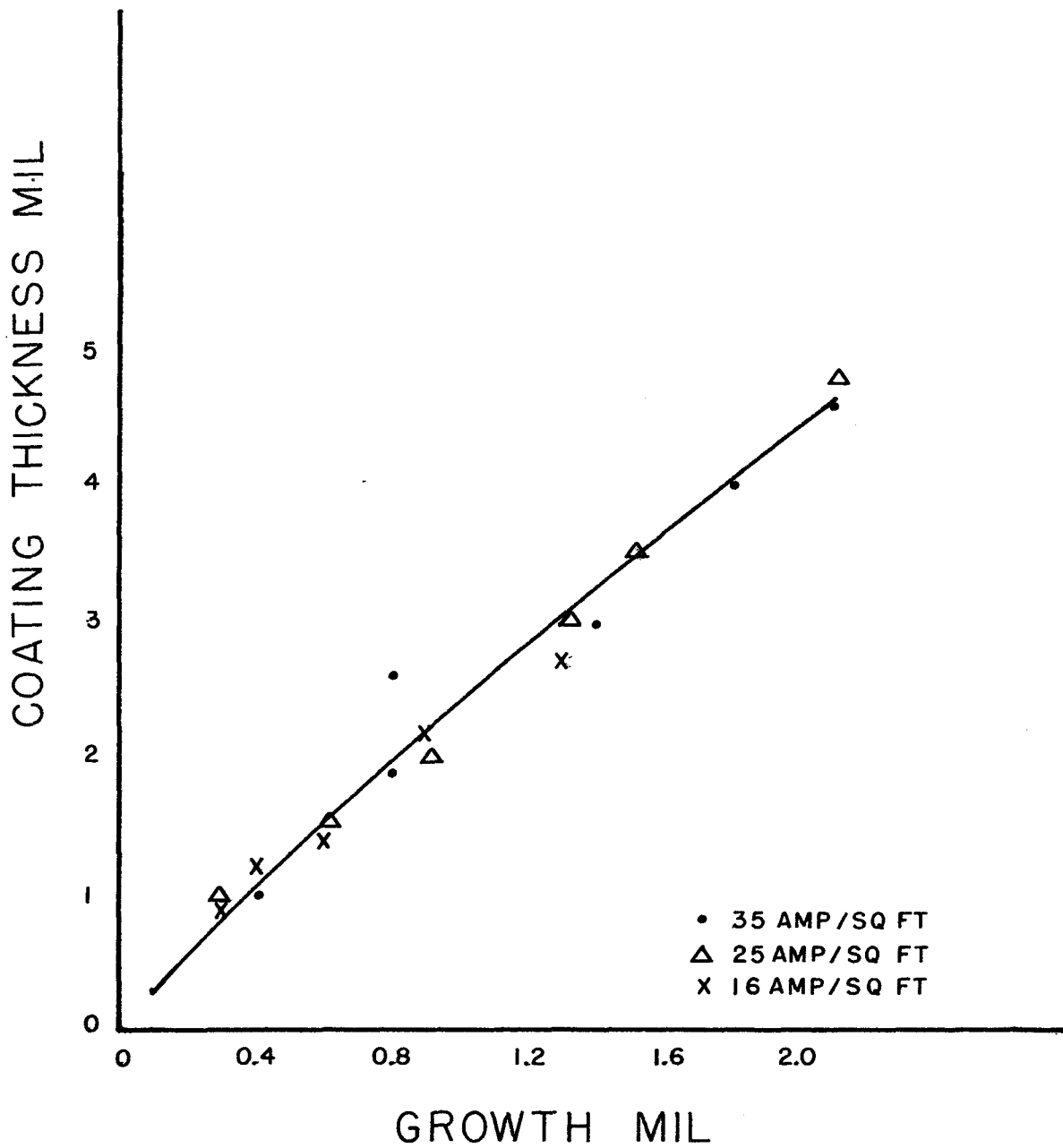
CURVE 6. Relation between Growth of the Part and Coating Thickness Formed at Different Temperatures on 2S-0 Aluminum.



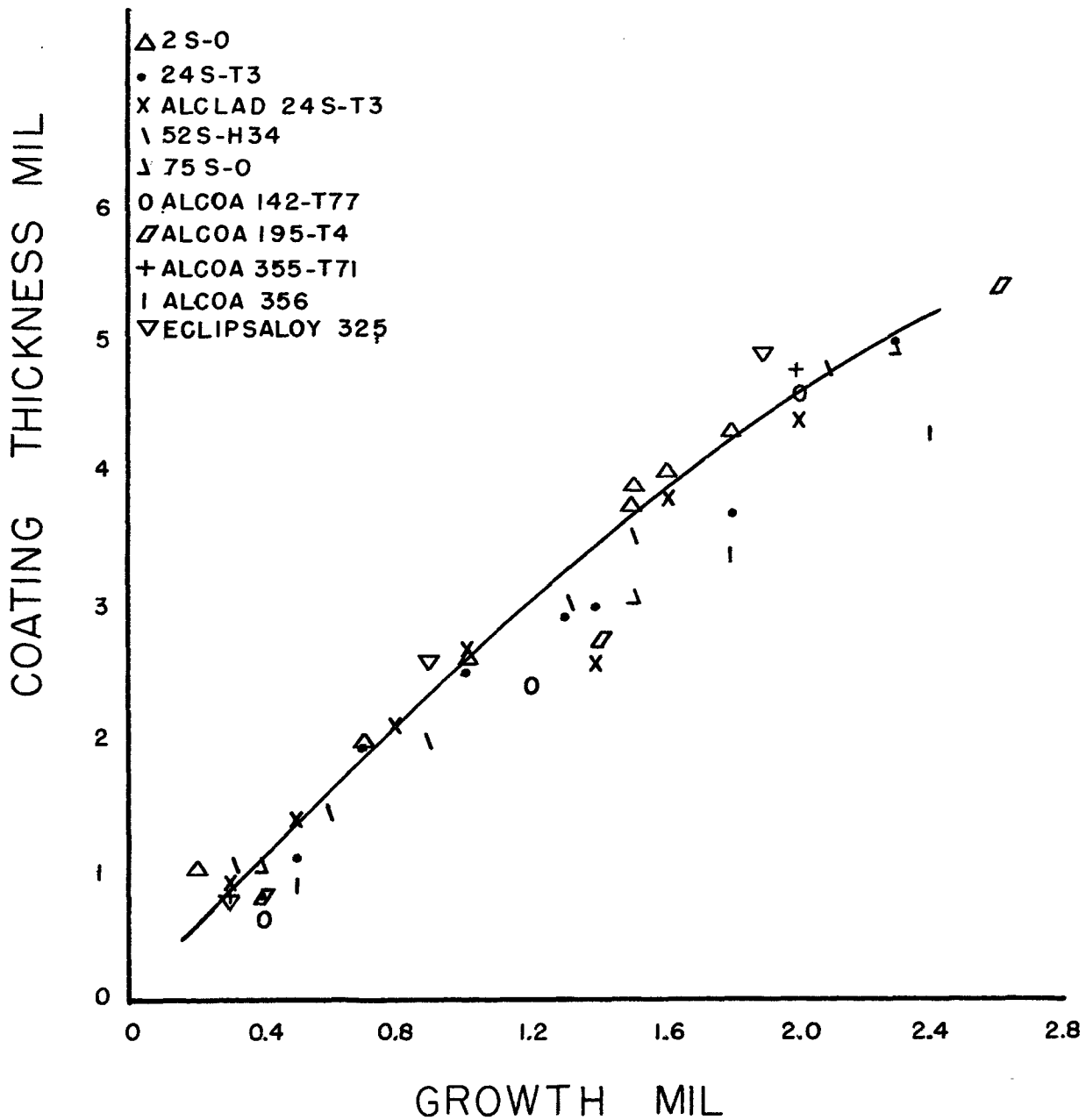
CURVE 7. Relation between Growth of the Part and Coating Thickness Formed at Different Current Densities on 2S-0 Aluminum.



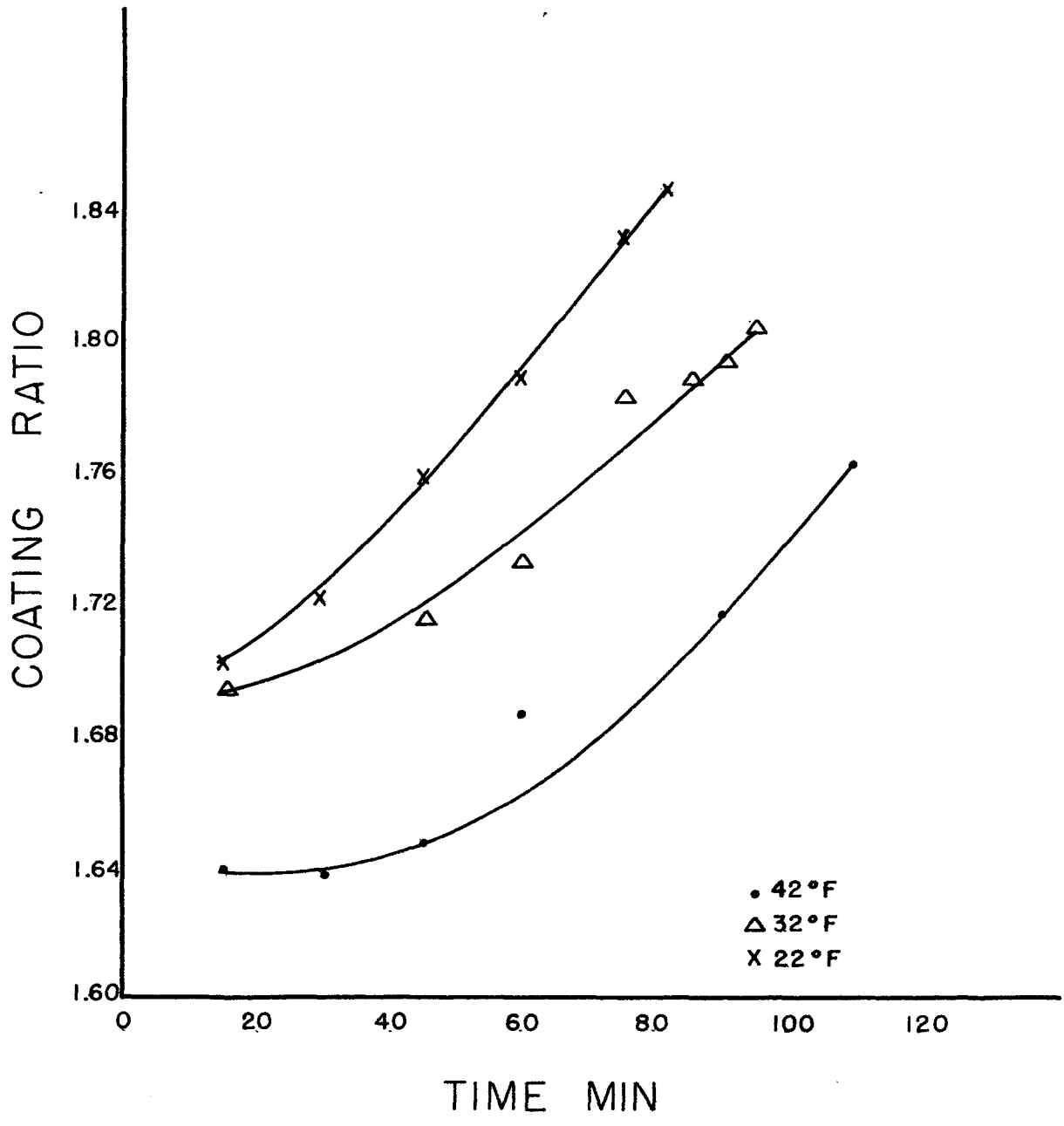
CURVE 8. Relation between Growth of the Part and Coating Thickness Formed in Different Strength Electrolytes on 2S-0 Aluminum.



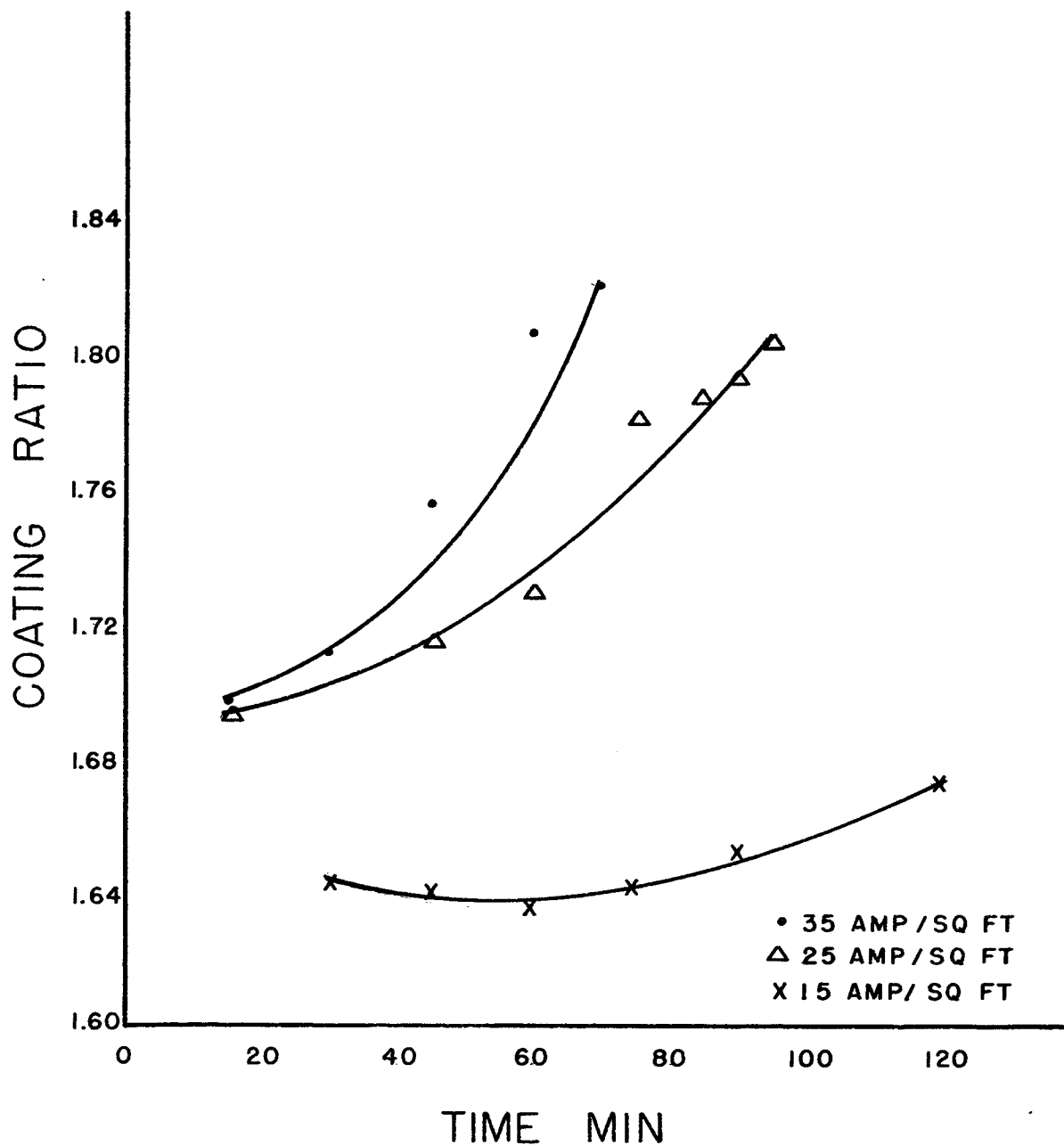
CURVE 9. Relation between Growth of the Part and Coating Thickness Formed at Different Current Densities on 52S-H34 Aluminum.



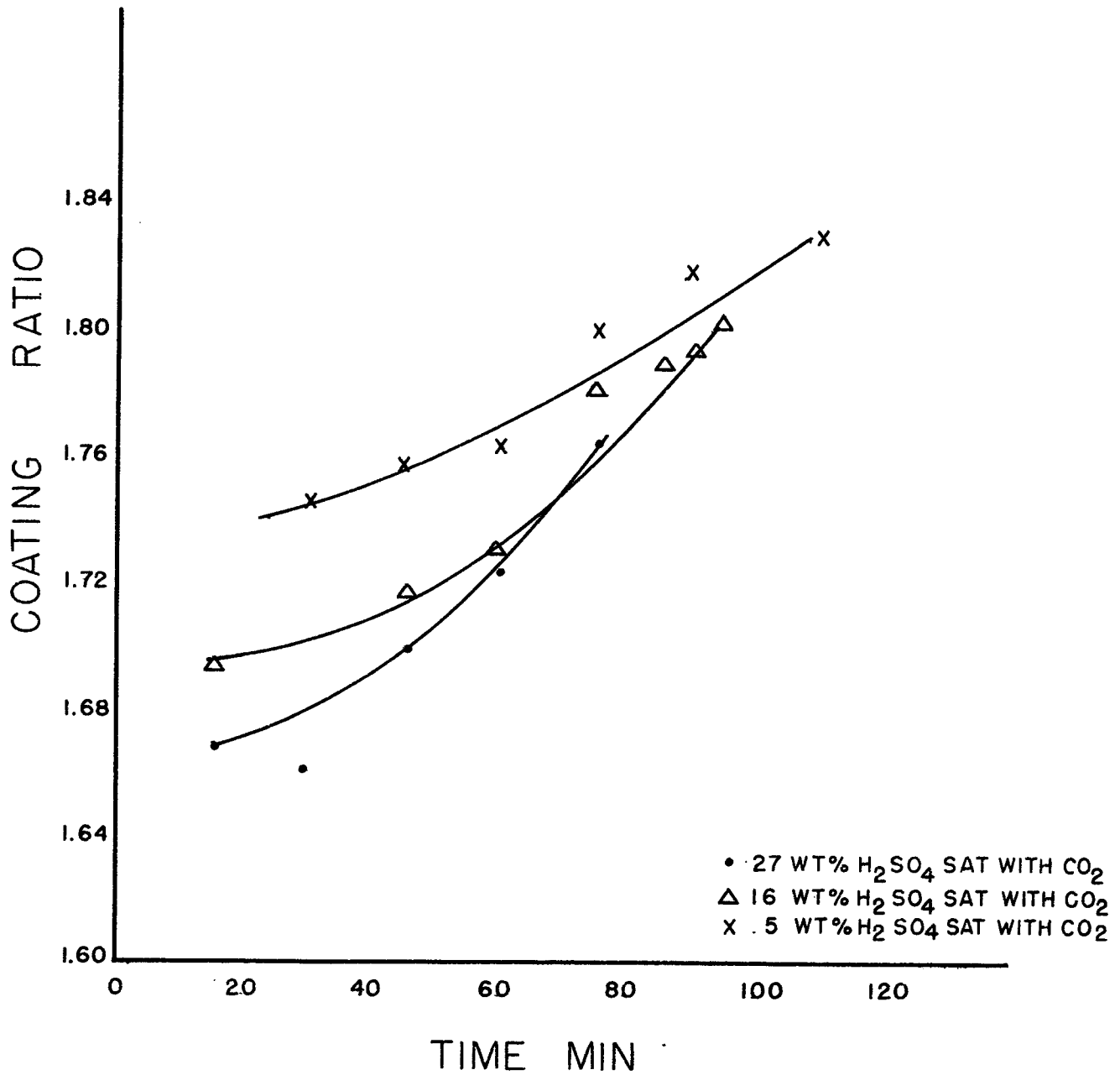
CURVE 10. Relation between Growth of the Part and Coating Thickness Formed on Different Aluminum Alloys under Similar Conditions of Temperature, Current Density, and Electrolyte Strength.



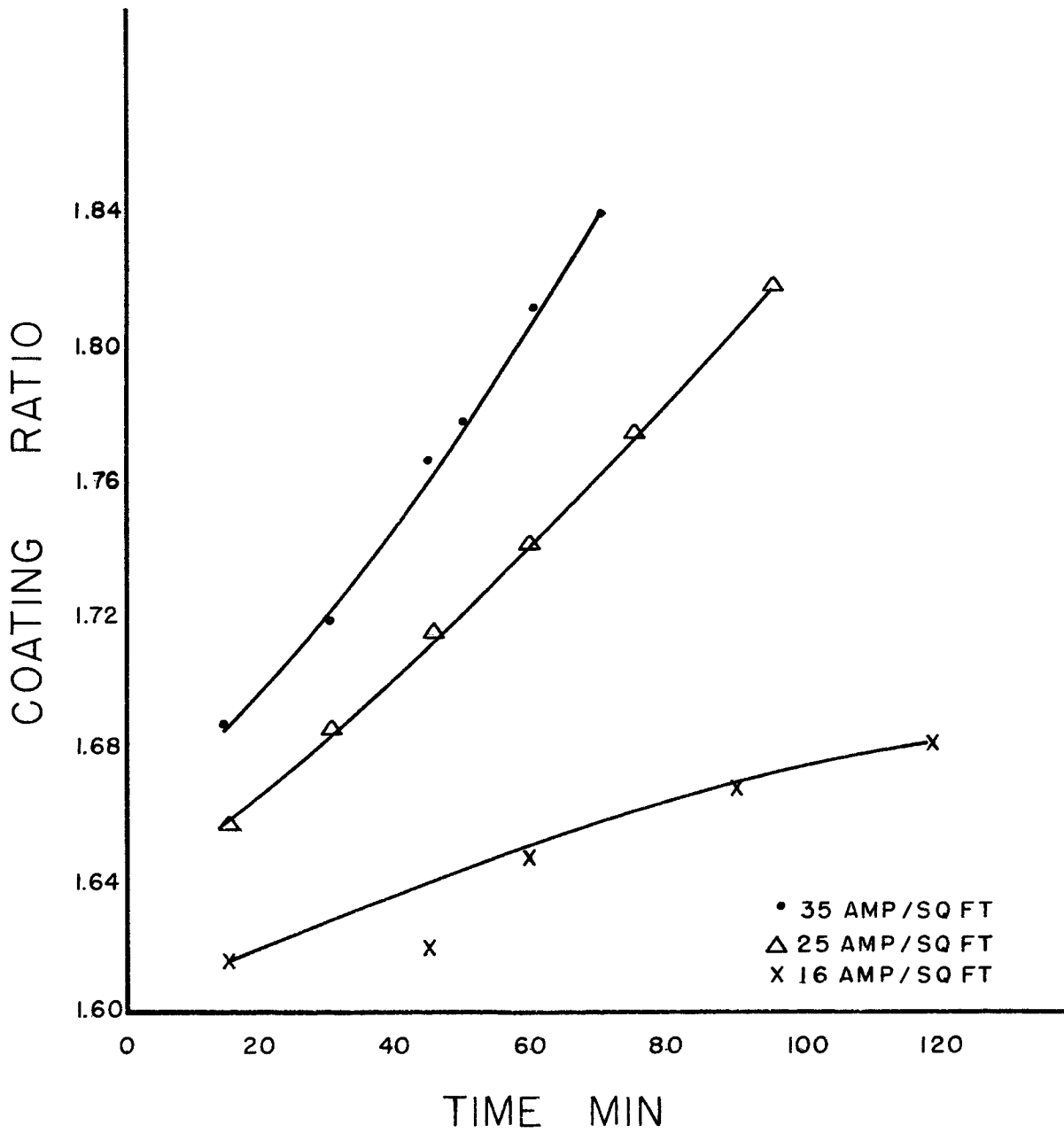
CURVE 11. Variation of Coating Ratio with Time for 2S-0 Aluminum Anodically Treated at Different Temperatures.



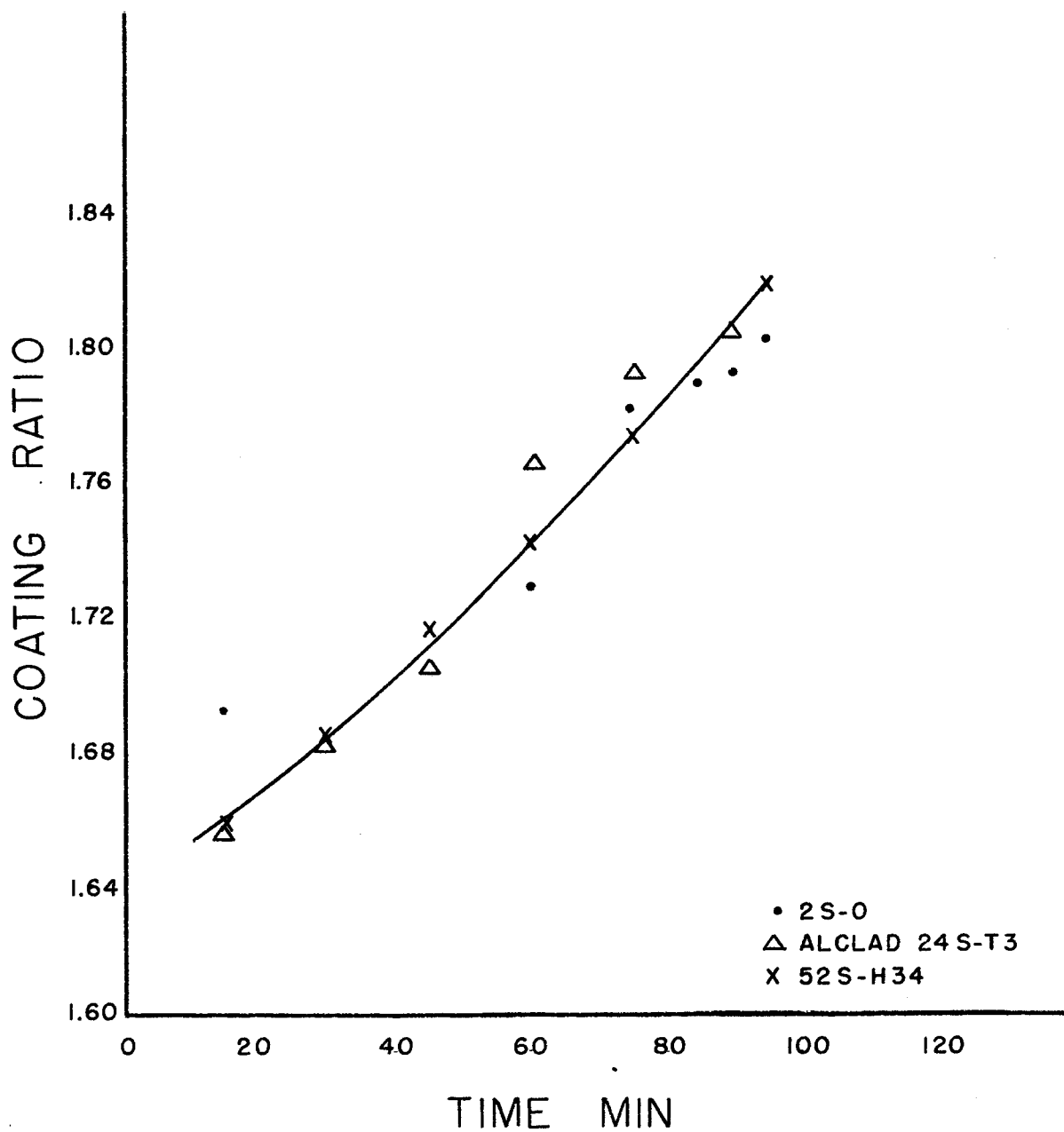
CURVE 12. Variation of Coating Ratio with Time for 2S-0 Aluminum Anodically Treated at Different Current Densities.



CURVE 13. Variation of Coating Ratio with Time for 2S-0 Aluminum Anodically Treated in Different Strength Electrolytes.



CURVE 14. Variation of Coating Ratio with Time for 52S-H34 Aluminum Anodically Treated at Different Current Densities.



CURVE 15. Variation of Coating Ratio with Time for Different Aluminum Alloys Anodically Treated under Similar Conditions of Temperature, Current Density, and Electrolyte Strength.

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APPENDIX

Acid Strength Titration

TOTAL 5 ml sample pipetted into a 400 ml beaker containing 200 ml distilled water. Titrated with sodium hydroxide with phenolphthalein indicator.

$$= \text{ml} \times N \times 0.88$$

FREE 5 ml sample pipetted into a 400 ml beaker containing 10 ml of a 45% potassium fluoride solution. Shake. Dilute to 200 ml with distilled water. Titrated with sodium hydroxide with phenolphthalein indicator.

$$= \text{ml} \times N \times 0.88$$

$$\text{EFFECTIVE} = \% \text{ FREE} + \frac{(\% \text{ TOTAL} - \% \text{ FREE})}{2}$$