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PERFORMANCE OF THIN FILM

HUMIDITY SENSORS

by

Joseph DelPico

DEPARTMENT OF METEOROLOGY
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Contract No. F 19628-67-0228
Project No. 6670
Task No. 667001
Work Unit No. 66700101

Scientific Report No. 1

15 October 1967

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Contract Monitor: Frederick Brousaides
Aerospace Instrumentation Laboratory

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AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS 01730

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ABSTRACT

Various hygroscopic materials have been considered for use as the thin film dielectric in a condenser, which is to be used as the humidity-sensing element in an electric hygrometer. One conductive condenser plate is made extremely porous so that water vapor may rapidly diffuse through it and into the dielectric thin film. Some electrical characteristic of the element (resistance, capacitance or impedance), which is a function of the amount of sorbed water vapor, is calibrated as a function of the atmospheric humidity. The requirement of such a dielectric is that it approach equilibrium rapidly and display both reversible and reproducible humidity-electrical characteristics.

Polymerous dielectrics have shown an extremely slow rate of response and it is suspected that the rate of Knudsen diffusion through many fine tortuous pores is responsible.

Anodic aluminum oxide films produced in a sulfuric acid electrolyte have recently shown a rapid rate of response as well as a reproducible response toward humidity changes. The major limitation hindering the use of such humidity sensing elements is their long-term calibration drift, which causes the elements to become less sensitive toward humidity variations. Results have shown that a change in the concentration of various species of chemisorbed water vapor initially present on the pore walls may be responsible for the observed calibration drift and that further experimentation in this area is warranted.

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NOMENCLATURE

C	Concentration (gr-moles/cm ³)
D	Ordinary diffusion coefficient (cm ² /sec)
\mathcal{D}	pore diffusion coefficient (cm ² /sec)
M	Molecular weight of water vapor (18)
N	Molal water vapor flux (gr-moles/sec-cm ²)
T	Temperature (degrees Kelvin)
r	Equivalent pore radius (cm)
x	Distance in direction of diffusion (cm)
Θ	void volume fraction (cm ³ /cm ³)
γ	tortuosity factor (unitless)

Subscripts

k	Knudsen pore diffusion
p	Ordinary pore diffusion
wa	Diffusion of water in dry air

Symbols

\AA	Angstroms (10 ⁻⁸ centimeters)
μ	microns (10 ⁻⁴ centimeters)

INTRODUCTION

Many materials are found to adsorb and desorb water vapor as the humidity of the atmosphere surrounding them is varied. Since water is highly conductive, most non-conductive materials (non-metals) will show a decrease in electrical resistance with increasing humidity. Materials displaying such a humidity dependent resistance may be utilized as the sensing element in an electric hygrometer. It becomes mandatory that any material which is to be utilized in such a capacity must approach equilibrium rapidly and display both reversible and reproducible humidity-resistance characteristics. At least one external dimension of such a material must be made small enough to allow the rate limiting phenomena, such as diffusion and adsorption of water vapor, to approach equilibrium rapidly.

The present study is mainly concerned with evaluating the use of anodic aluminum oxide films and polymeric films as the humidity-sensing material to be used in an electric hygrometer. The films are to be used as the dielectric in a plate condenser (See Figure 12). One of the condenser conductive plates is to be made porous so that water vapor may easily diffuse through it and into the dielectric film (See Figure 1).

An anodic aluminum oxide film is formed on the surface of an aluminum electrolyte which is used as the anode in an electrolytic bath (See Appendix II). The porosity thickness and structure of the film is known to be a function of the electrolyte composition, concentration, and temperature as well as the anodizing time and current density. Element sensitivity has been shown (7) to increase with increasing film porosity.

Sulfuric acid has generally been the electrolyte used since it produces a higher porosity film than other known electrolytes. The following anodizing conditions, which have been used by others (1) (4), were also used in the present studies:

Electrolyte	Sulfuric Acid
Concentration:	17.5% v/v
Temperature:	25°C
Current Density:	50 milliamps/square centimeter
Anodizing Time:	30 minutes

Films produced under the above conditions are found to have a large surface area for the adsorption of water vapor. Electron micrographs have shown the film structure to be composed of hexagonally spaced cylindrical pores which are both perpendicular and open to the film's outer surface (See Figure 14 and Figure 15). The pores are separated from the aluminum base by an extremely thin anodic aluminum oxide film (See Figure 14, b). Anodic aluminum oxide sensing elements which have been produced to date have shown the following advantages: very low cost, a rapid rate of response, a low temperature dependency above 0°C, no dependency on total pressure or air velocity, and a robust nature. The principle limitation hindering the commercial production of such elements has been an irreversible calibration drift. Investigators (7) have reported that this observed calibration drift becomes accelerated when the elements are subjected to relative humidities of greater than 80% over a prolonged period of time. Part of the present study was to determine the cause of the observed calibration drift in order to eliminate it or greatly reduce it and predict its residuum as a function of time and environment.

The possible modes of water vapor transport in a thin film are ordinary pore diffusion, Knudsen diffusion, physical adsorption and chemisorption (See Appendix I). The electrical characteristics of the anodic aluminum oxide element are believed to be a function of the amount of physically ad-

sorbed water vapor present on the pore walls. Physical adsorption, which is caused by secondary molecular forces, is completely reversible. The amount of physical adsorption at any specific pore location is principally a function of the relative humidity at that particular pore location and the chemical characteristics of the pore surface. Since ordinary pore diffusion is generally extremely rapid in comparison to Knudsen diffusion, an irreversible behavior may be shown if Knudsen diffusion becomes controlling. In other words, the rate of water vapor transfer through a fine pore structure becomes so slow that the pore water vapor concentration is seldom the same as the external water vapor concentration. This would cause the amount of physically adsorbed water vapor to be in equilibrium with the local pore water vapor concentration and not the external water vapor concentration. Knudsen diffusion through a fine pore structure may therefore be the cause of a long-term hysteresis effect.

Thus far chemical adsorption (termed chemisorption) of water vapor has not been considered. For chemisorption to occur, water vapor molecules must be capable of forming a chemical bond with the anodic aluminum oxide surface. The literature (10) shows that anodic aluminum oxide is composed of various hydrated forms of anhydrous Al_2O_3 (See Appendix III) and that prolonged heating would be expected to cause the anodic aluminum oxide to become less hydrated. Such hydrated water molecules present on the pore surfaces may be viewed as chemisorbed water vapor on an otherwise anhydrous Al_2O_3 surface. Such a chemisorbed surface can seldom be expected to be in equilibrium with its surrounding, due to the large activation energy requirement for desorption (See Appendix I). It is evident that these various chemisorbed species on the pore walls (various degrees of hydrated Al_2O_3) may not be in equilibrium with their surroundings and that the pore surfaces may be considered to be continually changing as the chemisorbed

species slowly approach their equilibrium degree of hydration. Since the amount of physically adsorbed water vapor present on the pore walls is a function of the chemical characteristics of the surface, a slow change in the degree of surface hydration on the pore walls would be expected to alter the amount of physically adsorbed water vapor at any given relative humidity. Therefore it is seen that chemisorption as well as Knudsen diffusion could be responsible for an observed calibration drift.

Elements were also produced using a hygroscopic polymeric material in place of the anodic film. The polymeric film selected was a linear polyether-urethane which is generally believed to be hygroscopic due to the physical adsorption of water vapor. Due to the extremely fine and tortuous pore structure of polymeric films in comparison to the regular pore structure of the anodic aluminum oxide film, it would be expected that the rate of response of a polymeric film element would be much slower than the rate of response of an anodic aluminum oxide element.

Part of the present investigation was to determine more about the physical structure of anodic aluminum oxide films formed in a sulfuric acid electrolyte. Electron micrographs were obtained so as to view the pore structure. The effect of varying the anodization time was also observed from film density measurements.

The major portion of the investigation involved element production and calibration as well as the effect of the elements storage environment on the calibration drift. One element was stored in each of the following environments: in a vacuum (at 25°C), in an oven at 600°C, and in an atmosphere having a 97% relative humidity.

It was expected that in a vacuum only dehydration would be possible, since no water vapor molecules are available for hydration, and at 600°C the surface dehydration would be greatly increased due to the available

activation energy. It is also expected that the rate of Knudsen diffusion would be increased in both a vacuum and at 600°C (See Appendix I). It was hoped that the effect of storage environment on the observed calibration drift would give some evidence of the presence of Knudsen diffusion or chemisorption (or both) which may be responsible for the observed calibration drift.

In summary, the present investigation was aimed at understanding the mechanisms involved in the operation of a thin film humidity sensor, with special consideration being given toward determining the cause of the calibration drift which is hindering the acceptance of the anodic aluminum oxide element as a useful hygrometer.

EXPERIMENTAL PROCEDURES

PRODUCTION OF ANODIC ALUMINUM OXIDE HUMIDITY SENSORS

Sample Preparation:

The aluminum chosen for anodizing was sheet aluminum, having a thickness of 0.0325 inches and an Aluminum Association Alloy (AAA) designation of 3003 (essentially pure aluminum containing 1.25% manganese). Rectangular elements, 1/2 x 3 centimeters, were cut from the sheet aluminum (See Figure 1) and buffed using a buffing wheel and a fine buffing compound. Buffing was continued until a uniform bright luster was produced. Particular attention was focused on the samples edges where buffing was continued until all visible cutting blemishes were removed. The elements were then washed, using Kimwipes soaked in benzene, to remove all traces of buffing compound and immersed in benzene to await anodizing.

Anodizing Bath Preparation:

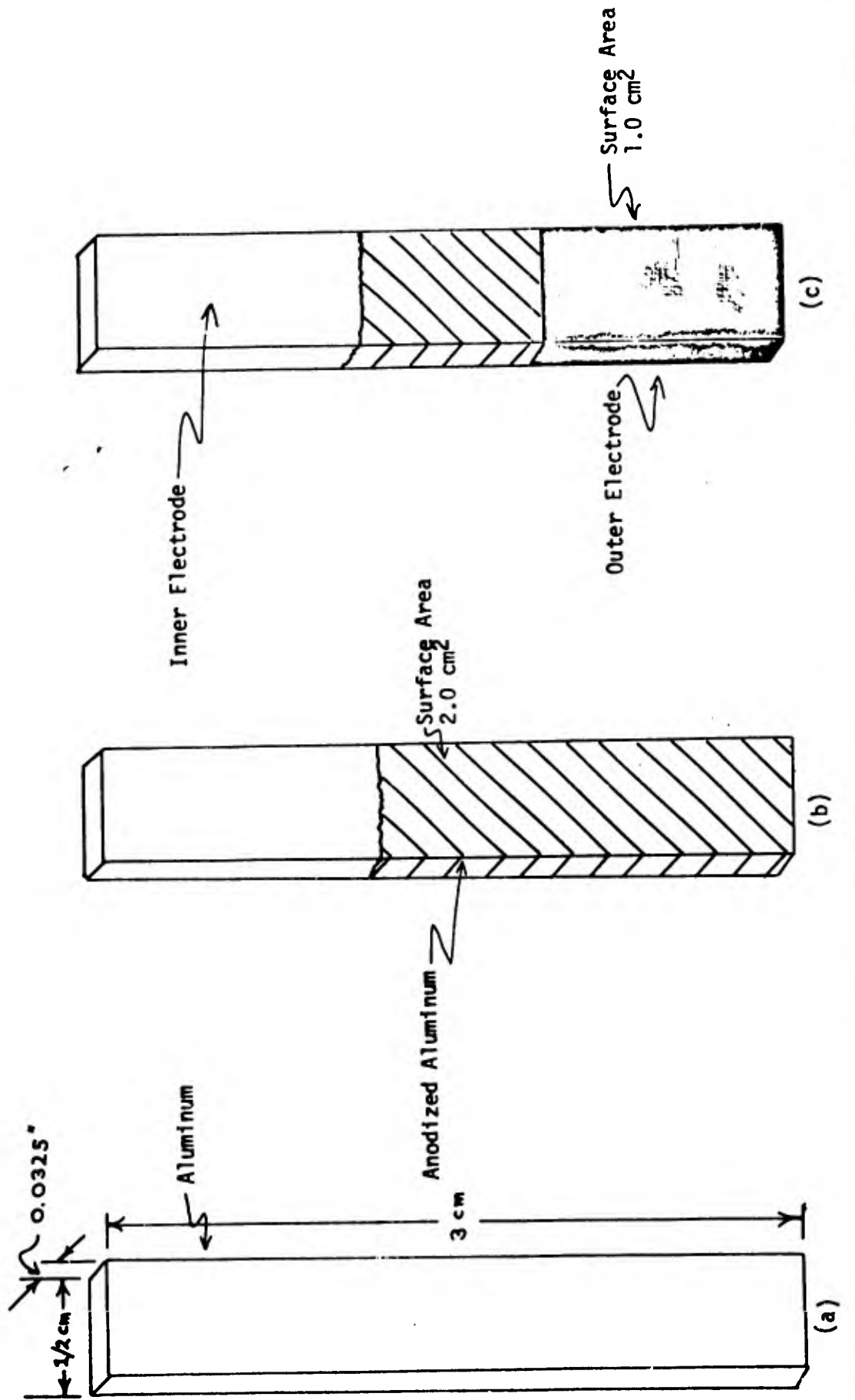
Although a number of electrolytes of varying concentration may be employed as the anodizing bath only the preparation of a 17.5% (v/v) sulfuric acid electrolyte, which was principally used in the experimentation, will be discussed. To 453 milliliters of distilled water into an empty beaker, 100 milliliters of Dupont reagent sulfuric acid (Max. 98.0% - Min. 95.0%) is added slowly while continually stirring. The solution is allowed to cool to the desired temperature of $25^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$ before use. Since the exact concentration of the sulfuric acid electrolyte is not a critical factor, titration techniques were not employed in the anodizing bath preparation.

Anodizing Apparatus and Procedure:

A 400 milliliter graduated beaker was used to hold the sulfuric acid

STAGES OF ELEMENT PRODUCTION

FIGURE 1



electrolyte, upon which was placed a 3-inch plastic petri dish cover. The petri dish cover was used to support the electrodes (See Figure 2). Two steel machine screws were fastened to the petri dish cover by the use of two nuts on each machine screw. A 2 x 8 centimeter strip of 0.0325 inch thick sheet aluminum (AAA 3003) was attached to the first machine screw and used as the cathode. A metal notebook clip was fastened to the second machine screw, allowing for easy and rapid implacement of the aluminum elements which were used as the anode. Holes were also drilled through the petri dish cover to allow for the venting of the hydrogen gas being produced at the cathode. The level of the electrolyte solution was adjusted so as to have the desired anodic element surface area (2.0 cm^2) below the solution (See Figure 2).

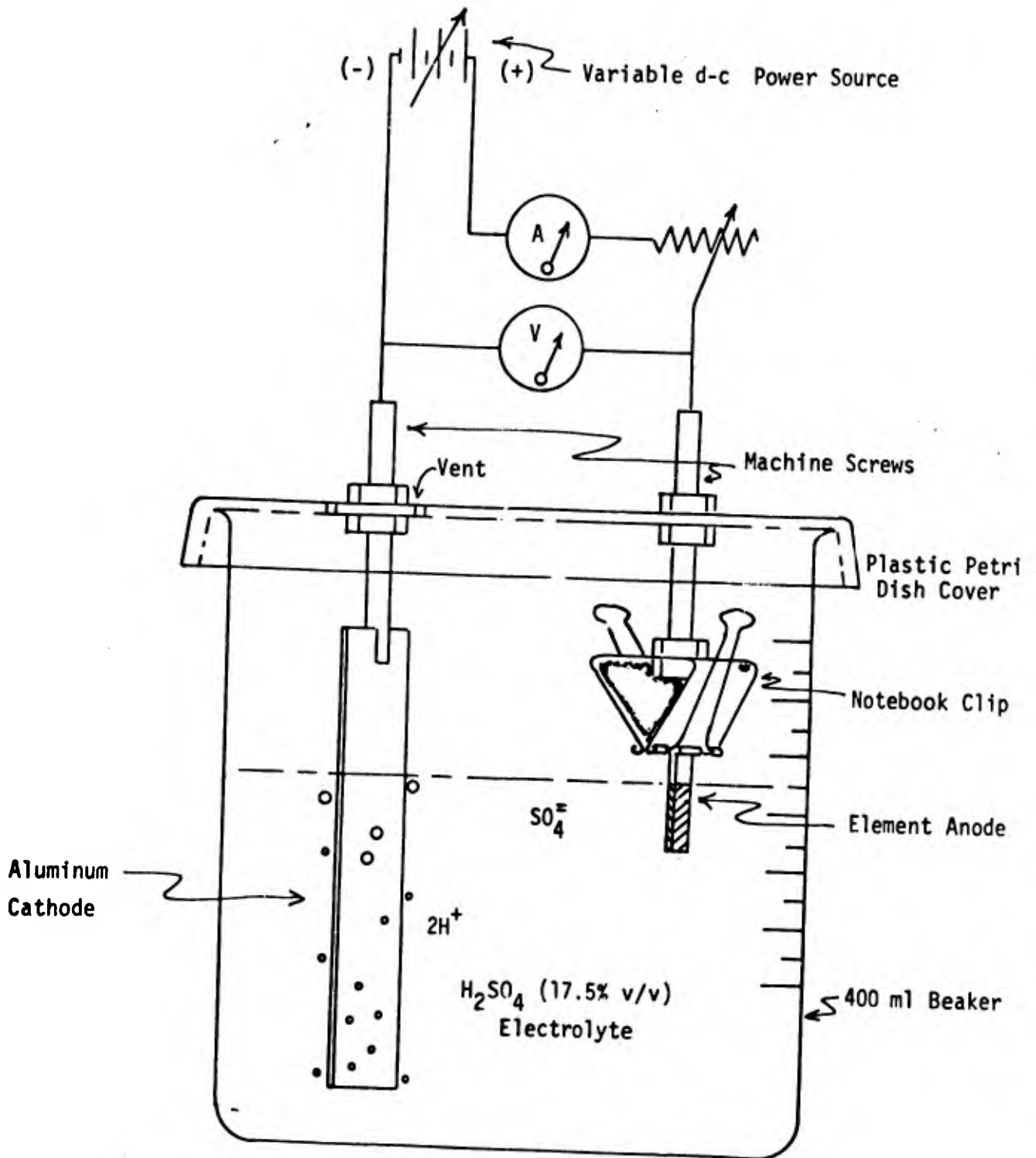
Direct current was obtained from an RCA-Regulator Power Supply WP - 23A, which converted the laboratory 115 volt, a-c power to an adjustable d-c power source. A milliammeter and a variable resistor were placed in series in the output circuit. The variable resistor, which had a full scale resistance of 86 ohms, was used to stabilize the current, since the d-c power supply was found to be more stable at higher voltages. A voltmeter was placed across the electrodes so as to measure the voltage across the anodic film. By the adjustment of the voltage from the d-c power source or the variable resistance (or both) the desired current density (50 ma/cm^2) could be obtained. As many as four elements could be anodized simultaneously, allowing greater element uniformity. It was found that the temperature of the electrolyte remained approximately constant at the room temperature of 25°C , throughout the anodization period.

Surface Neutralization:

Upon completion of the desired anodization period the elements were immediately rinsed under tap water and then allowed to soak in distilled

ANODIZATION APPARATUS

FIGURE 2



water for a two-hour period.

Although a number of basic solutions of varying concentration would appear to better neutralize the porous surface in which acid is entrapped, they were not used because of the uncertain effect which the salts from the neutralization reaction would have on the final humidity sensing elements characteristics.

Outer Electrode:

The outer electrode, which is to be placed over a portion of the aluminum oxide layer (See Figure 1) may be a metal physically evaporated over the surface, silver conductive paint sprayed over the surface, a metallic element chemically plated onto the surface, or colloidal carbon (Aquadag) painted over the surface. Colloidal carbon is by far the easiest to apply. The elements may easily be dipped into a 4 to 1 (distilled water - Aquadag) colloidal carbon slurry, so as to produce an outer electrode having the desired surface area (1.0 cm^2) and allowed to dry (See Figure 1).

Element Calibration Apparatus and Procedure:

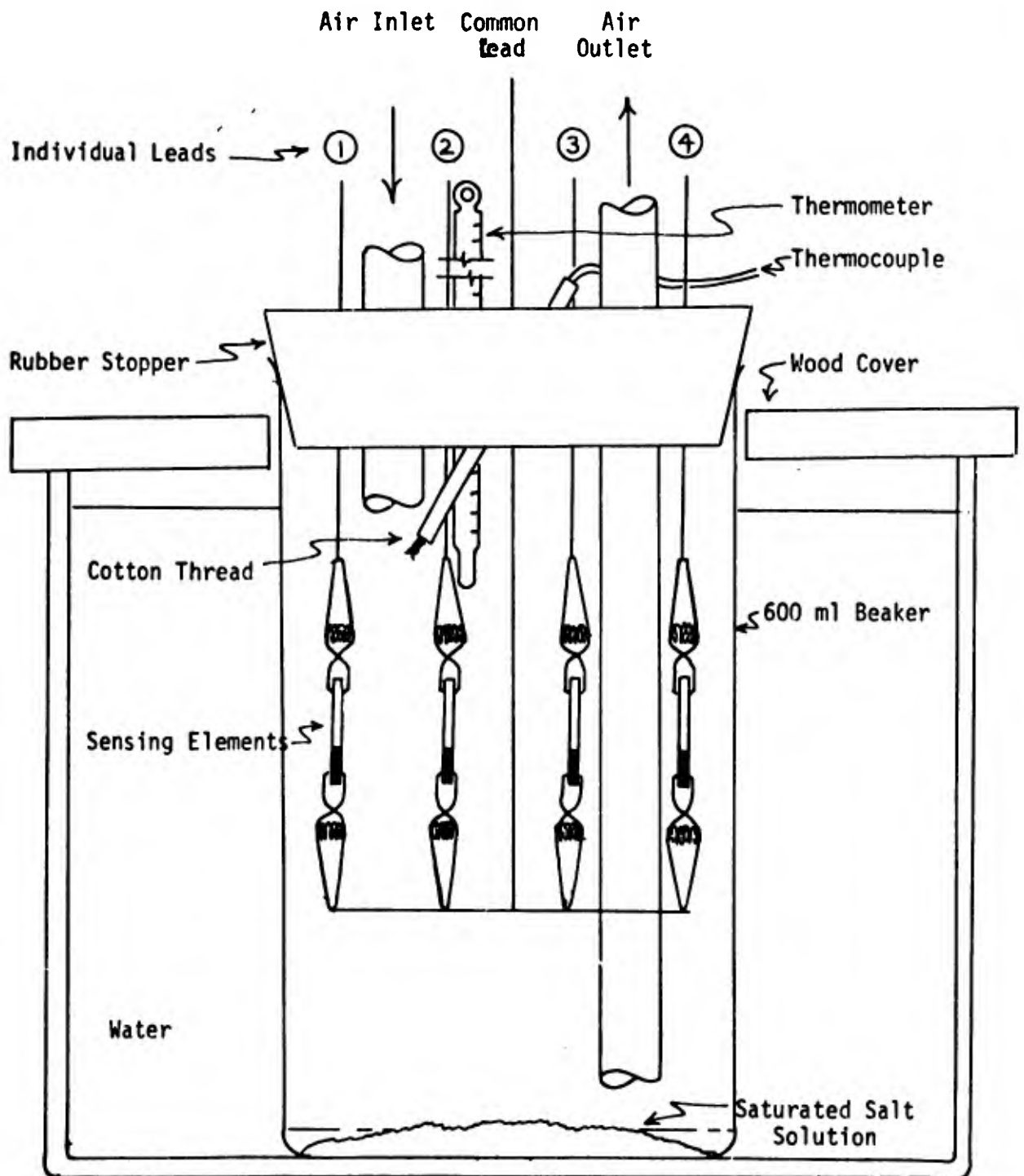
The element calibrating apparatus was built to allow individual calibration of four elements simultaneously (See Figure 3).

A 600 milliliter pyrex beaker was placed into a 6-inch diameter pyrex container. The space between the container and the beaker was filled with water at 25°C and a wooden cover placed over it. At the bottom of the beaker is placed a saturated salt solution. A rubber stopper which could be secured into the top of the beaker had the following inserted items:

- (a) an air inlet tube.
- (b) an air outlet tube.
- (c) a mercury thermometer.
- (d) a 3 millimeter diameter aluminum tube, inserted at an angle so as to have one end below the air inlet tube.
- (e) a common lead connected to four

ELEMENT CALIBRATING APPARATUS

FIGURE 3



Mueller clips (# 45c). (f) four individual leads all connected to Mueller clips.

The air inlet and outlet tubes were attached to an air circulating pump by two short sections of rubber tubing. Upon operation of the air circulating pump, air was drawn in from above the saturated salt solution and returned at the top of the beaker. The total volume of the system is estimated to be 700 milliliters.

Inserted into the 3 millimeter diameter aluminum tube was a copper-constantan thermocouple, the junction of which was wrapped with cotton thread. A reference junction was held in a thermos bottle containing crushed ice and water. The thermos bottle was covered by a cork stopper which contained the reference junction lead and a mercury thermometer. A Leeds and Northrup potentiometer (#238513) was used to measure the EMF produced by the temperature difference between the main junction and the reference junction. By the use of a standard conversion chart the EMF could easily be converted to the dry temperature at the main thermocouple junction. The main junction could be removed from the aluminum tube and the cotton thread covering it soaked in distilled water. By replacing the now wet main junction to just below the air inlet tube, with the air circulating pump running, the EMF which the potentiometer now indicated could be converted to the (so called) wet-bulb temperature. From the dry temperature and the wet-bulb depression, the percent relative humidity in the beaker could be obtained.

Four humidity sensing elements could be placed between the common lead and each of the individual leads by the use of the Mueller clips. The individual leads were clipped to the elements inner conductor (aluminum alloy 3003) and the common lead to the elements outer conductor (colloidal carbon). The Mueller clips contained teeth and covered very little of the

outer conductor surface. The tension on the Mueller clips was also greatly reduced so as not to damage the outer conductor.

After clipping the elements in place, the proper salt solution which will yield the desired percent relative humidity is placed in the bottom of the beaker and the rubber stopper (with inserts) secured to the beaker top. (If dry salt is first added to the bottom of the beaker followed by distilled water, time should be allowed for the heat of solution to dissipate.) Table I may be used in the selection of the proper salt. Due to the inadequate construction of the system the salt solution equilibrium relative humidity is seldom obtainable. Lithium chloride and potassium sulfate saturated salt solution yield values of 25 and 98 percent relative humidity respectively, after about a half hour waiting period (note that room relative humidity is approximately 63%). The air circulating pump is kept running continually.

At the end of the half hour waiting period the resistance through each element is measured and recorded by the use of a Keithley d.c. Electrometer, Model 610A. The temperature at the main thermocouple junction is also obtained and recorded. The main thermocouple junction is then removed, immersed in distilled water and replaced. The wet-bulb temperature at the main thermocouple junction is now recorded. From the available data, the relative humidity and one calibration point at that particular relative humidity for all four elements is obtained. The salt solution is then replaced by one yielding a different relative humidity and a second calibration point obtained for each element. Further points will yield the desired calibration curve for all four elements.

The thermometer, in the beaker, is used to verify that the temperature at the main thermocouple junction is the same as the air temperature, thereby indicating that the main thermocouple junction is dry.

TABLE IEQUILIBRIUM RELATIVE HUMIDITIES
FOR SATURATED SALT SOLUTIONS

<u>Saturated Salt Solution</u>	<u>Percent Relative Humidity at 25°C</u>
Lithium Chloride	12.0
Potassium Acetate	22.7
Magnesium Chloride	33.2
Potassium Carbonate	43.8
Potassium Nitrite	48.1
Magnesium Nitrate	53.4
Sodium Nitrite	64.3
Sodium Chloride	75.8
Ammonium Sulfate	80.3
Potassium Nitrate	92.0
Potassium Sulfate	96.9

The water bath surrounding the beaker was used to reduce the air temperature rise to a negligible value. The temperature rise was due to the energy imparted to the air by the air circulating pump. The bath may also be used to vary the temperature of calibration and thereby determine temperature coefficients (if detectable).

DETERMINATION OF ANODIC ALUMINUM PHYSICAL CHARACTERISTICS

Ten, 2 x 3 centimeter rectangular samples of 0.0325 inch thick sheet aluminum (AAA 3003) were cleaned and approximately 4 square centimeters of surface area of each anodized. The samples were anodized in sets having the following anodization time periods: 20, 30, 45, 60 and 120 minutes. The samples were next dried in an oven at 140°C and the weight and thickness of each recorded. Weight measurements were obtained using a Mettler balance having a precision of ± 0.0001 grams. Thickness measurements were obtained using a Lufkin micrometer caliper having a precision of ± 0.0002 inches. Upon removal by mechanical abrasion of 2 square centimeters of anodic surface from each sample, the samples were once again placed in the 140°C oven. On removal from the oven, the weight and thickness of each sample was once again recorded. The difference in sample weight divided by the difference in the sample thickness (in centimeters) yielded the density of the anodized aluminum surface of each sample. One-half of the difference in weight and thickness yielded the weight per square centimeter of surface area and the thickness of the anodized aluminum layer respectively.

ELECTRON MICROGRAPHS

Electron micrographs of both the polished aluminum surface and the anodized aluminum surface were obtained. The anodized surface was produced using a sulfuric acid electrolyte (17.5% v/v) over a 30-minute period at a current density of 50 ma/cm².

Using a medicine dropper, a solution of 2% parlodian in sec-butyl acetate was placed on the sample surfaces and allowed to dry. A 200-mesh nickel grid was placed on the dry parlodian and transparent Scotch tape placed over it. Upon removal of the tape from the aluminum samples, a parlodian replica of the aluminum surface was fixed to the grids. The grids were then removed from the tape and placed on a glass slide.

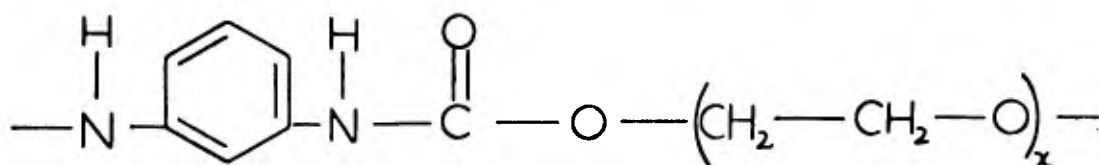
Due to the high porosity of the anodized aluminum surface, the parlodian film became so firmly attached that it could not be removed with Scotch tape. A small drop of concentrated Plymouth Rock Gelatine solution was placed over the parlodian and allowed to dry. When dry, the now hard gelatine drops were removed from the anodized aluminum surface. It was found that part of the anodized aluminum surface as well as the parlodian film had been removed with the gelatine drops. The gelatine was removed from the parlodian-anodized aluminum film by floating the gelatine drops in a 60°F water bath, replica side down. When all the gelatine was dissolved, the parlodian-anodized aluminum films were removed from the bath by placing a grid under the individual films and raising slowly. Upon drying the parlodian-anodized aluminum films were also placed on glass slides.

All the grids, including the ones containing a replica of the polished aluminum surface, were shadowed with a fine film of Chromium in a Kinney High Vacuum Evaporator, Model KSE-2. The angle of shadowing was 18.43 degrees such that a 4 millimeter long shadow on the final electron micrographs would be produced by a 1 millimeter high surface projection.

The electron micrographs were taken using a Phillips Electron Microscope, Model EM-200 and 35 millimeter film.

PRODUCTION OF POLYMEROUS ELEMENTS

In the hope of possibly replacing the anodized aluminum film described earlier by a hydroscopic polymerous film, a linear polyether-urethane film was coated over the aluminum samples (See Figure 1). Polyether-urethanes are suspected of being hydroscopic due to physically adsorbed water vapor. The following general structure linear polyether-urethane was used:



The coating was produced by dipping the elements into the linear polyether-urethane riding in a tetrahydrofuran vehicle and allowing them to dry. The film thickness could be varied by varying the concentration of the dipping solution.

The outer electrode was sprayed silver conductive paint (E-KOTE 40), since colloidal carbon would not adhere to the urethane surface.

RESULTS

A number of electron micrographs of both the buffed aluminum alloy (AAA 3003) surface and the anodized aluminum surface were obtained. The condition of anodizing were those given in the procedure and the anodization time was 30 minutes. Six plates which appeared to best represent the surface structure of both the buffed aluminum alloy and the anodic film were chosen. Plates 1 through 3 show the buffed aluminum surface structure and plates 4 through 6 show the structure of the anodic aluminum oxide film.

Figure 4 shows the anodizing voltage versus time over the initial 10 minutes of anodizing. The current density was held constant at 50 milliamps per square centimeter and the electrolytic bath conditions were those given in the procedure. The results show the average values of three runs, each of which were anodizing 2 square centimeters of surface area.

Figures 5, 6 and 7, show the film thickness, weight per square centimeter, and the density respectively versus anodizing time. Each data point represents the average of two runs. The density values (Figure 7) were calculated from the experimental values of the film thickness and weight per square centimeter. The anodizing condition as well as the experimental technique used is fully described in the procedure.

Figure 8 shows the absorption spectra of the anodic aluminum oxide film. The anodic aluminum oxide was scraped from samples anodized under the conditions given in the procedure. The vehicle used was Nujol mineral oil and the sample was contained between sodium chloride lenses. The anodic oxide scrapings were dried in an oven at 140°C before mixing with Nujol, so as to remove free or physically adsorbed water.

Figure 9 shows the rapid initial element aging. The time axis represents the time after anodizing was completed. The newly anodized surface was washed in distilled water and dried during the first 100 minutes after anodizing. The outer conductive coating (Aquadag) was then applied and allowed to completely dry before the first data recorded (at 120 minutes).

Figure 10 shows the initial first day element calibration curve and the 7th day calibration curve of the same element after being stored at approximately 62% relative humidity and 25° Centigrade.

Figure 11 shows the effect of the storage environment on the calibration drift of three elements. All three elements were produced simultaneously and showed the same initial (1st day) calibration. One element was stored for 17 days under each of the following environmental conditions: 1) 97% relative humidity (25°C), 2) vacuum and 3) 600 degrees Centigrade. At the end of the 17-day period all elements were immediately recalibrated.

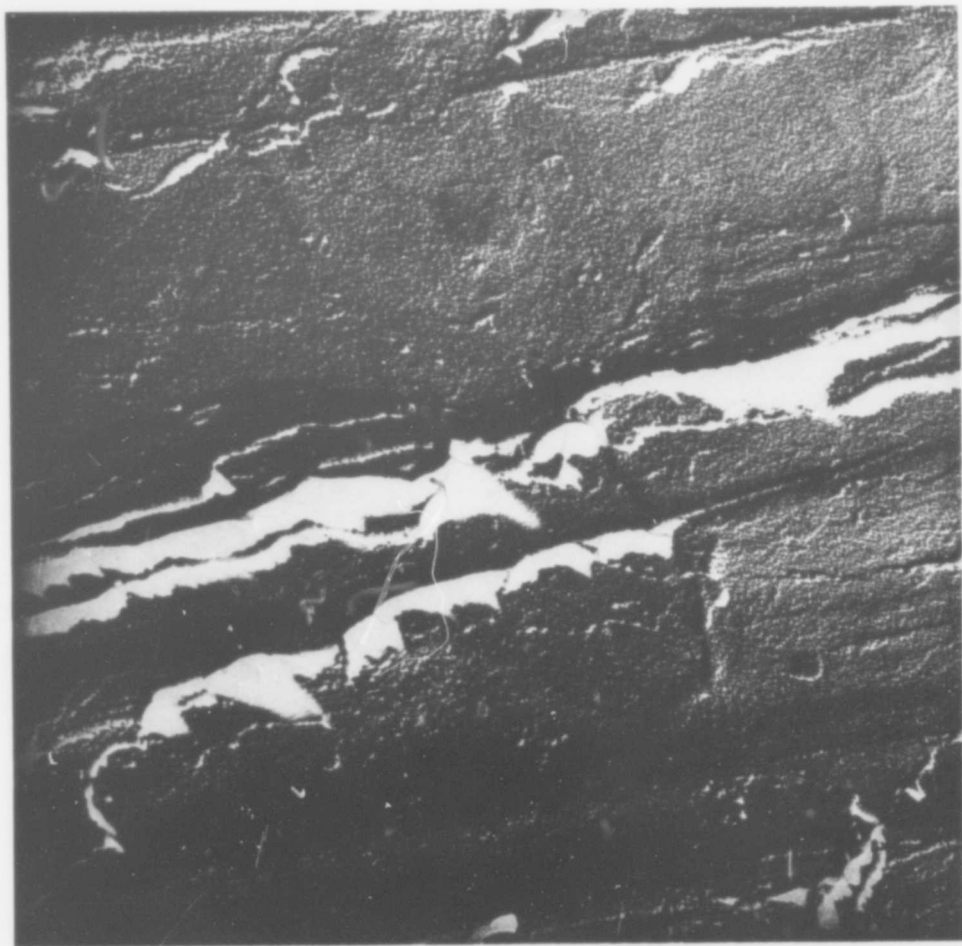
PLATE 1

BUFFED ALUMINUM SURFACE



1 millimeter = 510 \AA

PLATE 2
BUFFED ALUMINUM SURFACE



1 millimeter = 180 \AA

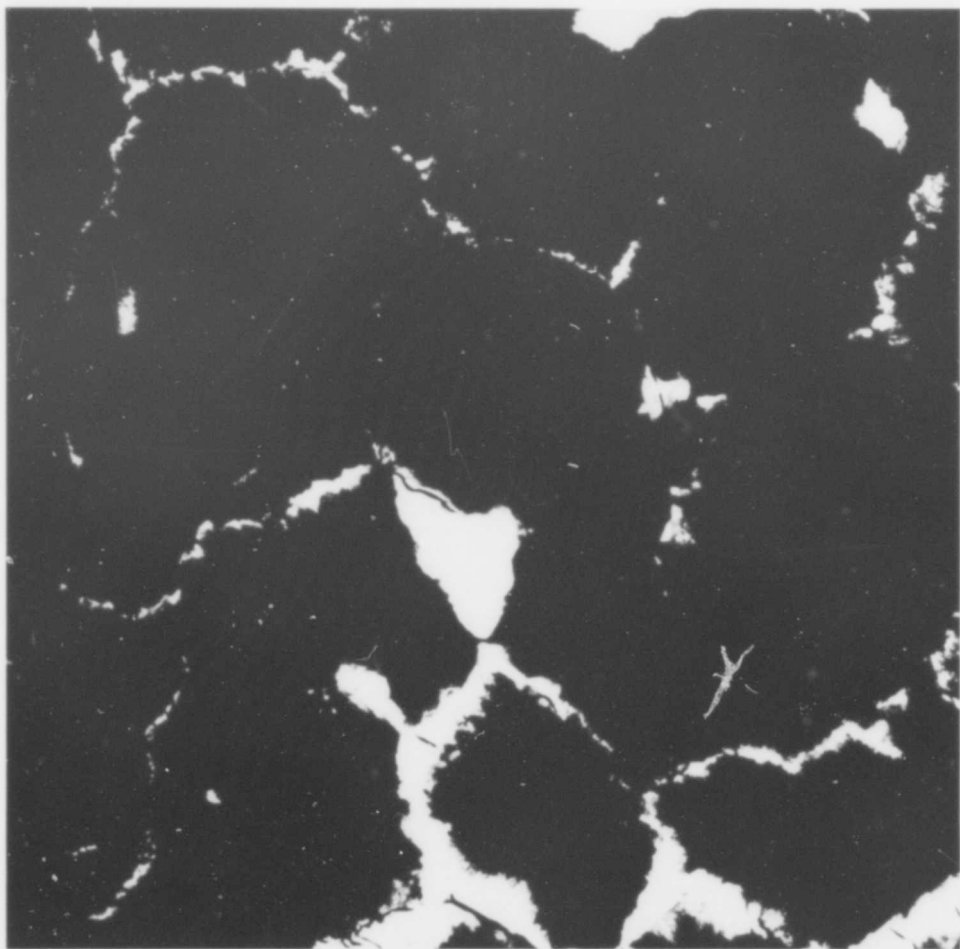
PLATE 3

BUFFED ALUMINUM SURFACE



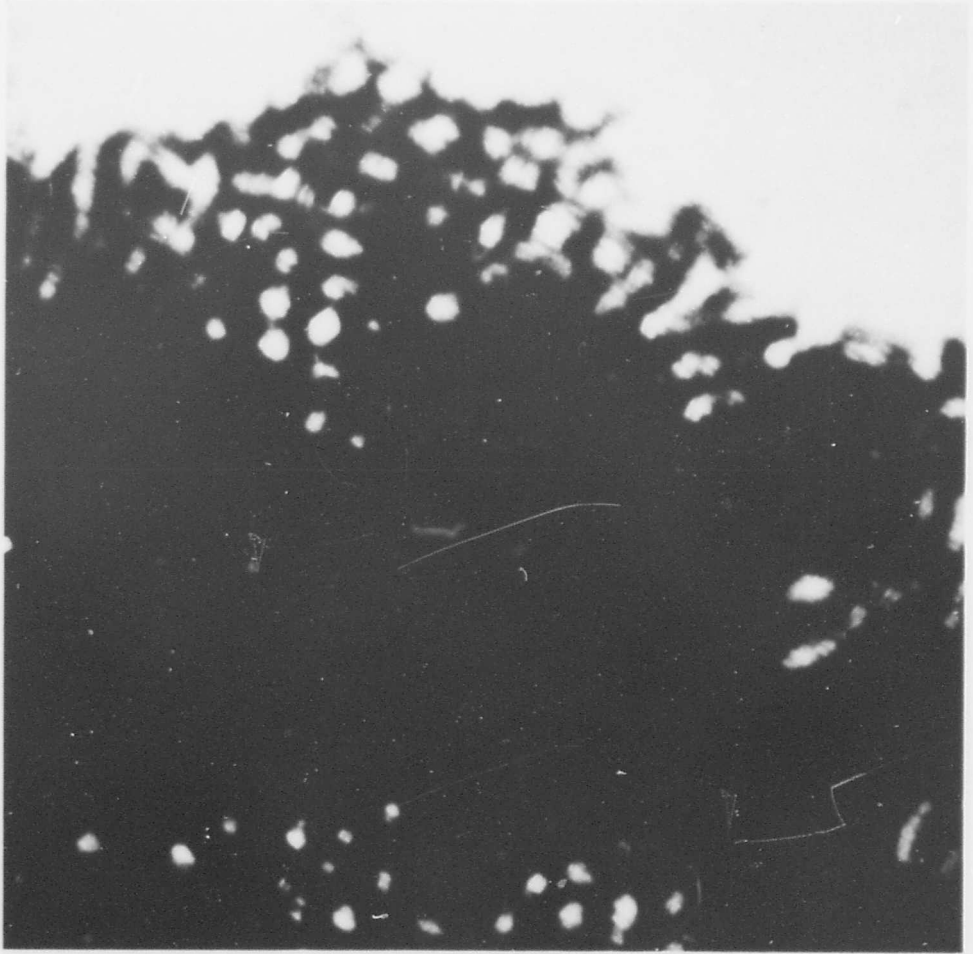
1 millimeter = 58 A^o

PLATE 4
ANODIZED ALUMINUM SURFACE



1 millimeter = 940 \AA

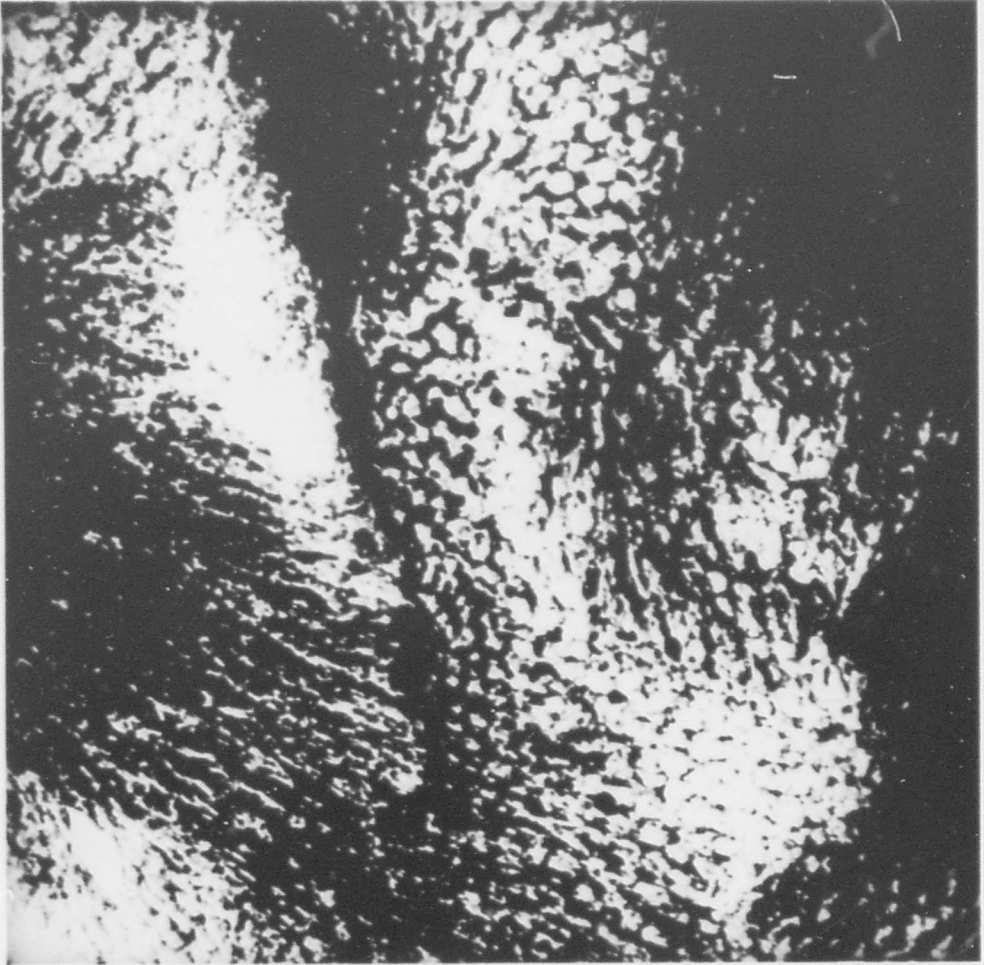
PLATE 5
ANODIZED ALUMINUM SURFACE



1 millimeter = 36 A°

PLATE 6

ANODIZED ALUMINUM SURFACE



1 millimeter = 22 μ

V O L T A G E

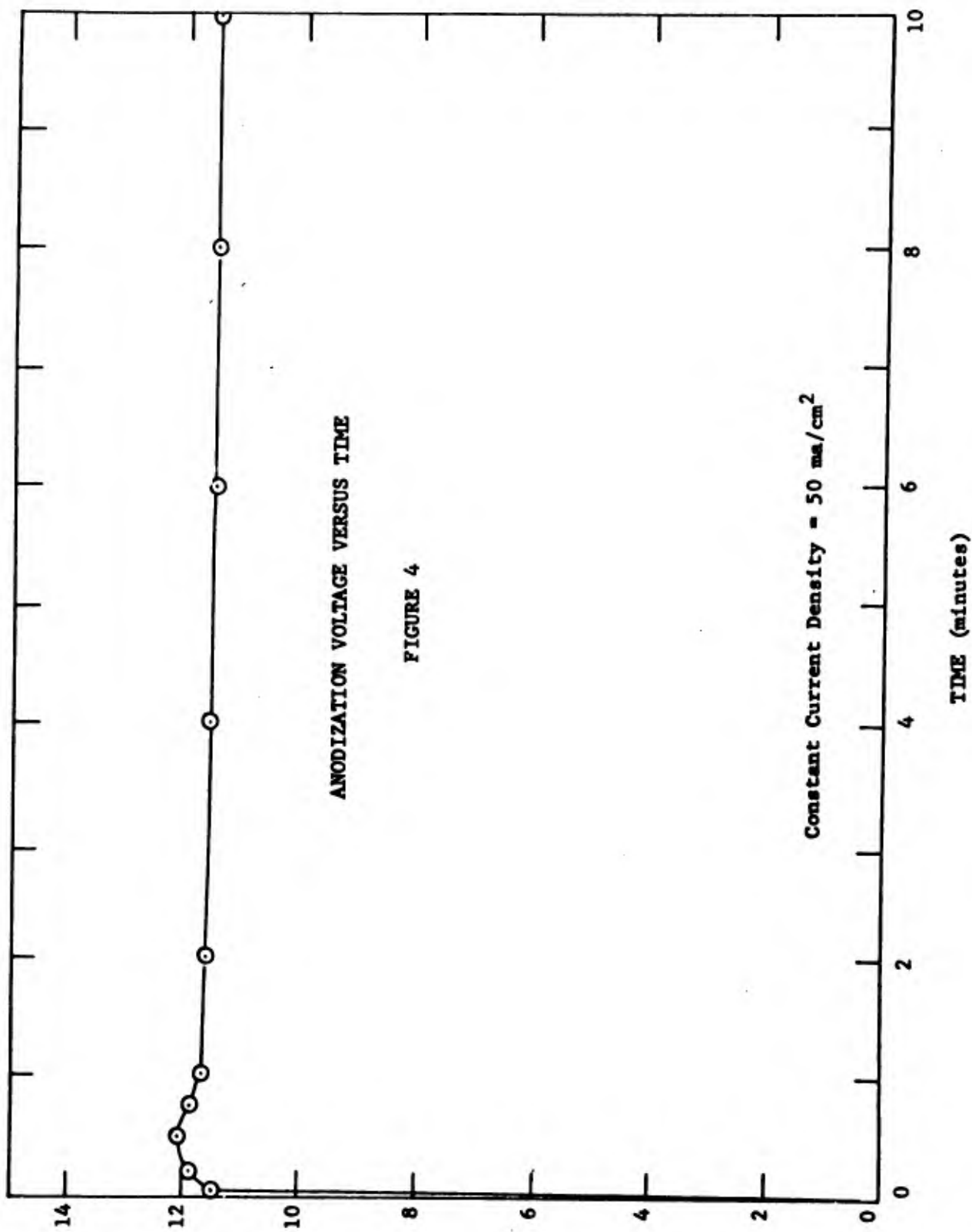
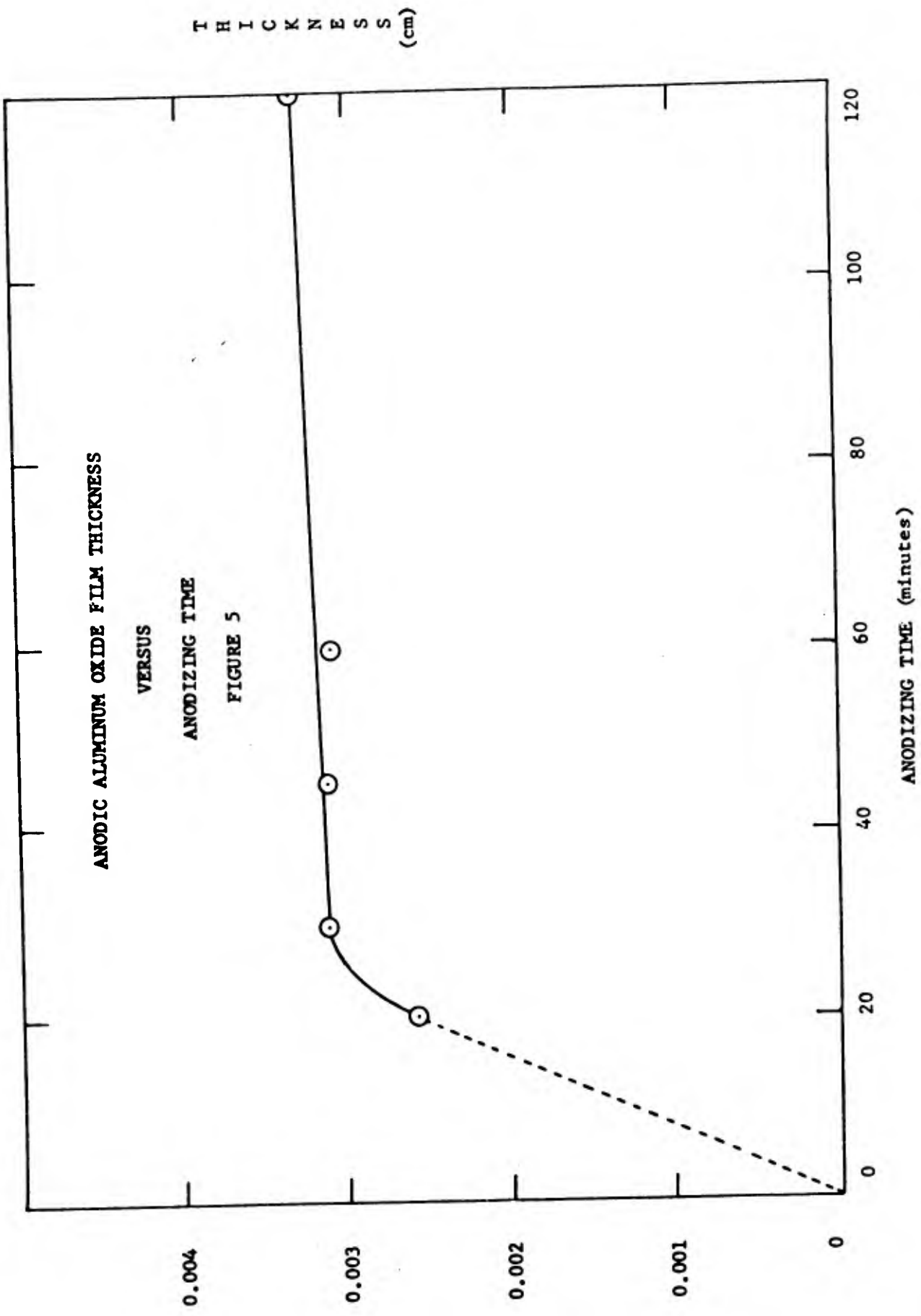
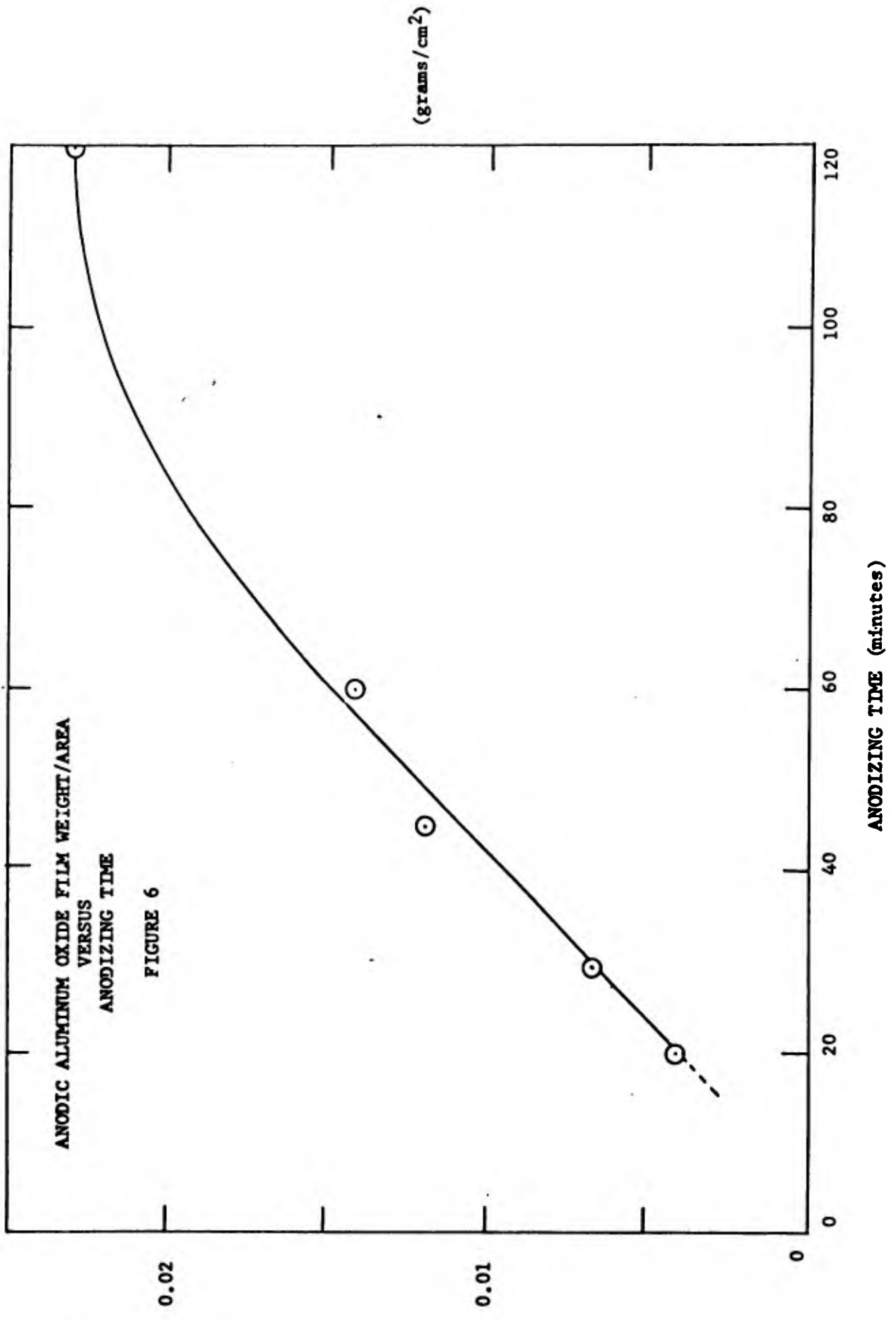
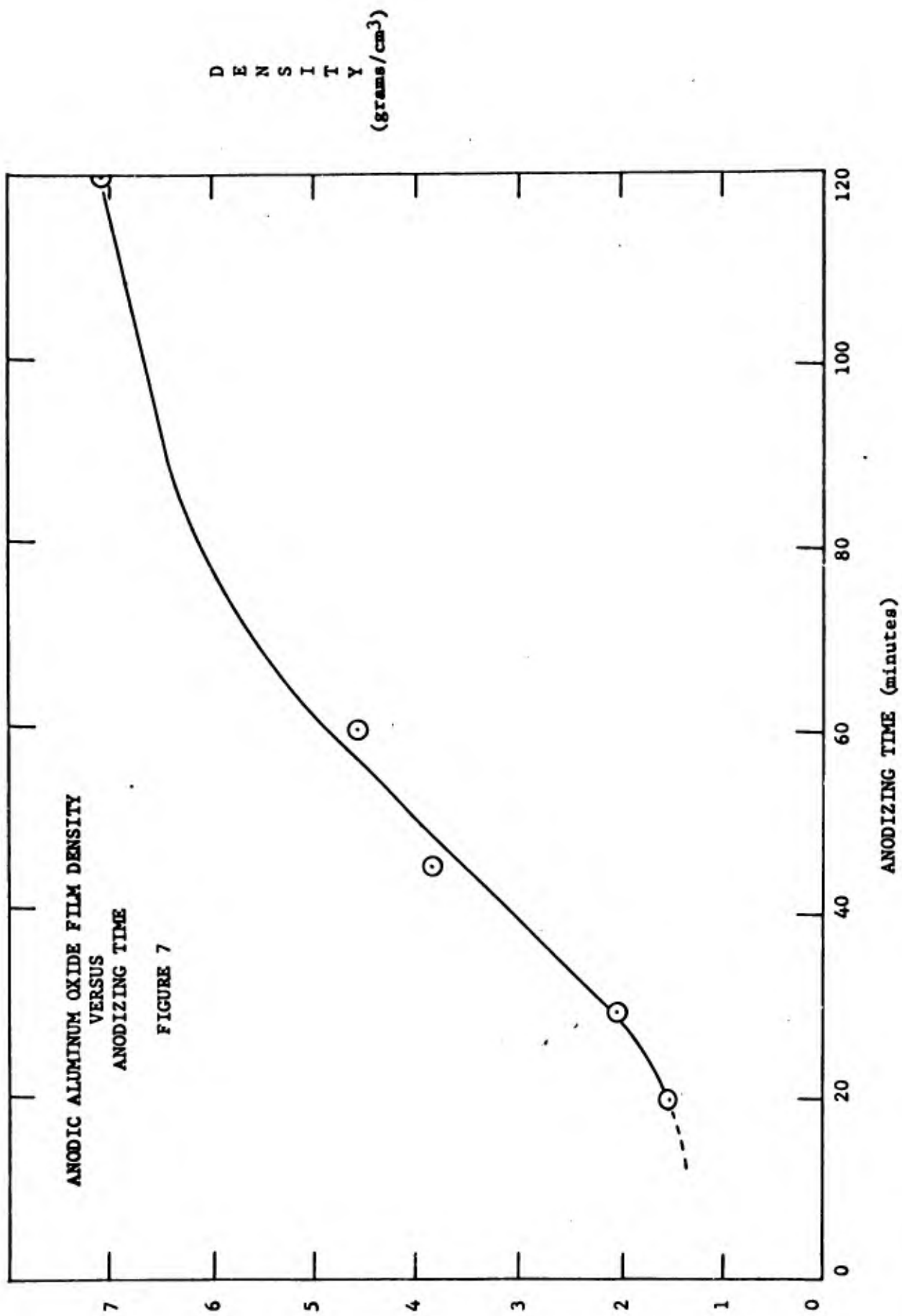
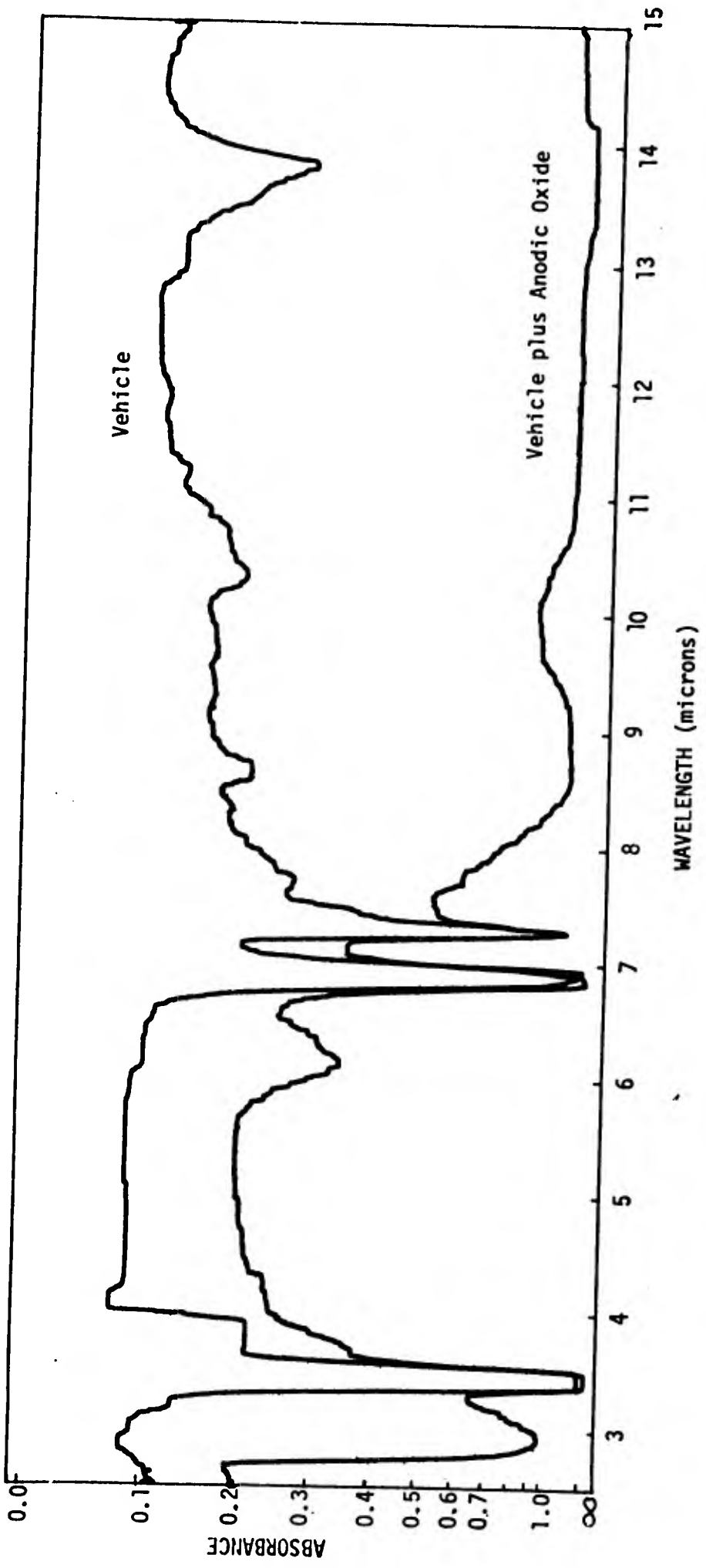


FIGURE 4





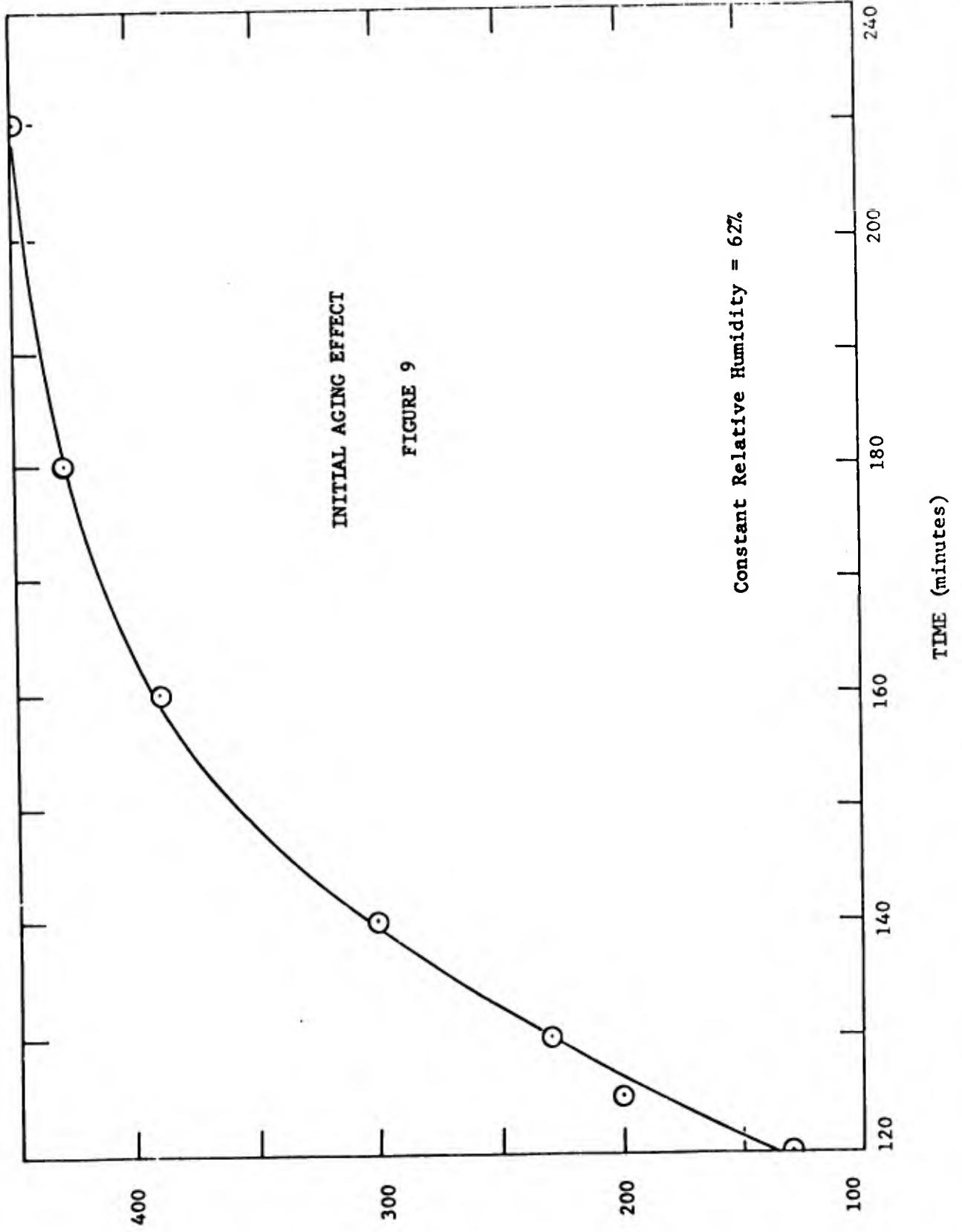




ANODIC ALUMINUM OXIDE INFRARED SPECTRA

FIGURE 8

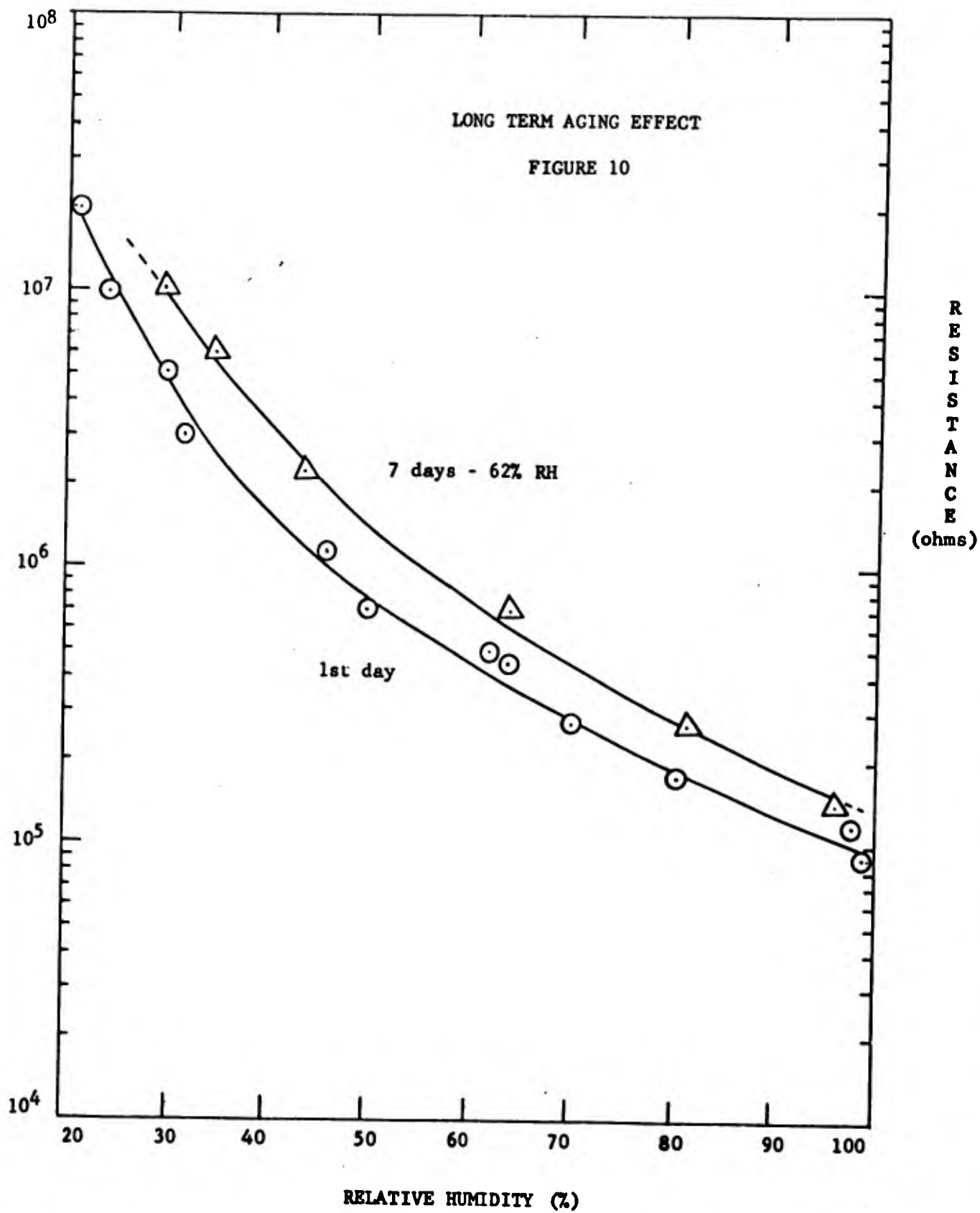
RESISTANCE
(ohms x 10⁻³)

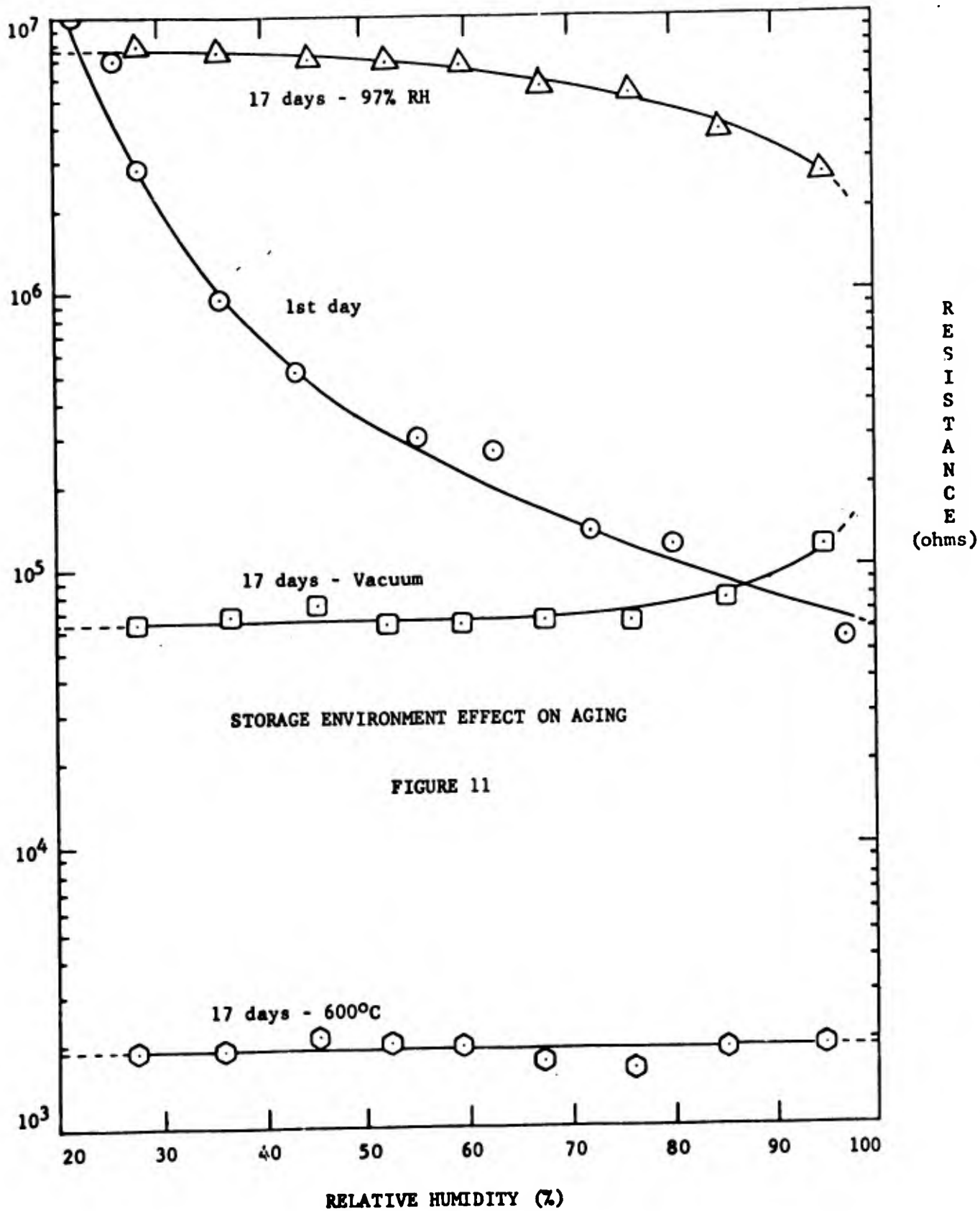


INITIAL AGING EFFECT

FIGURE 9

Constant Relative Humidity = 62%





DISCUSSION OF RESULTS

The first portion of the results (Plates 1-6 and Figures 4-8) is concerned with the physical structure and composition of the anodic aluminum oxide film. Plate 1 shows a 19,050X magnification of the buffed aluminum surface. The ridges which run across the page are due to the cutting effect of the buffing wheel. Plates 2 and 3 are 55,800X and 166,200X magnification respectively. Since the shadow projection is 4 times the surface projection (See Electron Micrograph Procedure) it may be concluded that the ridges are generally less than $5,000 \text{ \AA}$ in height. On Plate 3 the metallic crystals may be seen.

Plate 4 (11,375X) shows the anodic aluminum oxide crystal structure. The structure is roughly hexagonal, as shown by others (16), and the approximate diameter of the hexagonal crystals is $50,000 \text{ \AA}$. The film thickness, after a 30 minute anodizing period, is approximately 1 mil or $254,000 \text{ \AA}$. If the crystals extend to the aluminum alloy surface, their length will be approximately five times their hexagonal diameter. Plate 5 (274,300X) shows the hexagonally spaced pores which are present in the crystal structure (See Figure 15). The diameter of the pores is approximately 180 \AA . Plate 6 (456,750X) appears to show a torn portion of the anodic aluminum oxide film, which reveals hexagonally shaped pores approximately 100 \AA in diameter.

The electron micrographs of the anodic film do show the approximate pore dimensions and spacing reported by Jason (7), although Jason does not mention that this pore structure is the make-up of a roughly

hexagonal crystal structure.

Figure 4 shows that either the current density or the voltage may be fixed during the anodization process. At a fixed current density of 50 milliamps per square centimeter the EMF across the film rapidly approaches 11.5 volts. The curve may be examined in the following two sections: 1) the initial transient approach to 11.5 volts (0 to 2 seconds) and, 2) the relatively constant voltage (2 seconds to 10 minutes). During the initial two seconds of anodizing the film's resistance increased from 0 to 230 ohms and during the remaining section of the curve, it remained relatively constant (at approximately 230 ohms). It appears that the initial transient section of the curve may be responsible for the formation of the so called "non-porous layer" at the aluminum surface (See Figure 14,b), which has been described by Jason (7). During the remaining section of the curve the relatively constant resistance indicates that the pores being formed are filled with the conductive electrolyte and that further film formation does not increase the resistance. It should be noted that the electrical resistance produced by the anodic film began to increase again at approximately 20 minutes. From Figure 7 it may be seen that the film's density begins to increase rapidly at this point which may indicate that the pores are now being filled, causing the increase in resistance.

One portion of the above discussion does not appear plausible. Oxygen ions must migrate to the aluminum surface before they can oxidize the aluminum base to form anodic aluminum oxide. If the so called "non-porous layer" is initially produced, how do the oxygen ions migrate through such a non-porous layer? One possible answer may be that

this initial layer is actually a frothing layer of fine aluminum oxide particles, being agitated by the migration of ions. At this point it may be said that the correct answer to the above question and also to the question as to why a hexagonally spaced pore structure is formed at all would greatly help in the understanding of the film's physical structure.

Figure 5 shows that the rate of film growth (thickness) is greatly reduced between 20 and 30 minutes. Since the current density was held constant, the weight of film formed per unit time remains constant (see Figure 6). This indicates that the density of the film begins to rapidly increase between 20 and 30 minutes. This increase in density must cause a decrease in film porosity. This sequence of thickness changes in the sample, of a slight increase with time for 20 to 30 minutes, followed by rapidly decreasing sample width, has been observed by others. See Anderson (19) and Jenny (20). Since a high porosity film having a large surface area for physical adsorption of water vapor is desired, it would be recommended that elements not be anodized for more than 30 minutes (using the anodizing conditions described in the procedure). It may be noted that Figure 6, which is initially linear (due to constant current density), does not extrapolate to zero weight at zero time. The reason for this may be attributed to the initial loss of molecular diatomic oxygen.

The infrared spectra of anodic aluminum oxide (Figure 8) shows strong absorption bands from 2.8 to 4.0 microns and from 7.5 to 15.0 microns. The literature (10) shows that alpha and beta monohydrate phases, alpha and beta trihydrate phases as well as the anhydrous alpha phase show absorption peaks throughout the above regions. Since the infrared analysis is not quantitative, all that may be stated is that the anodic aluminum oxide appears to be a mixture of possibly all five of the above phases.

It should be mentioned that the term hydrate has been labeled as incorrect by an international symposium on alumina held in West Germany in 1957. The term hydrate is to be replaced by the term hydroxide. This distinction in nomenclature is intended to make clear the fact that water molecules are chemically attached to the Al_2O_3 structure and not physically adsorbed. Due to the many years of usage and the present use by most commercial suppliers of alumina, the term hydrate was used in this study, with the understanding that it refers to chemisorbed water molecules and not to physically adsorbed water molecules.

The second portion of the results (Figures 9-11) is concerned with the observed element calibration drift and its possible cause. Figure 9 shows the initial calibration drift of a newly-produced element at a constant relative humidity of 62%. It is noted that the rate of drift rapidly decreases and that it is in the direction of increasing resistance. After recording the data present on Figure 9, the same element was fully calibrated. The results of this first day calibration are shown on Figure 10. The element was then stored at approximately 62% relative humidity ($25^{\circ}C$) for seven days and then recalibrated. The results of the seventh day calibration are also shown on Figure 10. It may be noted that although the rate of calibration drift has decelerated, it is still significant enough to hinder the elements use without recalibration. As before (Figure 9), the direction of the calibration drift is towards an increase in resistance.

The fact that the calibration drift is in the direction of increasing resistance may at first lead to the possibility that a slow desorption is responsible. This would be the case if Knudsen diffusion of water vapor through a fine pore structure were occurring.

Other investigators (7) (4) have shown conclusively that the calibration drift becomes accelerated when the element is subjected to a high relative humidity (greater than 80%) over a prolonged period of time. If Knudsen diffusion of water vapor out of the element were responsible for this increase in resistance, the calibration drift should be decelerated when the element is subjected to a high relative humidity over a prolonged period of time (See Appendix I). It therefore appears that Knudsen diffusion is either not present or that its presence is insignificant and is being overshadowed by some other mechanism responsible for the observed calibration drift.

Since it appears that Knudsen diffusion through a fine pore structure is not responsible for the observed calibration drift, a second possibility is that chemisorption of water vapor on the pore walls causes the chemical characteristics of the pore surfaces to change and therefore the amount of physically adsorbed water vapor on the pore walls to also change. As mentioned earlier, the various hydrated phases of alumina (See Table II) may be viewed as different species of chemisorbed water vapor. In an attempt to dehydrate the chemisorbed species on the pore walls, one element was stored for 17 days at 600°C after an initial first day calibration. A second element was stored for 17 days at a relative humidity of 97% (25°C) and a third element was stored in a vacuum. All three elements were produced simultaneously and showed the same initial calibration curve which is shown in Figure 11. At the end of the 17 days' storage period all three elements were immediately recalibrated. These results are also shown in Figure 11. It is first noted that all three elements showed a loss in sensitivity. The resistance of the element stored at

97% relative humidity increased and the resistance of the element stored at 600°C decreased. These results, once again, support the earlier conclusion that Knudsen diffusion is not the cause of the observed calibration drift (See Appendix I). If we consider that the pore walls became highly hydrated after being stored at 97% relative humidity and very slightly hydrated after being stored at 600°C, one could infer that the highly hydrated species causes a larger amount of physically adsorbed water vapor on the pore walls than the lesser hydrated species. This inference is plausible since the amount of physically adsorbed water vapor on the pore walls is mainly a function of the relative humidity and the chemical characteristics of the pore walls (See Appendix I). At this point a plausible explanation for the observed calibration drift may be given as follows: Upon storage of an anodic aluminum oxide element in a humid atmosphere the pore walls chemisorb water molecules (further hydrate), which causes the amount of physically adsorbed water vapor to decrease and the element resistance to increase. The decrease in resistance shown by the elements stored in a vacuum and at 600°C (See Figure 11) is therefore due to dechemisorption (dehydration) of water molecules and an increase in the amount of physically adsorbed water vapor on the pore walls. The fact that the resistance decrease was less for the element stored in a vacuum could have been predicted since the needed activation energy of dechemisorption (See Appendix I) is available at a sufficiently high temperature.

The fact that all three elements displayed a loss in sensitivity is at first discouraging. After more careful thought one may ask the following: If the element initially showed an excellent sensitivity

and that chemisorption or dechemisorption of one or more chemisorbed species was responsible for such a loss in sensitivity, can the desired chemisorbed species be maintained on the pore walls? The answer to this question is not known at this time. The results showing the presence of chemisorbed species (Figure 11) were obtained using only one element at each of the three environmental storage conditions and have not at this time been repeated. Since the results do offer a plausible explanation of the observed calibration drift, it appears that they warrant further exploration. It is also apparent that if some intermediate hydrated phase (chemisorbed species) is responsible for the initial element sensitivity that a search for an equilibrium storage condition at which this chemisorbed species is stable is also warranted.

No results are shown for polymeric film elements since their rate of response was found to be extremely slow. It is expected that Knudsen diffusion through many fine tortuous pores is responsible.

CONCLUSIONS

- A The film structure of anodic aluminum oxide formed in a sulfuric acid electrolyte is one of roughly hexagonal crystals having a diameter of approximately 50,000 Å. These crystals contain hexagonally spaced pores approximately 150 Å in diameter.
- B Since a high porosity film is desired, the anodization period should not be more than 30 minutes (other anodizing conditions as stated in the procedure), due to a large increase in film density at this time.
- C Knudsen diffusion through a fine pore structure does not appear to be the cause of the observed calibration drift shown by anodic aluminum oxide sensing elements.
- D Initial results have shown that a change in the concentration of various species of chemisorbed water vapor on the anodic aluminum oxide pore walls may be responsible for the observed calibration drift and that further experimentation in this area is warranted.
- E Polymerous elements have shown an extremely slow rate of response which hinders their use as a thin film humidity sensor.

RECOMMENDATIONS FOR FURTHER WORK

- A Improve the procedure and techniques for obtaining electron micrographs of various anodic films. It is hopeful that the electron microscope may be used as a tool for the comparison of film structures.
- B Compare the characteristics (film density, pore structure and electrical characteristics) of elements produced from pure aluminum with those produced using aluminum alloy 3003. It is expected that aluminum alloy 3003 yields a more porous structure.
- C Compare the characteristics of elements anodized using alternating current with those anodized using direct current.
- D Run a series of tests on the characteristics of various outer electrodes. It is expected that colloidal carbon may show increasing resistivity with time. The assumption that the diffusion rate through the outer electrode is not the rate limiting process controlling the rate of element response should be validated.
- E Repeat the test for anodic aluminum oxide phase changes. Produce and calibrate a number of elements and store them as follows: (1) at various values of atmospheric relative humidity (over saturated salt solutions at 25°C), (2) at varying temperatures (0 to 600°C), (3) in a vacuum. Recalibrate all elements at 5, 10, 30, and 60 days.

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APPENDIX I

ADSORPTION-DIFFUSION MODEL

It is helpful to consider a solid material having a macro-micro pore size distribution. Such a material consists of a fine pore structure (micropores) which surrounds a coarser pore structure (macropores).

Molecules from the gaseous media surrounding the solid may become adsorbed on both the macro and micro pore walls, as well as on the solids external surface. These solid surfaces show a change in surface conductivity when the relative humidity of the gaseous media surrounding them is varied. This change is attributed to the adsorption of water vapor molecules, although other types of molecules present in the gaseous media may also be adsorbed. Adsorption phenomena may be subdivided into physical adsorption and chemical adsorption, the latter being termed chemisorption. Physical adsorption is caused by secondary attractive forces (van der Waal's), such as dipole interaction. Chemisorption involves the transfer of electrons and is similar in character to chemical bonding. The extent to which physical or chemical adsorption of water vapor occurs upon a surface depends largely upon the adsorbents chemical composition.

Physical adsorption of water vapor will occur on all surfaces provided that the relative humidity is sufficiently high, yet chemisorption will occur only if the adsorbent is capable of forming a chemical bond with the water molecules. Although physical adsorbed water vapor can occur on all surfaces, at a sufficiently high relative humidity, the amount adsorbed is still a function of the physical characteristics as well as the chemical composition of the surface.

At relative humidity values of 0.01 or less the amount of physical adsorption is negligible. Multilayer physical adsorption begins at a relative humidity somewhere between 0.1 and 0.4 and complete condensation to bulk liquid occurs at a relative humidity of 1.0. Chemisorption has a maximum limit of a complete monolayer, yet on most chemisorbed surfaces only a fraction of a monolayer is adsorbed⁽¹¹⁾. It is also possible for physical and chemical adsorption to occur simultaneously, yet all adsorption beyond the first monolayer must be considered to be physically adsorbed.

Physical adsorption requires no activation energy and is always an exothermic process. It is also completely reversible with equilibrium being established rapidly. Repeated heating and cooling will cause desorption and adsorption respectively without altering the adsorbent's surface. Heats of physical adsorption are found to be of the same magnitude as the heats of condensation (1000 cal/gr-mole). Chemisorption, contrary to physical adsorption, is often found to exhibit an activation energy and can, in rare instances, be endothermic. The activation energy requirement causes the rate of chemisorption to be appreciable only above some minimum temperature. Unlike physical adsorption, chemisorption is often highly irreversible causing the equilibrium amount of chemisorbed molecules to seldom exist. The possibility of more than one type of chemisorption occurring simultaneously also exists. The heats of chemisorption are usually far greater than the heats of physical adsorption, being comparable to heats of chemical reaction (20,000 - 50,000 cal/gr-mole). The heat of chemisorption is a measure of the bond strength found between the adsorbent and the adsorbate (water vapor).

The existing problem is to experimentally determine the exact types of adsorption occurring. Temperature variation is the main method of

distinguishing between physical and chemical adsorption. The amount physically adsorbed always decreases with increasing temperature, whereas the amount chemisorbed may become appreciable only above a specific temperature. Experimentally measured surface conductivity is expected to be altered by chemisorption as well as physical adsorption. Chemisorption may also alter the amount of physical adsorption since it must comprise a portion of the first monolayer. Therefore in cases where both chemisorption and physical adsorption occur simultaneously, the surface conductivity becomes a complex function of the types and amounts of adsorbed species. Infra-red methods may be useful in determining the exact structure of the different types of chemisorbed species, yet generally the small number of chemisorbed molecules in comparison to the large number of molecules upon which chemisorption has not occurred often causes extreme difficulties. The problem of exact adsorption identification is a complex one and only in extreme cases, where one type of adsorption greatly predominates, is the experimental analysis highly reliable.

Thus far the discussion has not considered pore diffusion in a macro-micro porous material. Consider the following transient situation: the relative humidity of the gaseous media in which the material is immersed is suddenly decreased. Water vapor immediately begins to diffuse out of all pores. Each of the following three modes of pore diffusion may exist⁽¹²⁾: ordinary diffusion, Knudsen diffusion and surface diffusion.

Ordinary diffusion and Knudsen diffusion result from a water vapor concentration gradient. Ordinary pore diffusion occurs in relatively large pores, which are filled with a dense gas phase (or liquid), while Knudsen diffusion is found to occur in fine pores or in larger pores having an extremely low total gas density. The distinction between ordinary and Knudsen pore diffusion is that molecules experiencing ordinary pore diffusion, being in a dense phase and relatively remote from any solid sur-

faces, largely collide with each other while molecules experiencing Knudsen diffusion, being in a rare phase and relatively closer to the pores surfaces than other gas phase molecules, largely collide with the walls of the pores and are momentarily adsorbed and then given off in random directions. In both ordinary and Knudsen diffusion the molal flux (N) of water vapor in a gaseous media relative to a fixed point in space can be described at any specific pore location by the following relation:

$$N = -D_p \frac{dC}{dx}$$

Where: N = molal water vapor flux (gr-moles/sec-cm²)
 D_p = water vapor pore diffusion coefficient (cm²/sec)
 C = water vapor concentration (gr-moles/cm³)
 x = distance in diffusion direction (cm)

It is evident from the above relation that the molal flux at any given concentration gradient is dependent on the water vapor pore diffusion coefficient (D_p). The pore diffusion coefficient must therefore take into account (be a function of) the particular pore geometry under consideration. The literature contains a large amount of experimentally obtained diffusion coefficients (D_{12}), which represent the relative diffusion of vapor 1 in a specific gaseous medium 2, remote from any solid surfaces. Theoretical relations yielding values of D_{12} become very complex when the second gaseous constituent is not a single component, but a homogenous mixture such as air, and seldom do the predicted and experimental values show good agreement. It becomes useful, when ordinary pore diffusion is occurring, to make the pore diffusion coefficient (D_p) a function of the experimentally determined diffusion coefficient (D_{12}), which is valid when solid surfaces are not present, and of two geometrical

variables. The following relation may be used:

$$D_p = \frac{D_{wa} \Theta}{\gamma}$$

Where: D_{wa} = diffusion coefficient of water vapor in air (cm²/sec)
 Θ = void volume fraction (cm³/cm³)
 γ = tortuosity factor (unitless)

The experimental value of D_{wa} is reported as 0.260 cm²/sec at a temperature of 25°C and a pressure of one atmosphere (12). The void volume fraction (Θ) of a porous material can vary from a value of zero, in a completely non-porous solid in which no diffusion occurs, to a value of one, where no solid surfaces exist ($D_p = D_{wa}$). The tortuosity factor (γ) is used to correct for changes in pore direction and varying pore cross section and range from one, for cylindrical pores at right angles to the solids external surface, to infinity, for pores so tortuous that the molal flux through them is zero.

In cases where Knudsen diffusion occurs the following relation gives the water vapor pore diffusion coefficient (D_p).

$$D_p = \frac{D_k \Theta}{\gamma}$$

Where: D_k = Knudsen diffusion coefficient of water vapor (cm²/sec)

The following relation may be used to determine the value of Knudsen diffusion coefficient (D_k) in cylindrical pores:

$$D_k = 9700 \cdot r \cdot \sqrt{T/M}$$

Where r = equivalent pore radius (cm)

T = temperature (degrees Kelvin)

M = molecular weight of water vapor (18)

It is noted that D_k is a function of a single component, water vapor, since molecular collisions (between water vapor and dry air) are considered to be negligible.

In the case of a macro-micro pore distribution both ordinary and Knudsen pore diffusion may be occurring in the macropores and micropores respectively. In this case the existing problem is to experimentally determine which of the two modes of pore diffusion is controlling the total diffusion of water vapor in the porous material. Theoretical relations predict that ordinary pore diffusion is inversely proportional to the total pressure and varies to the $3/2$ power with absolute temperature, whereas Knudsen diffusion is independent of the total gas pressure and varies to the $1/2$ power with absolute temperature. If either the temperature or pressure is varied experimentally, the controlling mode of diffusion may be determined.

In cases where a single pore size distribution exists and either ordinary or Knudsen pore diffusion is present, a variation in either temperature or pressure may also be used to determine which mode is present. A more complex situation exists when a single pore size distribution falls in the transition region between ordinary and Knudsen pore diffusion. By variation of the pressure the transition pore diffusion may be changed to ordinary or Knudsen pore diffusion thereby indicating the existence of the transition pore diffusion.

The third mode of pore diffusion is surface diffusion. Molecules that are absorbed on pore surface are often considerably mobile. Since the direction of diffusion is that of decreasing surface concentration and

that the adsorption concentration itself is a function of the local pore concentration, surface diffusion and gas-phase pore diffusion proceed in parallel.

Porous materials existing in a water vapor-dry air atmosphere often exhibit an irreversible adsorption of water vapor. From the above discussion, it may be concluded that physical adsorption and ordinary pore diffusion generally proceed at a rapid rate in comparison to chemisorption and Knudsen diffusion respectively. In cases where both chemisorption and Knudsen diffusion occur, the extremely slow rate of either or both can be attributed to the occurrence of an irreversible adsorption. In the event of chemisorption or Knudsen diffusion occurring alone, the extremely slow rate of either can be responsible for the irreversible adsorption.

APPENDIX II

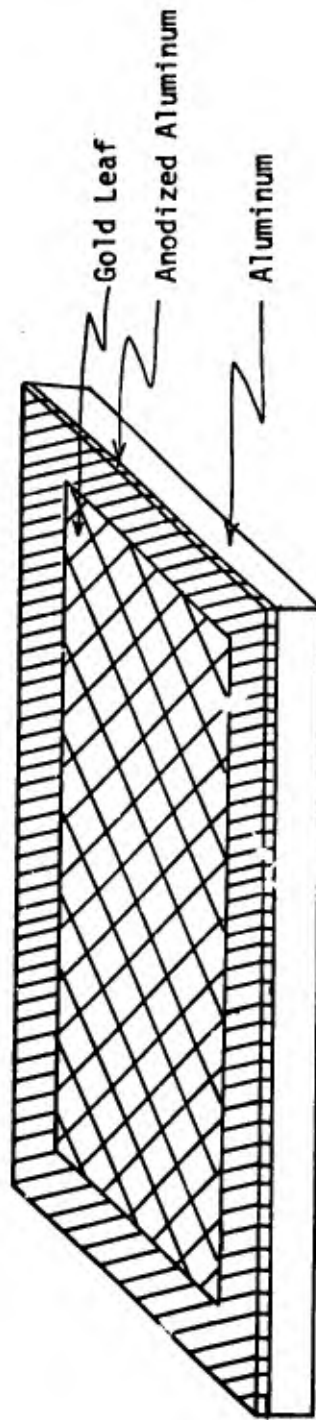
ANODIC ALUMINUM OXIDE HUMIDITY SENSORS

The earliest reference in the literature describing the use of an anodic aluminum oxide film as a humidity sensor (hygrometer) was a U. S. patent by Koller in April of 1941. Koller's patent described a plate condenser formed by anodizing an aluminum surface and depositing a gold leaf electrode on the oxide surface (See Figure 12). The electrical impedance of such a plate condenser was found to be a function of the atmospheric humidity (15).

An anodic aluminum oxide film is produced on the surface of an aluminum electrode, which is made the anode in an acidic bath. Oxygen ions will be liberated at the aluminum anode and hydrogen gas will be liberated at the cathode (See Figure 13). The oxygen ions produced at the anode, by the passage of current through the solution, react with the aluminum to produce an oxide film. The oxide film becomes part of the electrical circuit, being sufficiently porous to allow oxygen ions to flow through it. Since aluminum oxide has a high electrical resistance, a constant current density must be maintained by increasing the voltage across the film. The physical structure of an anodic aluminum oxide film is found to be a function of the following variables: electrolyte, electrolyte concentration, electrolyte temperature, anodizing time, and current density or voltage. By the adjustment of the above variables a large variety of thicknesses and porosities may be produced. Since the exact physical structure of the anodic aluminum oxide film determines the

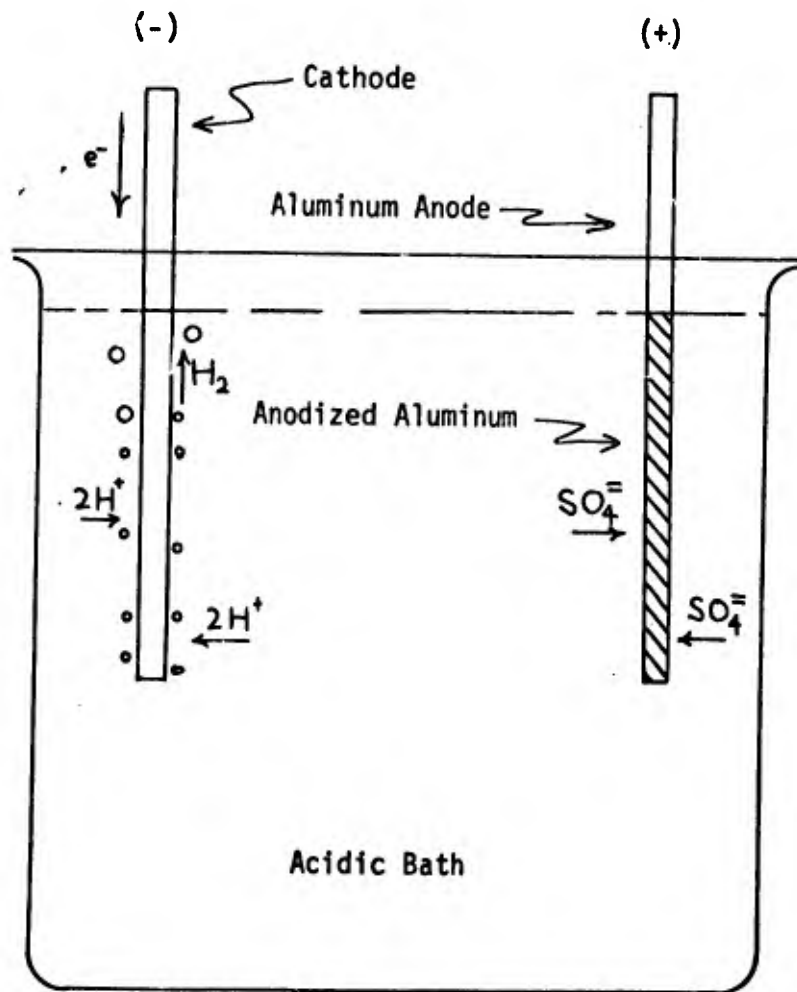
KOLLER HYGROMETER

FIGURE 1.2

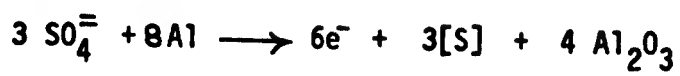


SULFURIC ACID ANODIZATION

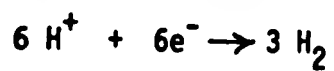
FIGURE 13



Reaction at Anode:



Reaction at Cathode:



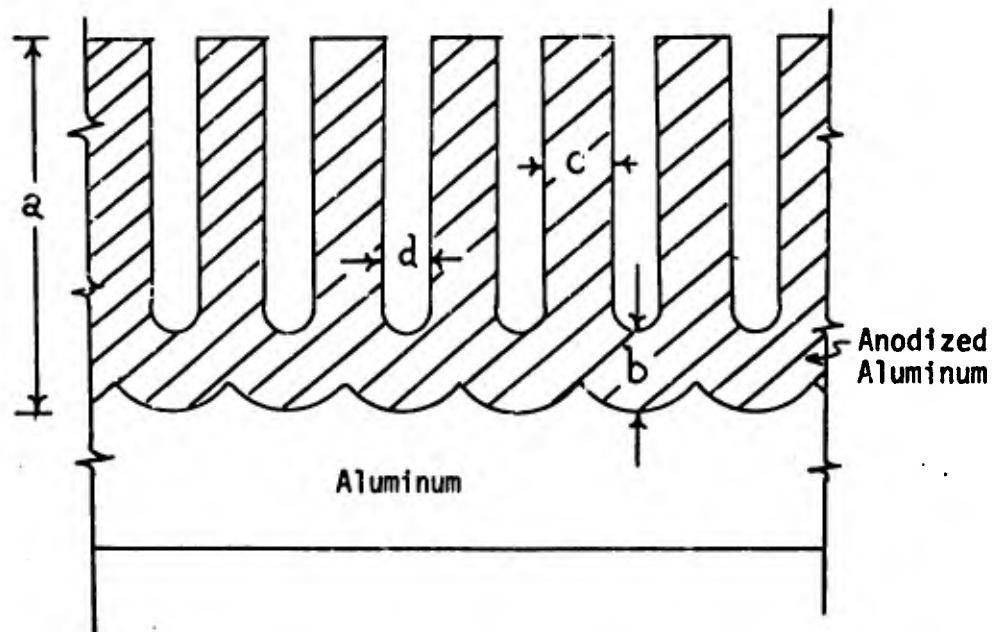
films water vapor sorption characteristics, the resistance and capacitance of a condenser, which uses an anodic aluminum oxide film as the dielectric is also a function of the above variables. Jason and co-workers (6) studied the effects of electrolyte variation on the electrical characteristics (resistance and capacitance) of such condensers at various values of the atmospheric relative humidity. Results showed that all electrolytes used displayed decreasing resistance and increasing capacitance with increasing relative humidity and that a sulfuric acid electrolyte produced an element of showing the greatest sensitivity. Density measurements of the oxide films formed also confirmed that a sulfuric acid electrolyte produced a higher porosity film (7).

Booker (6), using electron-micrographs, and others studying anodic aluminum oxide films produced in a sulfuric acid electrolyte have proposed a structural model of cylindrical pores, hexagonally spaced and perpendicular to the films outer surface. The pores are open to the external surface of the film but do not extend to the aluminum base. Next to the aluminum base is an extremely thin film of non-porous anodic aluminum oxide. Figure 14 shows the structure and approximate dimensions of an anodic aluminum oxide film produced in a sulfuric acid electrolyte. Although the physical structure of anodized aluminum oxide is not critically dependent on the purity of the aluminum anodized, small amounts of manganese cause the ordinarily colorless oxide film to become a pale gray color.

The condensers outer electrode, which is deposited over the oxide film, must have a high porosity such that water vapor may easily diffuse through it. It may be a chemically or vacuum deposited metallic element, or any other imaginable porous conductive surface. The highly porous nature of the oxide film, having large tubular pores open to the films external surface, allows for a rapid rate of water vapor diffusion into and

STRUCTURE OF ANODIZED ALUMINUM FILM
FORMED IN SULFURIC ACID ELECTROLYTE

FIGURE 14



Thickness of oxide layer (a)	30 to 127 μ^*
Pore base thickness (b)	$\sim 500 \text{ \AA}$ or less
Pore spacing (c)	450 to 600 \AA
Pore diameter (d)	190 to 300 \AA^*
Pore density	$13 \times 10^9 \text{ cm}^{-2}$
Pore volume/volume of oxide layer	13% [*]
Pore surface area	$0.2 \text{ meter}^2/\text{cm}^2$ [*]

*Depending on anodization conditions

out of the pores as well as a large surface area for adsorption to occur upon. Jason (4) explains that at a low relative humidity the path of least electrical resistance is through the complete oxide film (since dry air has a higher resistance than the oxide film) and as the relative humidity increases the surface conductivity on the pore walls increases, due to the adsorption of water vapor, causing a path of lesser resistance. At high relative humidity values an extraordinarily large dielectric constant of greater than 1000 is observed. Jason explains that the pore walls, having adsorbed large amounts of water vapor, serve as part of the outer condenser plate and that the thickness of the dielectric (b, Figure 14) is now approximately 500 Å. This reduction in distance between the conductive plates (aluminum and water) lowers the dielectric constant to the approximate value of alumina. Jason (7) goes to great lengths to explain the analogy between an electrical circuit, made up of capacitors and resistors, and the electrical properties of a single pore as the relative humidity is varied. Although the analogy, which contains five adjustable parameters, is capable of simulating the electrical characteristics of a single pore, it is evident that a more realistic model would be one involving diffusion and adsorption phenomena.

Data on the adsorption characteristics of various types of alumina have been presented by the chemical and aluminum industries (12) (10), for the utilization of alumina as a chemical catalyst. The results have shown that water vapor adsorption is principally a function of the relative humidity and comparatively insensitive toward temperature. It should be noted that the above conclusion came about while exploring temperatures in the 20°C and above range, where most chemical reactions proceed at a rapid rate. Jason (6) showed that the electrical characteristics of his anodic aluminum oxide humidity sensing elements were relatively insensitive

toward temperature variations from -15°C to 80°C (with relative humidity held constant). Jason observed that as the temperature was further reduced to -30°C a large increase in resistance and decrease in capacitance occurred, accompanied by a lower sensitivity toward relative humidity. Underwood and Houslip (15) searched for a temperature dependency, using elements produced by Jason. The temperature was varied from 18.4°C to 35°C and relative humidity values were held below 0.10. Results showed that a slight temperature dependency is indeed present. Chleck (2) tested the use of similar aluminum oxide elements as the sensing element to be employed on radiosonde balloon flights. His results showed that the electrical characteristics of such elements were a function of the absolute humidity. Although his results do show a decrease in sensitivity toward absolute humidity, as the temperature is increased from -80°C to 20°C , they remain contradictory to past results. Since relative humidity is itself a function of temperature and absolute humidity, it appears that the most accurate method of calibrating such sensing elements would be to make some electrical characteristic of the element (such as resistance, capacitance or impedance) a function of both temperature and absolute humidity. From a temperature reading, generally easily obtainable, and a value of some electrical characteristic, the absolute humidity may be determined. The relative humidity may then be obtained from the available data, if desired. The above method would involve a laborious calibrating procedure, especially since elements produced thus far have not displayed a reproducible uniformity. Since anodic aluminum oxide humidity sensing elements also display aging effect, to be discussed later, it appears that such a laborious method of calibrating individual elements is not yet warranted. In summary, it appears that: (a) Although a temperature dependency is present, its magnitude is small for temperatures above 0°C and that anodic aluminum oxide humidity sensing elements may be considered

a function of relative humidity without appreciable error. (b) Below 0°C, where presumably solid-state conduction is present, the electrical characteristics of such elements cannot be considered solely a function of relative humidity.

Investigators appear to be in agreement that the equilibrium electrical characteristics of anodic aluminum oxide humidity elements are not a function of the total pressure.

A number of investigators have recorded electrical response versus time for sensing elements subject to a relative humidity step function. Jason and Cutting (4) show that electrical equilibrium is established in less than 2 minutes for step function as large as 80% relative humidity. Chleck and Brousaides (3) report that approximately 63% of the electrical response was found to occur within 2 and 1/2 seconds. It should be mentioned that if ordinary pore diffusion (See Appendix I) through the oxide film is the rate limiting process, the response time should be inversely proportional to total pressure, yet vary to the 3/2 power of the absolute temperature.

Jason (6) showed that elements subjected to varying high and low relative humidity values showed no immediate hysteresis effects. He also observed that a long-term aging effect caused the element's initial calibration to be invalid. The rate of such a calibration drift appeared to decrease with time and the direction of drift was such that the element had a lower electrical sensitivity towards relative humidity variations. The rate of aging (calibration drift) is also found to be a function of the relative humidity in which the element is stored. Jason (6) reported that the rate of aging increases with the storage relative humidity and that it becomes so accelerated near saturation that the element soon loses all sensitivity toward relative humidity. Jason states that the possible cause of the observed aging effect may be that conduction ions present at

the pore surfaces tend to experience solid diffusion inward.

Chleck and Brousaides (3) have reported that the normal gas pollutants present in our atmosphere have no effect on element response. Since the equilibrium response is a function of the conductivity of the adsorbed species present on the pore walls, it is likely that the response of other vapors would be a function of their particular concentration, temperature and degree of molecular polarization. Jason (6) has reported that ammonia vapor, which has a higher polarization than water vapor, shows a greater electrical response than water vapor. In our atmosphere the main polar gases to be contended with are carbon dioxide, carbon monoxide, nitrogen dioxide and sulfur dioxide, all of which are present at such a low concentration that their effects would be expected to be negligible.

The aluminum oxide sensing elements may be produced in a variety of shapes. Jason prefers cylindrical shaped condensers whereas Chleck and Stover (13) have produced plate condensers.

The main advantages of anodic aluminum oxide sensing elements are their robust nature, extremely low cost, rapid rate of response, low temperature dependency (above 0°C) and their independence of total pressure and air velocity.

The principle limitation of such elements, which must be overcome before they may be suitably used as the sensing element in an electric hygrometer, is their irreversible calibration drift (aging). The question of what causes irreversible drift is not fully answered in the literature, and to repeat, the following drift behavior is known: (a) The rate of drifting increases for elements stored at a higher relative humidity. (b) Drifting is found to be in the direction of increasing apparent relative humidity, such that the resistance is increased and the capacitance decreased for a constant relative humidity.

APPENDIX III

ANODIC ALUMINUM OXIDE

The intent of the following discussion is to determine possible characteristics of an anodic aluminum oxide film, formed in a sulfuric acid electrolyte. It is hopeful that such a discussion may lead to the cause of the aging effects found in anodic aluminum oxide humidity sensors (See Appendix II), which thus far has hindered their use commercially. Incorporated in the discussion will be electron micrograph evidence of the film structure as well as literature concerning the various phases of alumina and their changes.

Electron micrographs (16) have shown anodic aluminum oxide to have a hexagonal crystal structure. Such a hexagonal crystal structure leads to the conclusion that the arrangement of the unit cells which make up the crystal may also have a hexagonal structure (See Figure 9). Higher resolution micrographs (6) reveal that the crystals have cylindrical pores which are hexagonally spaced.

Much of the literature refers to anodized aluminum oxide as Al_2O_3 , which is supposedly the smallest subdivision of the crystal lattice which contains a whole number of atoms. Al_2O_3 is also known as alpha alumina (10) or the mineral corundum, whose natural occurrence is found in rock or igneous rock. Alpha alumina is found to have a roughly hexagonal crystal structure, similar to anodic aluminum oxide, yet does not display the high porosity found in anodic aluminum oxide crystals.

There are also a number of other alumina minerals found in nature, often termed bauxite. The name bauxite has come to be used to cover any aluminum ore consisting of reasonably pure hydrated aluminum oxide. Table II gives a summary of the common alumina phases which have been

ANODIC ALUMINUM CRYSTAL STRUCTU.

FIGURE 15

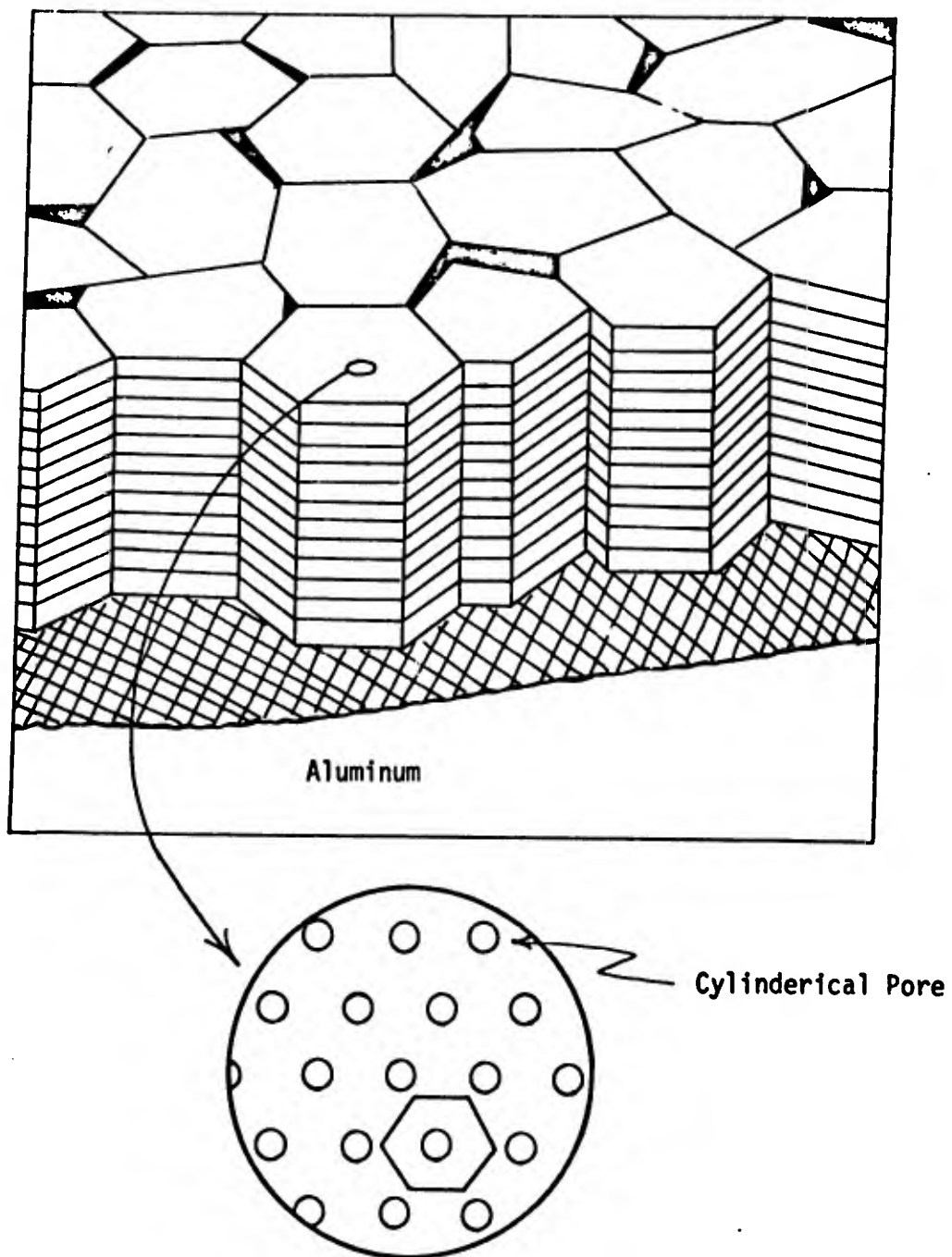


TABLE II

ALUMINA NOMENCLATURE

ALCOA NAME (10) (PHASE)	FORMULA	COMMON NAME	CRYSTAL STRUCTURE
Alpha	Al_2O_3	Corundum	Hexagonal
Alpha Monohydrate	$Al_2O_3 \cdot H_2O$	Bohmite	Orthorhombic
Alpha Trihydrate	$Al_2O_3 \cdot 3H_2O$	Gibbsite	Monoclinic
Beta Monohydrate	$Al_2O_3 \cdot H_2O$	Diaspore	Orthorhombic
Beta Trihydrate	$Al_2O_3 \cdot 3H_2O$	Nordstrandite	Monoclinic

observed.

Bergmann (10) who studied the electrolytic oxidation of high purity aluminum in a dilute electrolyte, observed the formation of predominantly amorphous products. He reported an average degree of hydration from $\text{Al}_2\text{O}_3 \cdot 2.94\text{H}_2\text{O}$ to $\text{Al}_2\text{O}_3 \cdot 3.02\text{H}_2\text{O}$ containing varying amounts of beta alumina trihydrate and alpha alumina monohydrate, the proportion of which appeared to be dependent on the electrolyte used.

In search of chemical catalysts it was found that the trihydrated aluminas may be partially dehydrated by prolonged heating. The product was a lesser hydrated alumina containing a fine pore structure (activated alumina). In general the higher the temperature used, the shorter the time period required to dehydrate to a desired level. The trihydrated aluminas are stable at normal temperatures and may be easily reduced to alpha monohydrate by heating. Further dehydration of alpha monohydrate is found to be more difficult since alpha alumina becomes stable at greater than 1100°C , when formed from the trihydrates.

The term hydrate has recently been labeled as incorrect and the term hydroxide used to replace it. This distinction in nomenclature tends to confirm that the water molecules are chemically attached to the Al_2O_3 structure and not physically adsorbed.

The above discussion leads to the belief that porous anodic aluminum oxide films formed in sulfuric acid electrolyte may possibly be a mixture of a non-hydrated phase and various hydrated phases of Al_2O_3 . Since atmospheric moisture is readily accessible to the pore surfaces, it is possible for phase transitions to occur on the pore walls. It is believed that the electrical effect shown by the anodic aluminum oxide humidity sensing elements is due to physically adsorbed water vapor on the pore walls and that the amount of water vapor physically adsorbed is a function of the

surface chemical characteristics. If the chemical characteristics of the pore walls change with time, possibly becoming more hydrated, it is probable that the amount of physically adsorbed water on the pore walls will also be varied (possibly a lesser amount). This would result in a decrease in electrical sensitivity and possibly the aging effect presently observed in anodic aluminum oxide humidity sensing elements.

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3. ABSTRACT Various hygroscopic materials have been considered for use as the thin film dielectric in a condenser, which is to be used as the humidity sensing element in an electric hygrometer. The requirement of such a dielectric is that it approach equilibrium rapidly and display both reversible and reproducible humidity-electrical characteristics. Polymerous dielectrics have shown an extremely slow rate of response and it is suspected that the rate of Knudsen diffusion through many fine tortuous pores is responsible. Anodic aluminum oxide films produced in a sulfuric acid electrolyte have recently shown a rapid rate of response as well as a reproducible response toward humidity changes. The major limitation hindering the use of such humidity sensing elements is their long-term calibration drift, which causes the elements to become less sensitive toward humidity variations. Results have shown that a change in the concentration of various species of chemisorbed water vapor initially present on the pore walls may be responsible for the observed calibration drift and that further experimentation in this area is warranted.	

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Humidity Sensor						
Hygrometer						
Porous Hygrometer						
Thin Film Hygrometer						
Electric Hygrometer						
Anodized Aluminum Hygrometer						
Aluminum Oxide Hygrometer						
Polymerous dielectric Hygrometer						
Water Vapor Absorption in Porous Solids						

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