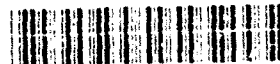


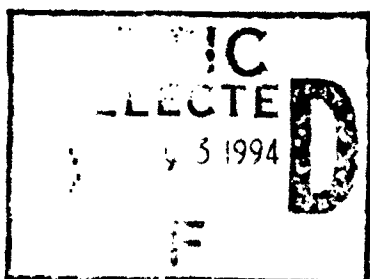
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THIN METAL FILMS AS CORROSION INDICATORS

Richard B. Belser
Niels Engel

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia



MARCH 1960

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Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia. THIN METAL FILMS AS CORROSION INDICATORS, by R. B. Belser and N. Engel. December 1959. 77 p. illus. tables (Proj 7312; Task 73122) (WADC TR 59-759) (Contract AF 33(616)-3879) Unclassified Report Thin metal films were evaluated as corrosion indicators for packages. Over 500 films deposited on glass substrates were examined by exposure in sealed containers at 25°C and at known relative humidities of from 0 to 70 percent. Iron, copper, manganese, magnesium and bimetal iron-copper films were studied. Although pure metal films did not corrode to a significant degree at 70% R. H. additions of sensitizing materials such as acid fumes (over)	UNCLASSIFIED	UNCLASSIFIED
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Richard B. Belser

Niels Engel

*Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia*

MARCH 1960

Materials Laboratory
Contract No. AF 33(616)-3879
Project No. 7312

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FOREWORD

This report was prepared by the Engineering Experiment Station of the Georgia Institute of Technology, 225 North Avenue, N. W., Atlanta, Georgia, under USAF Contract No. AF 33(616)-3879. This contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73122, "Corrosion and Corrosion Prevention". The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Harold L. Stevens acting as project engineer.

This report covers work conducted from 15 November 1958 to 31 December 1959.

The work of the project has been conducted by Mr. Richard B. Belser, Associate Professor Research, Project Director, and by Dr. Niels Engel, Mr. A. P. Youmans, Mr. Frank E. Hankinson, and Miss Dorothy A. Brine, Research Assistants.

The present report is the third technical report issued during this project, being preceded by Wright Air Development Center Technical Report No. 57-662, ASTIA Document No. 155 516 and WADC Technical Report 59-149, ASTIA Document No. 214886.

ABSTRACT

The purpose of the research conducted was to study the properties of thin metal films in relation to their proposed use as integrating indicators of corrosive conditions existing over a period of time within sealed packages. In particular the evaluation of iron films as corrosion indicators was desired.

During the period of this report over 500 films deposited on glass substrates were examined by exposure in sealed containers at 25°C and at known relative humidities in the range of 0 to 70 percent; electrical resistance changes and area destruction were recorded. The specimens consisted predominantly of iron films but included approximately 50 films of manganese, 30 films of magnesium, and 50 bimetal films of iron and copper.

The observed behaviors confirmed results previously reported and extended knowledge of the basic corrosion behavior of thin metal films. In short, thin iron films deposited by vacuum evaporation onto glass slides which are essentially clean did not corrode in a manner observable to the eye at 25°C and 70 percent relative humidity in periods greater than 60 days. Careful electrical measurements, on the other hand, indicated small electrical resistance changes of one to five percent during the same period. Efforts made to increase corrosion rates by roughening the substrate, placing the film in tension, partially oxidizing the film, or employing bimetal configurations of iron and copper were only partially successful in that the corrosion rate was increased by a factor of two or three but data scatter remained large.

Iron film specimens sensitized with a salt spray such as NaCl or with HCl acid fumes exhibited rapid corrosion rates, i.e., extensive area destruction or large resistance increases in 24 hours. Similarly rapid corrosion effects were observed when films were inadvertently sensitized by chemical fumes coming from nearby laboratories through the ventilation system, by fumes released from soldering fluxes, or from acid bottles opened in the laboratory during processing. Films which had been thus sensitized exhibited relatively rapid corrosion at 25°C and at relative humidities above approximately 35 percent; hence, such films became essentially coarse integrators of conditions of temperature and relative humidity.

It was evident that metal films, as usually prepared, were frequently inadvertently sensitized during fabrication and storage and that the various degrees of sensitization experienced contributed to the large data scatter observed. The scatter of corrosion rates prevents use of the films as precisely calibrated individual indicators of corrosion rates; on the other hand, their use as corrosion indicators in statistically valid numbers appears practical. In addition, it is apparent that

films register the event of sensitization when exposed at 25°C and above a relative humidity of 35 percent and that sensitized films register the event of rise of relative humidity above 35 percent. Likewise, it is probable that a coarse integration of conditions of temperature and relative humidity may be obtained up until the time the film becomes nearly totally destroyed.

Bimetal films of copper and iron and films of manganese and of magnesium exhibited, generally speaking, essentially the same corrosion characteristics as films of iron with the exception that in general their corrosion rates were slightly greater.

Concurrent studies of bulk metal specimens, and the occurrence of inadvertent sensitization of these specimens at the same time as film specimens, revealed the importance of sensitization effects in corrosion; these implied that large corrosion losses in packaged metal goods could be avoided by proper care in minimizing or removing sensitizing influences during processing and packaging.

A method of studying the corrosion of films of the semi-refractory and refractory metals by measuring the temperature coefficient of resistance of metal films in vacuo and in air over the range 25°C to 600°C was presented. It was shown that only films of gold and platinum survived temperatures of 600°C without oxidation. Films of iridium exhibited only relatively minor oxidation and films of chromium began oxidizing at about 550°C. Films of other metals exhibited rapid oxidation at 400°C or below. Overcoatings of silicon monoxide provided considerable protection of films of the various metals from oxidation. The method of study outlined appears to be a useful one for further exploring the corrosion properties of the refractory metals and for studying protective coating systems.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



I. PERLMUTTER
Chief, Physical Metallurgy Branch
Metals and Ceramics Division
Materials Laboratory

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SECTION I

INTRODUCTION

The need for a sensitive, easily inspected, economic corrosion indicator which integrates with respect to time the total exposure of packaged material to corrosive conditions has been pointed out in previous work sponsored by the Materials Laboratory of Wright Air Development Center^{1,2,3,4}.

The Engineering Experiment Station of the Georgia Institute of Technology, under Contract No. AF 33(616)-3879, was assigned the task of conducting a further study of "Thin Metal Films as Corrosion Indicators." The work of the first and second years has been reported in Wright Air Development Center Technical Reports Nos. 57-662⁵ and 59-149⁶, respectively. An exploratory investigation of the corrosion rates and behaviors of nine metals and two bimetal pairs exposed to controlled conditions of relative humidity and temperature was made. Of the metals examined films of iron and bimetal films of iron and copper were selected for more intensive study.

It was demonstrated that, in addition to being affected by the temperature and relative humidity of the environment during exposure, the corrosion rate of a metal film was affected by the substrate choice, the substrate cleaning technique and the temperature at which the film was deposited or to which it may have been raised subsequent to its deposition but prior to its exposure. The number of parameters requiring control in order to produce films of similar corrosion rates resulted in a need for further studies that would establish films of the desired reliability as corrosion indicators.

By careful control of substrate cleaning and film deposition procedures iron films which exhibited no visible corrosion in over 140 days at 25°C and 70 percent relative humidity were obtained.

With the condition of virtually no corrosion established an effort was made to return to the films corrosion inducing agents which would provide specimens of controlled corrosion rates. A variety of attempts was made to nucleate corrosion. These attempts included the heating of the deposited films in vacuo; undercoating or overcoating of the iron films with selected metallic salts; the deposition of iron films by sputtering; vaporization of iron oxide onto iron films; partial oxidation of the films by the discharge from a Tesla coil; heating of a portion of the film in air; and fabrication of bimetal films in various configurations.

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Manuscript released by authors 31 December 1959 for publication as a WADC Technical Report.

The employment of metallic salt contaminants on or under iron films resulted in relatively rapid corrosion rates at 25°C and at relative humidities above approximately 35 percent. However, salt sensitized specimens were only temperature and humidity integrators in the sense that the influence of the salts overrode the effect of other sensitizing agents which might be present in the environment of interest.

Although these salt sensitized specimens may be considered as a partial solution to a corrosion indicator, provided specimens of consistently controlled corrosion rate can be obtained in large quantities, a need still remained for an unsensitized indicator which would exhibit sensitization if it occurred. To accomplish this mission further studies of the basic corrosion properties of metal films were necessary. This report covers the progress on these further studies.

SECTION II

APPARATUS AND PROCEDURES

A. General

The general apparatus and procedures for depositing metal films on glass or plastic substrates and conducting corrosion rate studies have been detailed in Wright Air Development Center Technical Reports 57-602 and 59-149. In short, microscope slides of soft glass were halved and cleaned by standard chemical techniques. These, or clean plastic substrates of similar size, were inserted in a vacuum chamber and coated with films of iron or another metal by means of the evaporation technique; the evaporation was normally conducted at a pressure of approximately 2×10^{-5} mm of mercury. The prepared films were then inserted in constant humidity chambers consisting of glass containers into which a humidity controlling solution of sulfuric acid or glycerine had been previously introduced^{7,8}. A temperature of approximately 25°C was obtained by storing the containers in a temperature controlled room. Effects of corrosion were determined by recording over a period of time visual observations of area destruction of the thin metal films or by electrical measurements of changes in the electrical resistances of the films.

During the period of this report the procedures and equipment have been modified and improved where feasible. The major modifications are reported in succeeding sections.

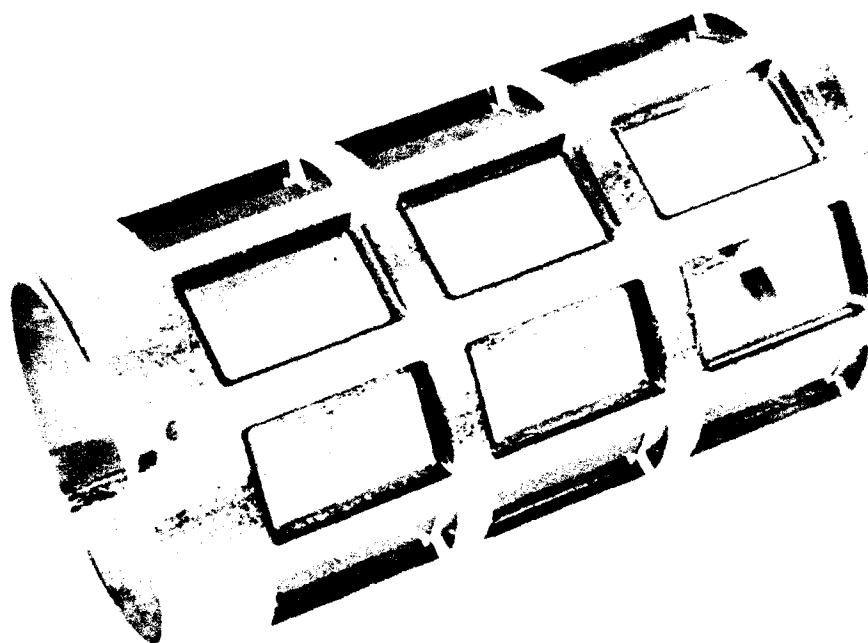
B. Apparatus

1. Vacuum System Overhaul

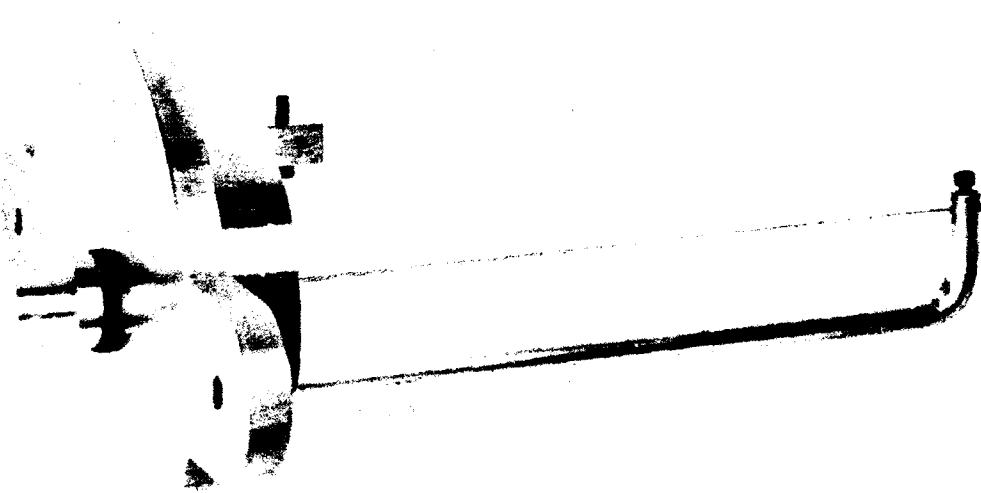
The primary vacuum system used on the project had been in operation somewhat over two years and the pumping times to the pressure of 2×10^{-5} mm of mercury had increased to an unreasonable period. The procurement of a new VEECO helium leak detector Model MS9AB furnished an opportunity for a complete check of the system. This revealed a number of small leaks in the valves controlling the inlet to the mechanical pump and leaks in several chamber headers. These leaks were repaired and the pumping time to 10^{-5} mm of mercury dropped to the normal time of about 15 minutes.

2. Work Holder Mask for Coating 12 Specimens Simultaneously

A work holder mask has been fabricated from a 6-inch long section of 3-inch I.P.S. (3-1/2 inch O.D.) Schedule 40, Type 304 stainless steel pipe as shown in Figure 1. Into a 180° sector of this piece were machined 12 openings of 7/8 x 1-3/8 inches with corners of 1/8-inch radius. The outer surface of each opening was milled to form a rabbetted



A. WORK HOLDER MASK



B. FILAMENT AND HEADER

Figure 1. Work Holder Mask and Filament for Preparation of 12 Iron Film Specimens.

step $3/32$ " wide and $3/32$ " deep to hold one-half of a glass microscope slide and to mask its edges by approximately $1/16$ inch.

A header plate was constructed from a brass plate $3/8$ " thick. A single lead-through, insulated from the plate, was inserted at the center. The ground lead consisted of a copper rod of $1/4$ " diameter fastened one inch below the center electrode. At its opposite end it was bent 90° toward the center in the form of an "L" with the short leg $1-3/8$ inches long. The rod serves as one electrode and as the support for the evaporation filament.

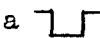
A piece of brass pipe $7/8$ -inch long, of the same outside diameter as the stainless steel work holder, and a lug made of $1/2$ -inch square brass stock, $1-1/4$ inches long, support the work holder mask. The ring, lug and headplate were joined by silver soldering. The lug extends $1-1/16$ inches beyond the ring and is drilled and tapped for a machine screw of No. 6-32 thread. A hole drilled in the work holder permits it to be attached to the lug by means of the screw.

3. Improved Headers

Two additional headers for the 4-inch diameter pyrex pipe chambers were constructed. These were equipped with four electrical leads of large diameter as shown in Figures 2 and 3. Small O-ring sandwiches between the aluminum electrode and a threaded stainless steel tube were held securely by a brass screw cap. Not only do the O-rings serve as vacuum seals but also as electrode insulators. With this arrangement only a very small portion of the gasket material was exposed to the atmosphere of the chamber.

4. Filaments

A reexamination of filament materials and configurations was made with respect to evaporation of two metals simultaneously. Wire filaments of tungsten, molybdenum and tantalum were examined for most favorable evaporation performance. The wires were placed under slight tension to prevent buckling during heating. Of these metals, wires of stranded tungsten proved the more favorable for iron and tantalum the more favorable for copper and gold.

Whereas wire filaments, stranded or monofilament, were found satisfactory for films deposited of a single metal they were less satisfactory for the preparation of bimetal layers, primarily because of the small metal charge utilizable at a single run and rapid destruction of filaments by large charges. A $1/4$ inch wire ribbon filament in the form of a  was found to be satisfactory for long runs. Tantalum was selected for the reason that it was not embrittled by successive heating. The portion connected to each lead and up to the trough proper was made of double thickness by spot welding two thicknesses of ribbon together.

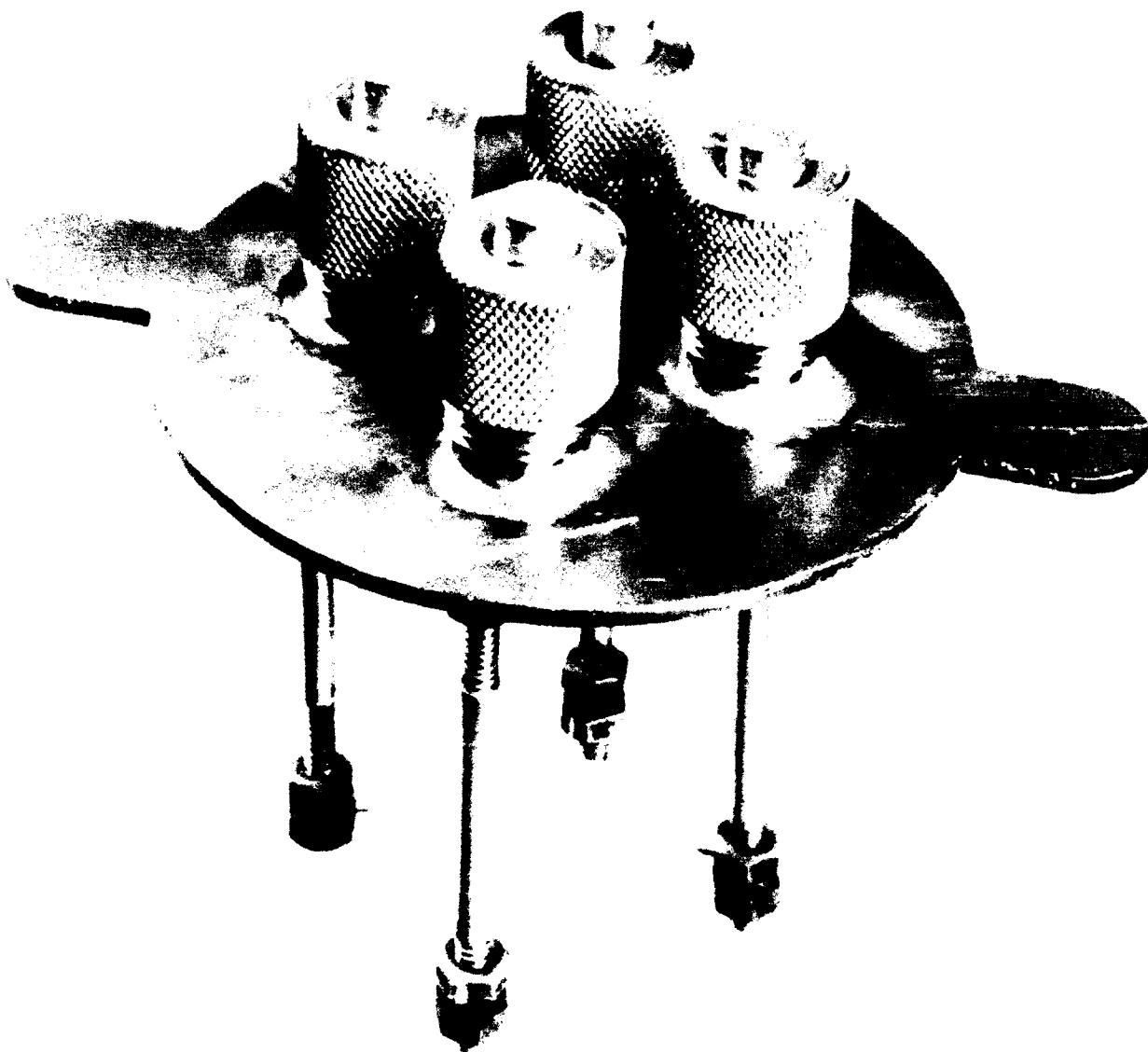


Figure 2. Vacuum Chamber Header with Large Diameter Electrical Leads Sealed to and Insulated from the Header Plate by "O" Rings.

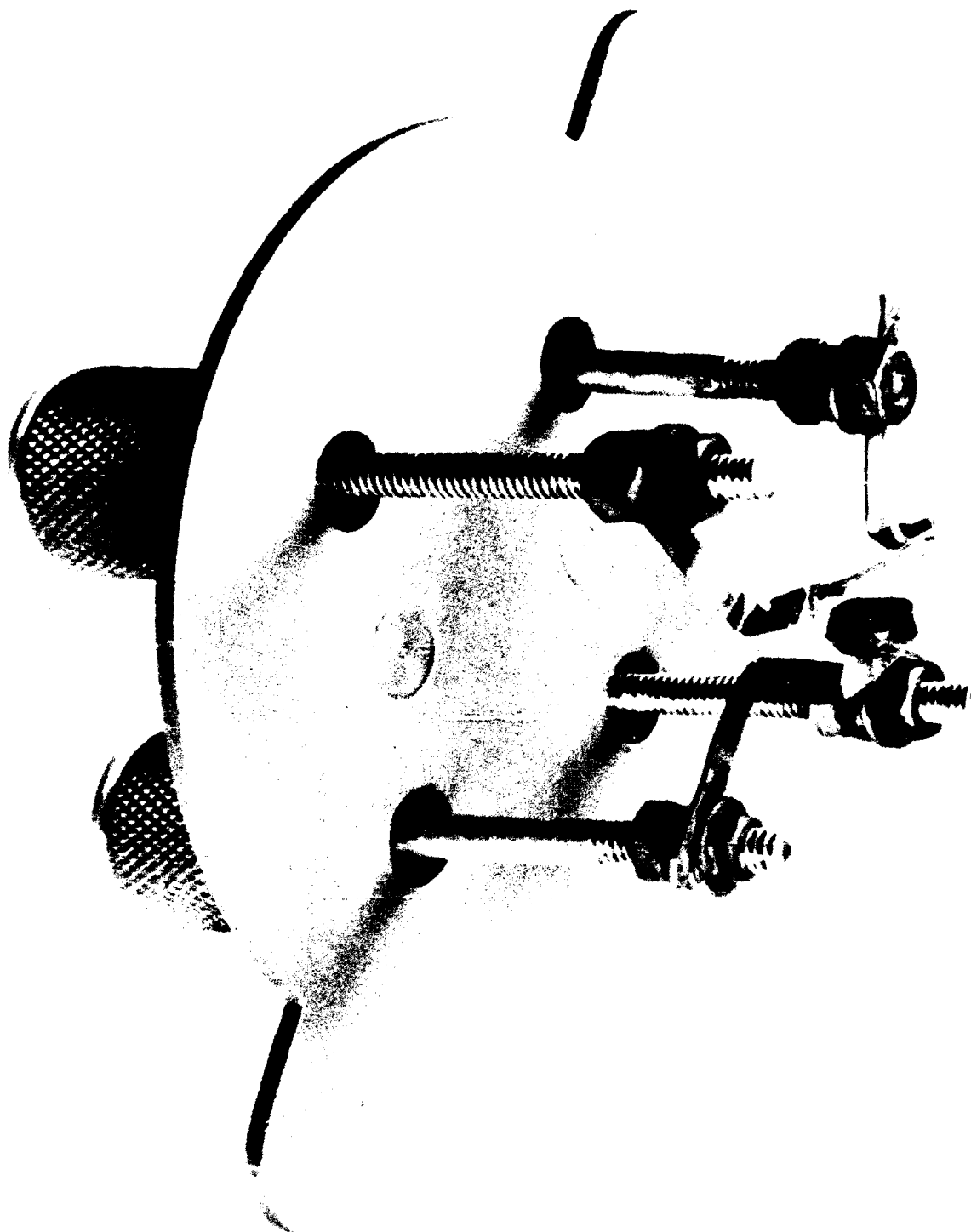


Figure 3. Header with Tantalum Ribbon Filaments Attached (Note double thickness leading to center section.)

Thus the ribbon was relatively cool except for the hot center portion. The temperature of this section was controlled by means of a Variac feed and an optical pyrometer. A pair of filaments is shown in Figure 3, preceding. The temperatures and evaporation rates from two filaments were controlled by two separate Variacs after individual calibration of each filament with the optical pyrometer.

5. Fastex Movies

In order to make a proper choice of filaments Fastex movie equipment was employed to photograph behavior of various metals on selected filament materials. Pictures were taken at approximately 500 frames per second. On the basis of these records ribbon filaments of tantalum were chosen for simultaneous evaporation of the copper and iron.

6. Electrical Resistance Measurements

Apparatus for measuring the resistance of metal films through a temperature range such as 25°C to 600°C has been described in detail in Wright Air Development Center Technical Report 57-600 and in a paper⁹. The film was normally deposited on a tubular substrate of Vycor or fused quartz so as to overlay terminations consisting of a fired platinum bright film at each end of the substrate as shown in Figure 4. To the platinum bright was bonded a silver wire by means of silver paste. The film was temperature cycled in a tube furnace which could be evacuated and then filled with a desired atmosphere. This is shown in Figure 5.

Temperatures within the furnace were monitored by means of a chromel-alumel thermocouple and a potentiometer. Resistances were measured by means of a Wheatstone Bridge.

C. Procedures

1. Cleaning

The cleaning procedures outlined in paragraph II, C, 1 of Wright Air Development Center Technical Report 59-149 were continued during the period of this report. In general the primary cleaning procedure used for glass substrates was as follows:

- a. Soft glass microscope slides were scrubbed with warm Alconox solution;
- b. rinsed with warm tap water;
- c. immersed in chromic acid cleaning solution for five to ten minutes;
- d. rinsed with tap water;

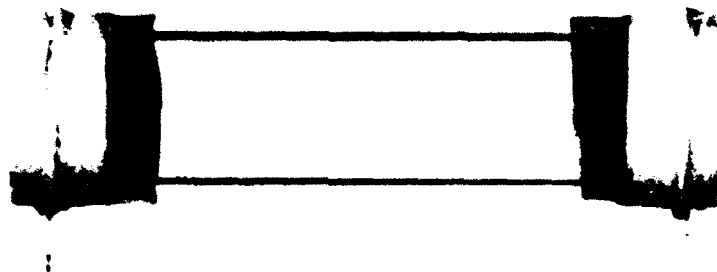
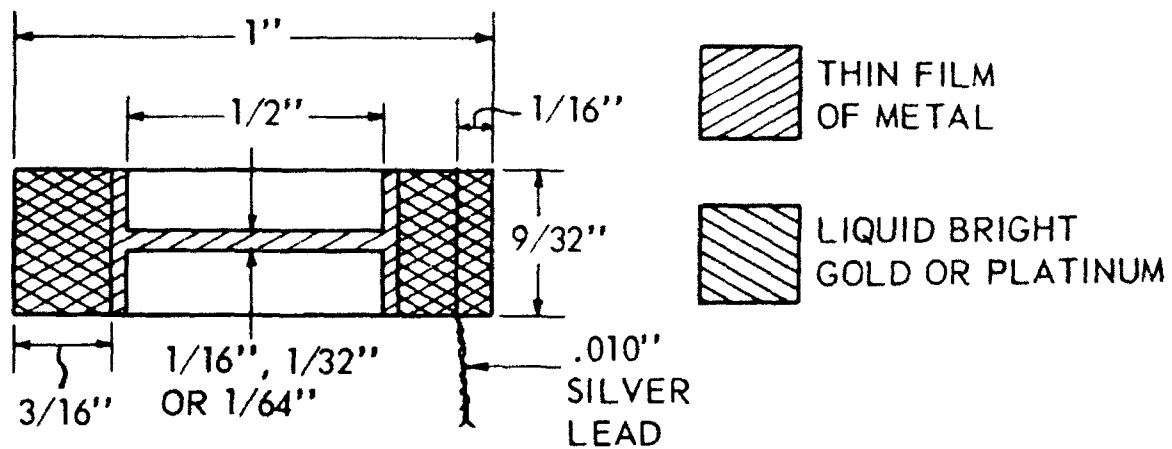


Figure 4. Configuration of a Film Resistor Examined for Corrosion by Measuring its Temperature Coefficient of Resistance.

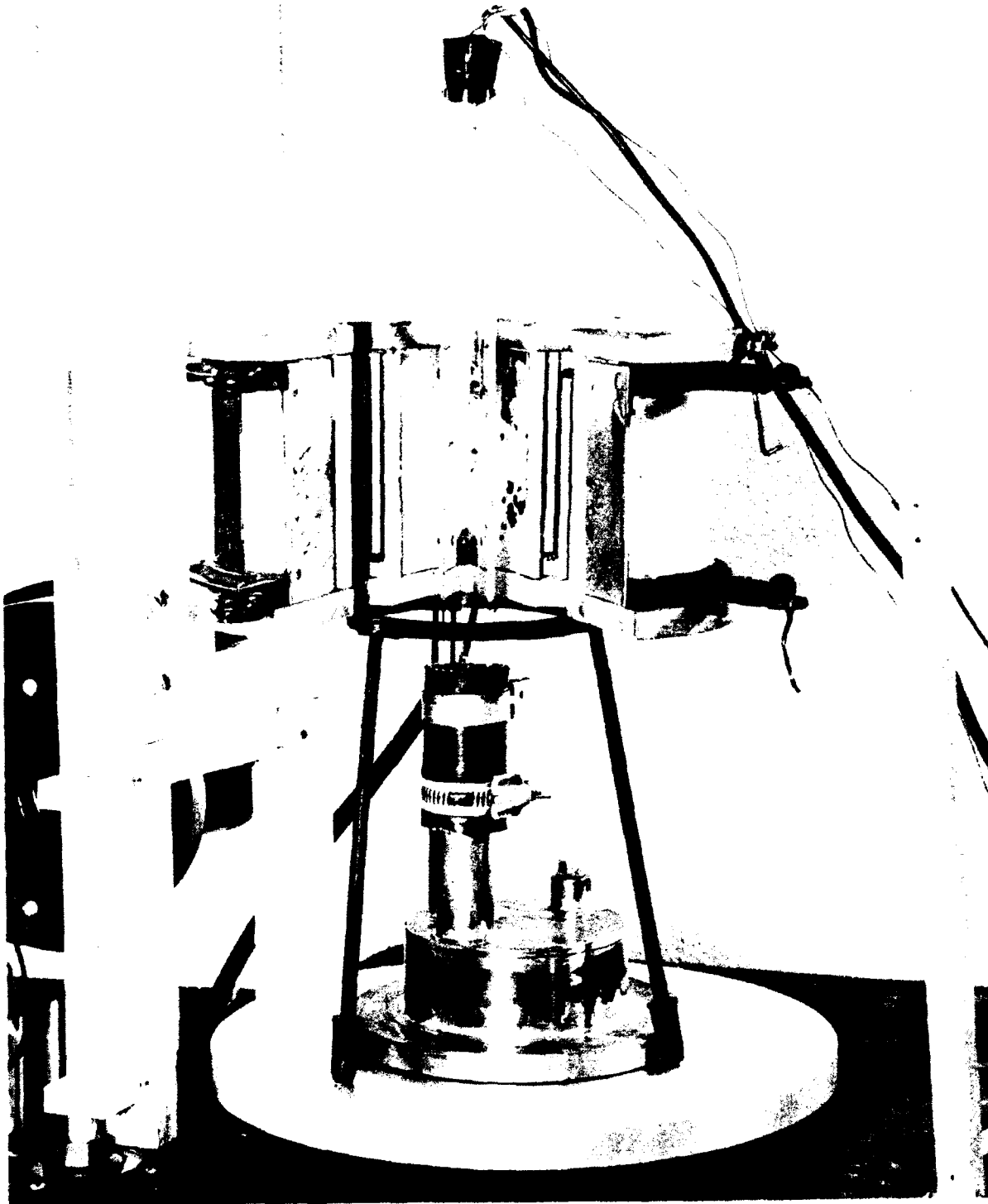


Figure 5. Tube Furnace in which Film Resistors were Temperature Cycled
in vacuo and in Air.

- e. rinsed with distilled water;
- f. rinsed with methanol;
- g. dried with hot air from a blower.

All handling of the slides subsequent to step (a) was done with special tweezers designed to grasp only the edges of the slides.

Slides only occasionally showed water marks and these slides were discarded.

Cleaning of microscope slides by ultrasonic techniques in a five-gallon container driven by a 5 Kw ultrasonic transducer was examined but no appreciable improvement in film adherence or corrosion behavior was noted in the few experiments run.

Flaming of slides with an oxy-hydrogen flame in lieu of an air-gas flame gave an apparent improvement in adherence of iron films subsequently deposited on the glass surface. However, flaming had already been discarded as a cleaning technique and this method was not adopted as a permanent feature of necessary cleaning for the glass substrates.

2. Storage

The large gallon jars used during the preceding two years were replaced by quart glass jars with gasket sealed lids. All electric lead-in entrances were sealed with beeswax. A resurvey of humidity controlling solutions was made. Dilute H_2SO_4 was chosen as the humidity controlling agent. Figure 6 shows a new storage chamber.

3. Storage under Tension

Small plastic jigs were made up to hold one microscope slide each. A screw through the jig at the approximate center of the slide permitted a bending stress to be exerted on the slide; the film was located on the opposite side from the screw and was thus stressed in tension. The jig assembly with a mounted specimen is shown in Figure 7. The film specimens thus mounted were suspended in storage chambers of selected relative humidity.

D. Magnesium Films

Magnesium films were deposited on glass slides in a series of narrow interconnecting lines by means of a conical shaped piece of magnesium rotated at high speed. Electrical resistances of specimens were measured during storage at selected humidities.



Figure 6. Glass Specimen Sealed in New Container. Humidity Controlling Solution in Bottom of Jar.

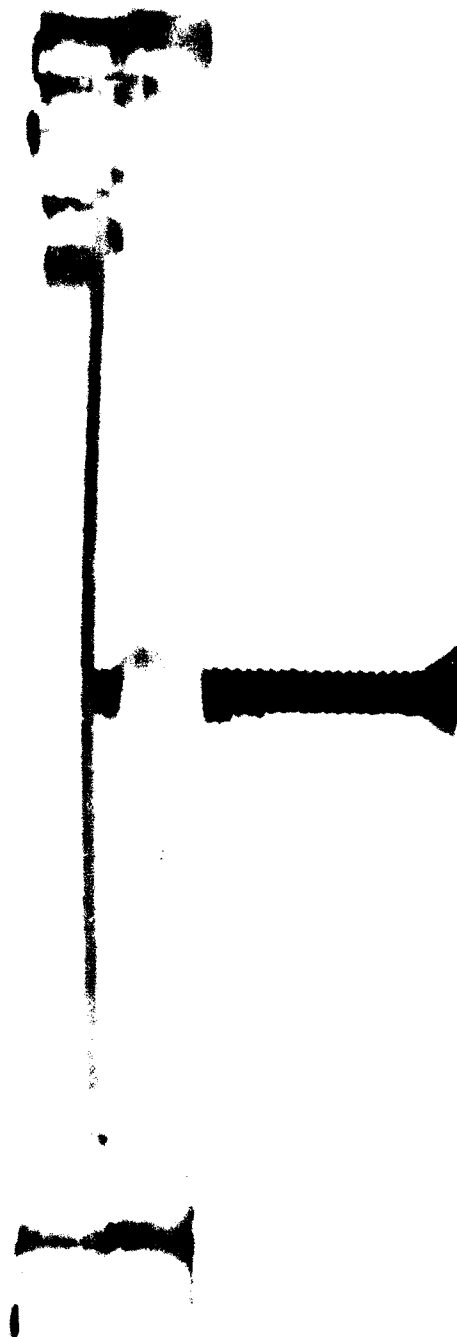


Figure 7. Film Specimen Mounted in Bending Jig.

E. Corrosometer

A corrosometer, received from Crest Instrument Corporation* about 11 August 1959, was placed in operation near the end of the period of this report. The corrosometer, based on the principle of a Self Balancing Double Kelvin Bridge, allows rapid measurement and recording of electrical changes in films exposed to the various conditions of temperature and relative humidity. In theory, the effects of various methods of film preparation, sensitization or the protective coating of films may thus be studied with a minimum waiting period. Experiments with the corrosometer are reported in Section III, H, 2.

* Sante Fe Springs, California.

SECTION III

EXPERIMENTAL WORK

A. Introduction

During the preparation of the final report for the work of the second year, a contrast in corrosion rates of iron films deposited on glass during the first and second years was clearly set forth. Whereas the films made during the first year exhibited visually detectable signs of corrosion in 24 to 72 hours, those fabricated in the second year frequently exhibited no signs of corrosion in 60 days. The reasons for this large difference in corrosion rates were not readily apparent since the corrosion rates of the first period essentially agreed with the earlier work of Mr. David Roller. There was, however, a greater variation in the data obtained than is desirable for proper interpretation of it; and the reasons for this had not been determined.

A review of the former substrate cleaning system incorporating washing with a detergent, rinsing, blotting dry and flaming revealed, in the light of the further work, the latter two cleaning stages as subject to suspicion. A series of tests was then devised to indicate more clearly the influence of these stages on the corrosion rates of iron films subsequently deposited on the respective substrates. A portion of the results of these was reported in Wright Air Development Center Technical Report No. 59-149, and some additional work is included in this report.

The slow corrosion rates of films deposited on substrates cleaned by the "acid" method* indicated a need for a corrosion nucleating or sensitizing system. Two partially satisfactory systems had been found in the salt spray sensitization method and in bimetal films, as has been discussed in the reports cited. The latter methods, however, required further work for a proper choice of the contaminating salt species and for specimen preparation techniques. The delineation of ranges of relative humidity and temperature in which desired sensitivity may be realized was also necessary.

As the work progressed it became evident that additional basic information and a review of information previously obtained concerning the parameters affecting the corrosion rates of thin films was necessary in order to have any chance of achieving corrosion indicators of reproducible rates. Hence, studies were directed toward obtaining further knowledge concerning the basic parameters affecting the corrosion of thin metal films and toward studies of bimetal films, at the sacrifice of more extensive studies of salt sensitized films and of corrosion rates of iron films in the presence of vapor corrosion inhibitors.

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*The same as that outlined in Section II, B, 1.

Some additional experiments on films of magnesium and manganese were conducted and a study of the oxidation of metals by means of measurements of the temperature coefficient of electrical resistance of films over a temperature range of 25°C to 600°C is reported.

B. Examination of Cleaning Variables

1. General

As the work had progressed it had become more and more evident that unknown variables were contributing to a large scatter in the corrosion rates measured for iron films. Hence, there were sensitizing influences present in the laboratory which were being overlooked. A careful survey of each step in processing of the films and in their storage was then instituted.

Sources of corrosion sensitization were traced to one or more of the following: fumes from a nearby laboratory utilizing FeCl_3 baths for etching, HCl acid bottles opened during a processing step, soldering on adjacent laboratory benches with acid type fluxes, breathing of the storage chambers, and the cleaning steps which included blotting or flaming.

2. Iron Film Specimens Studied using Old Cleaning and Storage Methods

In order to trace these various influences a considerable amount of rechecking of experiments was done in the initial portion of the year's work. Corrosion measurements of some 280 films were conducted and are reported in Table I. These were primarily concerned with variables introduced by the cleaning techniques. Concurrently, however, checks were made of sources of corrosive influence that were obviously sensitizing the films during processing, usually during the time the films were being mounted in the humidity containers and being connected electrically to the socket used for rapid connection of the films to a Wheatstone Bridge for resistance measurement.

Films 231-240 and 241-250 are examples of iron films which exhibited no corrosion in 140 days; and films 141-150 and 211-220, using what was termed "standard" cleaning and "acid" cleaning respectively, similarly exhibit no corrosion in 60 days.

Standard cleaning included blotting and flaming the substrates but no immersion in chromic acid; acid cleaning included immersion in chromic acid but no blotting and flaming; acid-heater-shutter means that the substrate received the acid cleaning, was heated in vacuo and the initial pulse of evaporating iron was caught on a shutter before the balance of the evaporating material was allowed to coat the glass substrate.

The flaming and blotting steps were omitted in the specimens of numbers greater than 300 as the experiments gave some evidence that these

contributed to sensitization of iron films deposited subsequently on the glass substrates. However, there were obviously other conditions sensitizing the films as shown in the film series 381 through 430. These causes were not traced absolutely but were ascribed to fumes coming into the laboratory from outside sources since a correlation with experimental activity in nearby chemical laboratories was found. Likewise in the groups composed of specimen 311-370, it is apparent that corrosion began after about 30 days. This is ascribed to breathing of the containers when the outside air was highly contaminated.

Units 311-370 were prepared in the period 10-15 March 1959 and a careful examination of electrical resistance data revealed resistance increases beginning about 20-25 March. This is the same period 381-430 were made; the latter films had extremely rapid corrosion rates. Hence, it is concluded that sensitization fumes in the laboratory must have seeped into the containers.

3. Iron Films Studied using New Cleaning and Storage Methods

As a result of the experiments outlined above the entire film processing and storage technique was changed from that described in Wright Air Development Technical Report 59-149 to that described in Section II, B, 1, of this report.

Again a series of iron film specimens was prepared to use as a control group. Other experiments included studies of the effect of substrate temperature, the effect of surface roughness and the effect of external stress. A summary of these studies is recorded in Table II and is further detailed for representative specimens in Figure 8. These studies, although not continued for as extensive periods as those reported in Table I, present more uniform data than the previous studies and generally agree with conclusions that might be expected.

Twelve specimens of iron films deposited on cold substrates and exposed at 25°C and 70 percent relative humidity revealed 6.5 percent average increase in electrical resistance in 42 days. Twelve specimens similarly prepared, but scratched longitudinally at equally spaced intervals of about 1/16", exhibited only about 7.2 percent increase in resistance in 44 days.

Twelve units deposited on cold Pyrex substrates and post heated to 455°C changed only about one percent in 14 days. A comparison of the relative rates is best visualized from the data for typical specimens of each group displayed in Figure 8.

4. Other Effects

a. Effect of Surface Increase

Sixteen iron films deposited on glass surfaces, sandblasted previously to a frosty appearance, exhibited about 14 percent electrical resistance increase in 34 days.

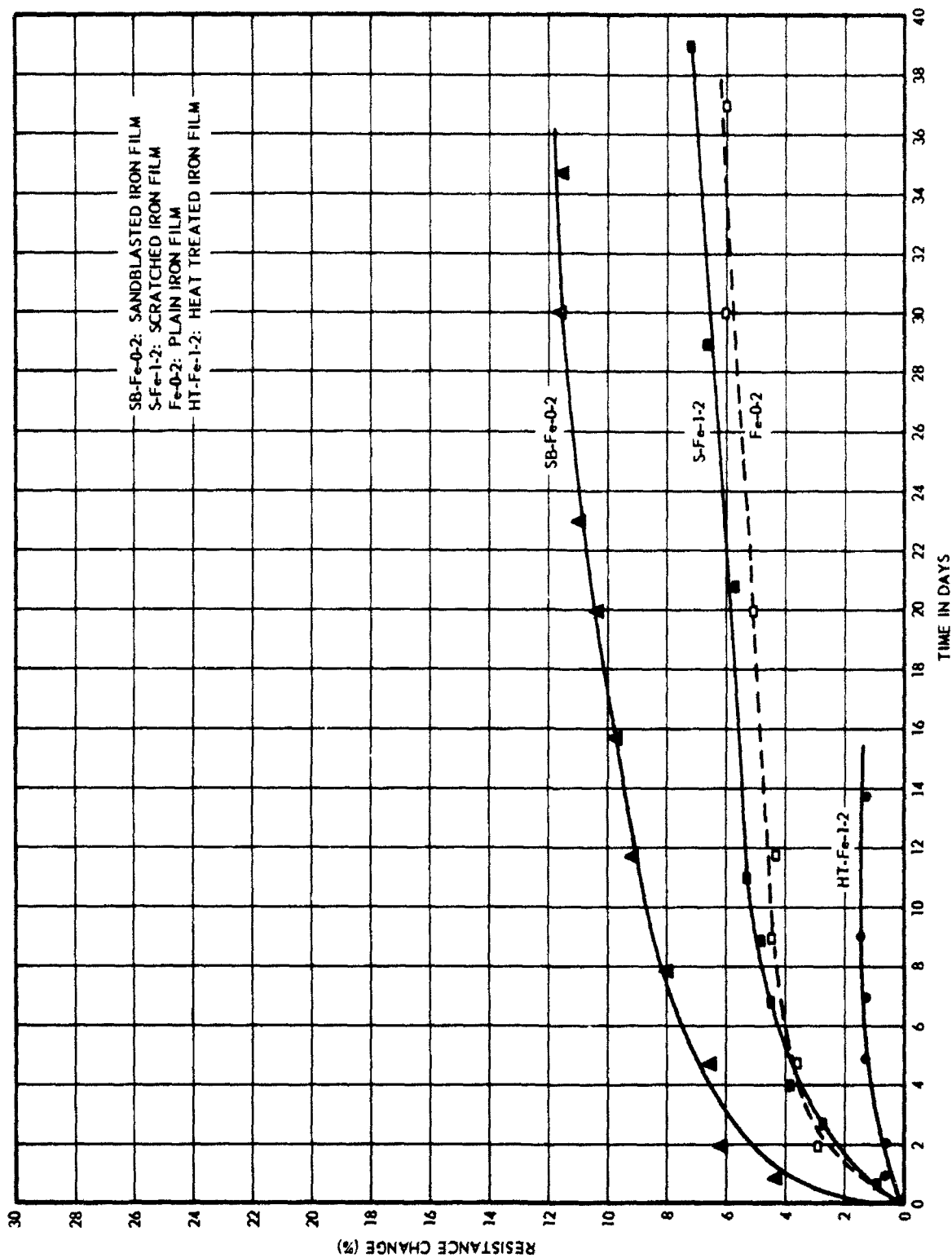


Figure 8. Data Exhibiting Corrosion Rates of Typical Iron Film Specimens Prepared after Revision of Cleaning and Storage Procedures.

b. Effect of Thickness

Iron films tapered in thickness were prepared by evaporating iron onto a substrate located so that the evaporating atoms struck it at incident angles in the range 90 degrees to some very small angle. The resultant films over the length of a microscope slide varied in thickness from a value at one end near 1000 Angstroms to a value of less than 100 Angstroms at the other end. Electrical connections were made to the film at five positions spaced approximately $1/4$ the length of the specimen apart.

The specimens were exposed in chambers at 25°C and 70 percent relative humidity and records of electrical resistance changes were maintained for a period of 25 days. During a period of 20 days the thicker sections changed in resistance only six percent whereas the thinnest one changed 77 percent. A careful analysis of these data indicated that direct oxidation of the film for some 25 to 50 Angstroms must have occurred. Whereas this was an insignificant amount at 1000 Angstroms it became a relatively large proportion of the thinner film. This corrosion could not be detected by simple visual observation. A plot of corrosion data for a typical very thin film is shown in Figure 9.

Although it can readily be seen that the percentage resistance change for the thinner sections was sufficient to give an indication of the occurrence of corrosion in the exposure chambers it is unlikely that such films would be practical, i.e., the rate, being extremely sensitive to thickness, would be subject to large scatter when specimens were prepared in quantity. Furthermore, the corrosion observed was probably the growth of a film of a protective type of oxide in contrast to that of the porous unprotective type normally encountered on bulk steel specimens subjected to the more common and the more economically important electrolytic type of attack occurring at temperatures of 25°C and at relative humidities about 35-40 percent.

c. Effect of Post Heating

Twelve iron films were deposited on cold Pyrex substrates and post heated to 455°C for 18' in vacuo. These specimens corroded only about one percent in 14 days.

d. Iron Films in Bending Jigs

Four films of iron, mounted in bending jigs to place the film in tension as displayed previously in Figure 7, exhibited no corrosion visible to the eye in 60 days.

5. Summary

In general, it may be stated that iron films deposited on clean but cold substrates and not sensitized during fabrication or mounting

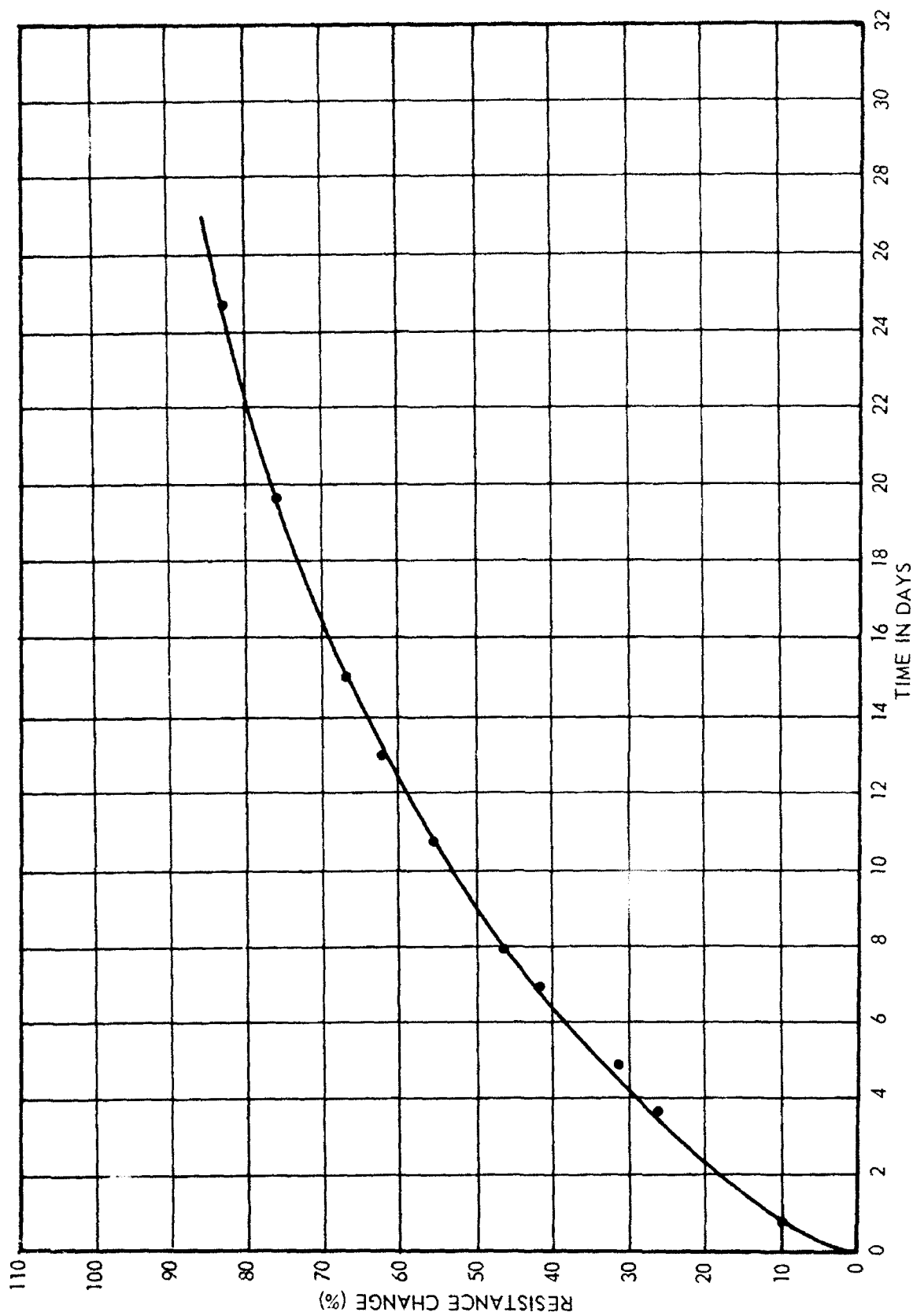


Figure 9. Plot of Corrosion Data for a Very Thin Iron Film ($< 100 \text{ \AA}$) Exposed at 25°C and 70 Percent Relative Humidity.

corrode only a few percent in a period of 60 days at 25°C and 70 percent relative humidity; considerably less corrosion than this is displayed when the substrate is heated to about 450°C during deposition or when annealed by post deposition heating in vacuo. If the surface area of the substrate be increased by etching or sandblasting, corrosion rate increases may be doubled. Studies of the tapered films indicated that corrosion rates may be increased by reducing the thickness of the films to values less than 200 Angstroms. However, films of this thickness appear to be impractical from the standpoint of preparation.

C. Studies of Salt Treated Films

As mentioned previously studies of salt treated specimens were conducted only during the early part of the last year's work. As the effect of the salt tended to override all other variables in the study except temperature and humidity it was decided to expand the primary effort of the project in studies of unsensitized films and to trace sources of sensitization being encountered without intent.

Eighty specimens were prepared by a method of spraying the salt solution onto the substrate with an atomizer and subsequently baking the substrate. The metal film was then deposited over the salt. The data collected are exhibited in Table III. It is apparent that a very small quantity of NaCl or NH_4Cl solution will sensitize the metal to relatively rapid corrosion rates. Non-uniformity in application resulted in non-uniformity of corrosion rates. There was a definite relative humidity level, about 35 percent, below which corrosion did not occur and above which corrosion was quite rapid.

D. Studies of Bimetal Films

1. General

During the first two years of this work extensive studies of bimetal layers of iron and copper overcoating one another in various geometries have been reported. In general, the result of a second more noble metal in contact with the iron is to accelerate the corrosion of the iron. The percent resistance changes for the "ladder" configuration, as explained in Wright Air Development Technical Report 59-149, was up to 39 percent in 60 days when the substrate was cold and about 16 percent when the substrate was heated to 450°C during deposition. A large part of the increase occurring was noted during the first ten days.

An alternate system that it would appear might accelerate corrosion is simultaneous evaporation of two metals onto a single substrate. This results in a film which has high stress within it and electrolytic cell material scattered through it. The result of an initial experiment is reported below.

2. Early Experiments

A set of bimetal films was formed by the simultaneous evaporation of copper and iron from separate filaments. The shutter in the system allowed the substrates to be exposed to the evaporating metal only after the evaporation of each metal had begun, and allowed evaporation cut off at a selected time such that the film sample was a relatively uniformly mixed bimetallic specimen.

Since the films were prepared in a mask and shutter system which held only two slides simultaneously the specimens were prepared in pairs. Because of control difficulties in adjusting exact rates of evaporation of two different metals considerable variation exists between pairs in thickness, initial resistance value, and rates of corrosion. The resistance data obtained for the films prepared is shown in Table IV.

If one extracts from this table the data for three specimens of similar initial resistance and thickness, namely films Nos. 433, 435, and 436, one finds that the behavior of film No. 433 represents the approximate average of the three. Likewise the behavior of films 431, 432, and 438 are similar, although the thickness of No. 438 is considerably less than that of the other two films.

The scatter in the initial resistance values is related to the different mixtures of the metals occurring during simultaneous evaporation; and low initial resistances are frequently correlated with complete segregation at some level of one metal from the other. Hence, one might have a continuous thin film of copper or of iron at the top or bottom of the film. This would contribute to a very low initial resistance measurement and may also account for a low corrosion rate.

A very interesting aspect of the corrosion behavior, however, may be observed by plotting values for the average percent increase in initial resistance obtained for a series of films such as those noted, i.e., 433, 435, and 436 or of films 437, 439, and 440 exposed at 25°C and 70 percent relative humidity. The corrosion thus indicated is relatively rapid as shown in Figure 10 and, for an extended period, up to 50 days, is almost directly proportional to time of storage.

3. Subsequent Experiments

A number of different approaches to alloy formation were subsequently made. The metals iron and copper were evaporated simultaneously from a single filament onto a hot substrate (450°C). This resulted in segregation, at the filament temperature used, because of the differences in vapor pressure and in melting points, 1083°C and 1533°C respectively. Separate filaments were then employed. However, because of the variation in evaporation behavior of the metals as outlined in the preceding section, III, D, 2, difficulty in control still existed even though data for temperatures versus voltages of the filaments were obtained by means of an optical pyrometer and a voltmeter.

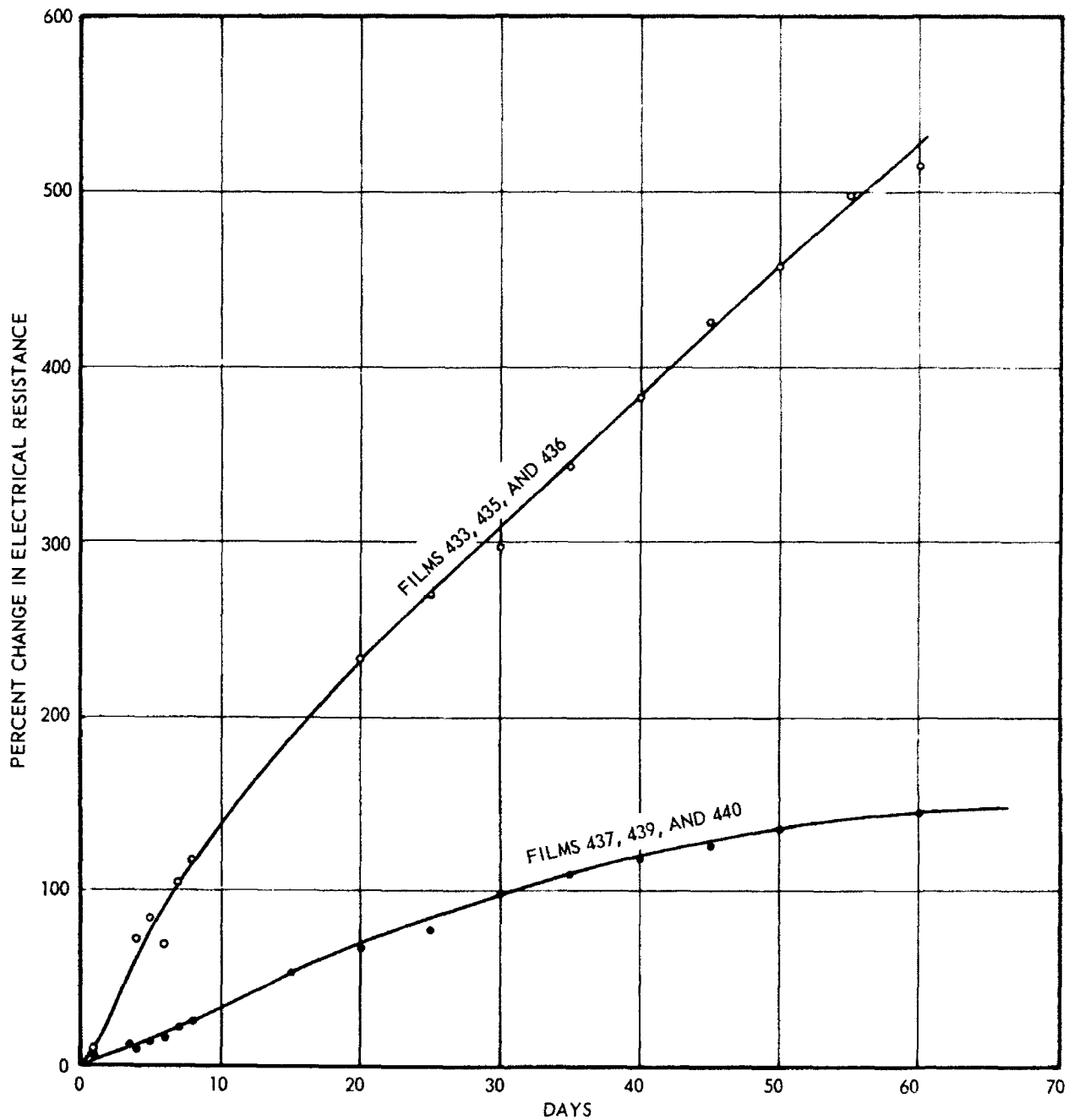


Figure 10. Plots of Electrical Resistance Data for Bimetal Films of Iron and Copper Prepared by Simultaneous Evaporation of the Metals onto a Glass Substrate, Subsequently Stored at 25°C and 70 Percent Relative Humidity.

Subsequently, films made by evaporation of successive layers of copper plus iron were given a heat treatment in vacuo to accelerate the diffusion of the two metals through each other. This process required a temperature cycle to nearly 550°C for a period of 20 minutes. During this period the glass slide actually softened and partially collapsed. Subsequently films were deposited on Pyrex substrates and heated as high as 750°C in vacuo. No specimens satisfactory for corrosion testing were obtained by this method.

A total of 24 films made by the various methods, except the last, were examined. The data obtained are exhibited in Table V.

One series of eight films consisting of successive layers of Cu + Fe without diffusion were also exposed at 25°C and 70 percent relative humidity. No appreciable corrosion occurred during a test period of 25 days.

4. Summary

In general, bimetal films of iron plus copper exhibited corrosion rates at 25°C and 70 percent relative humidity more rapid than that for films of iron only. For iron plus copper films the ladder configuration proved most satisfactory and rates up to 39 percent in 60 days were experienced in experiments reported in Wright Air Development Center Technical Report No. 59-149. Although films prepared by simultaneous evaporation of copper and iron have relatively high corrosion rates, difficulties in control of alloying proportions of the films contributed to a very large scatter in the corrosion rates observed. It is possible that control methods for properly proportioning the two metals could be worked out but this was not accomplished in the time allotted for the work under this contract.

The diffusion method of mixing films of iron and copper did not work out satisfactorily, as it required the heating of substrates to temperatures above 600°C. Iron and a second metal other than copper and more compatible with iron, i.e., either forming an intermetallic compound with it or more soluble in it, would probably interdiffuse more satisfactorily and give more uniform corrosion rate measurements.

E. Other Films

1. Magnesium Films Frictionally Applied

A series of films was prepared by frictional application of magnesium to glass as described in earlier work by Mr. Belser^{10,11}. A typical film is shown in Figure 11. Sixteen specimens were prepared and exposed at 25°C and 70 percent relative humidity and 12 at 40 percent and 25°C. Additional control specimens were exposed in a sealed jar containing a small volume of concentrated sulfuric acid for maintenance of

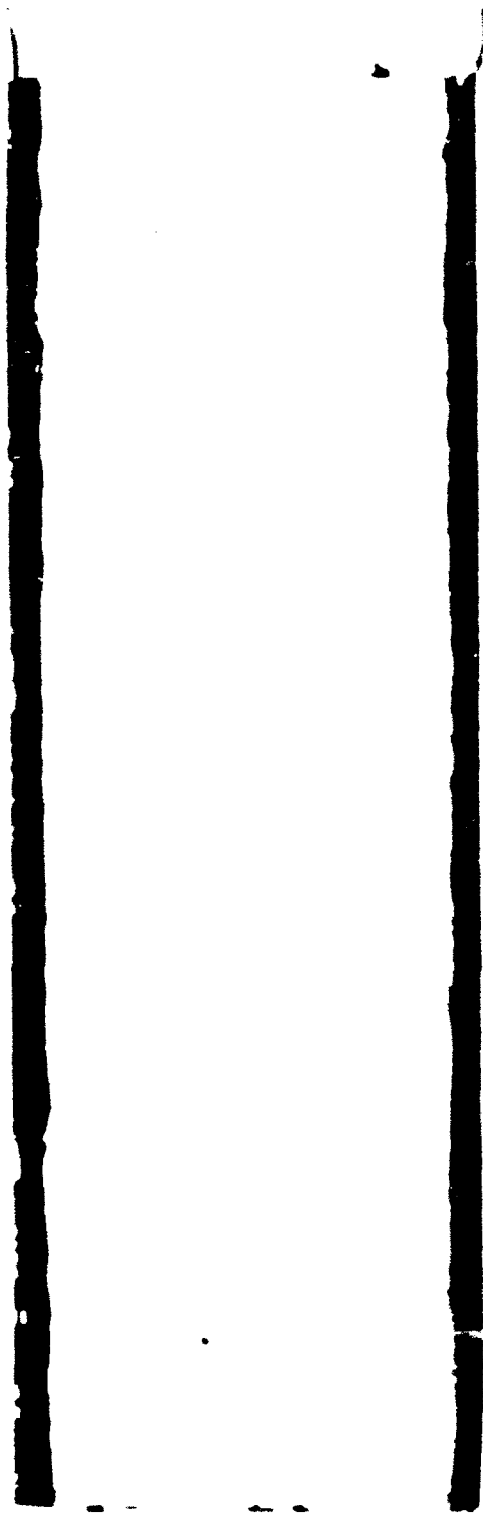


Figure 11. Glass Slide with a Frictionally Applied Magnesium Film in Narrow Lines.

a low humidity. Resistance measurements of the latter specimens revealed virtually no change whereas those exposed at 70 percent humidity underwent increases in resistance of 4 to 14 percent in 30 days. The specimens exposed at 25°C and 40 percent relative humidity likewise underwent resistance changes of one to four percent. The spread of resistance versus time plots is shown in Figure 12.

The magnesium films, frictionally applied to glass, exhibited corrosion rates characteristic of other metal films examined. A maximum corrosion of about 14 percent at 25°C and 70 percent relative humidity was experienced in 30 days while at 40 percent relative humidity; less than four percent corrosion was revealed.

2. Iron-Iron Oxide Films

One set of two films of iron-iron oxide was formed in the following manner. First an iron film was deposited by evaporation; next the film was annealed at 500°C in vacuo for ten minutes; then dry oxygen was introduced to the chamber while the film was still hot; next the chamber was reevacuated; and finally another layer of iron was deposited by evaporation. The two films exhibited electrical resistance increases of 10 and 16 percent respectively in 18 days.

However, the two specimens examined do not furnish sufficient basis from which to draw conclusions with regard to corrosion rate indicating values of such films.

F. Studies of Temperatures of Rapid Direct Oxidation of Metal Films

1. General

In previous studies conducted under Contract No. AF 33(616)-3870, "Electrical Conductivity of Metallic Films," reported in Wright Air Development Center Technical Report 57-660, it was shown that the plots of the temperature coefficient of resistance data of a metal film conducted in vacuo and in air could be utilized to detect the temperature at which the film began to corrode rapidly in air.

2. Studies of Iron and Nickel Films

This technique was used to study the corrosion of films of iron deposited on a Vycor substrate. A film of iron was deposited on a hot (400°C) Vycor tube which had previously been terminated at each end with baked platinum bright and a silver wire which was bonded to the platinum with silver paste. The dimensions of the film under test were approximately 1/2" x 1/32" and those of the Vycor tube were 1" x 9/32" diameter. After preparation the specimen was heated to 600°C in vacuo and its resistance was recorded at 50°C temperature intervals. The film was cooled and then heated a second time but in an atmosphere of air. The resistance

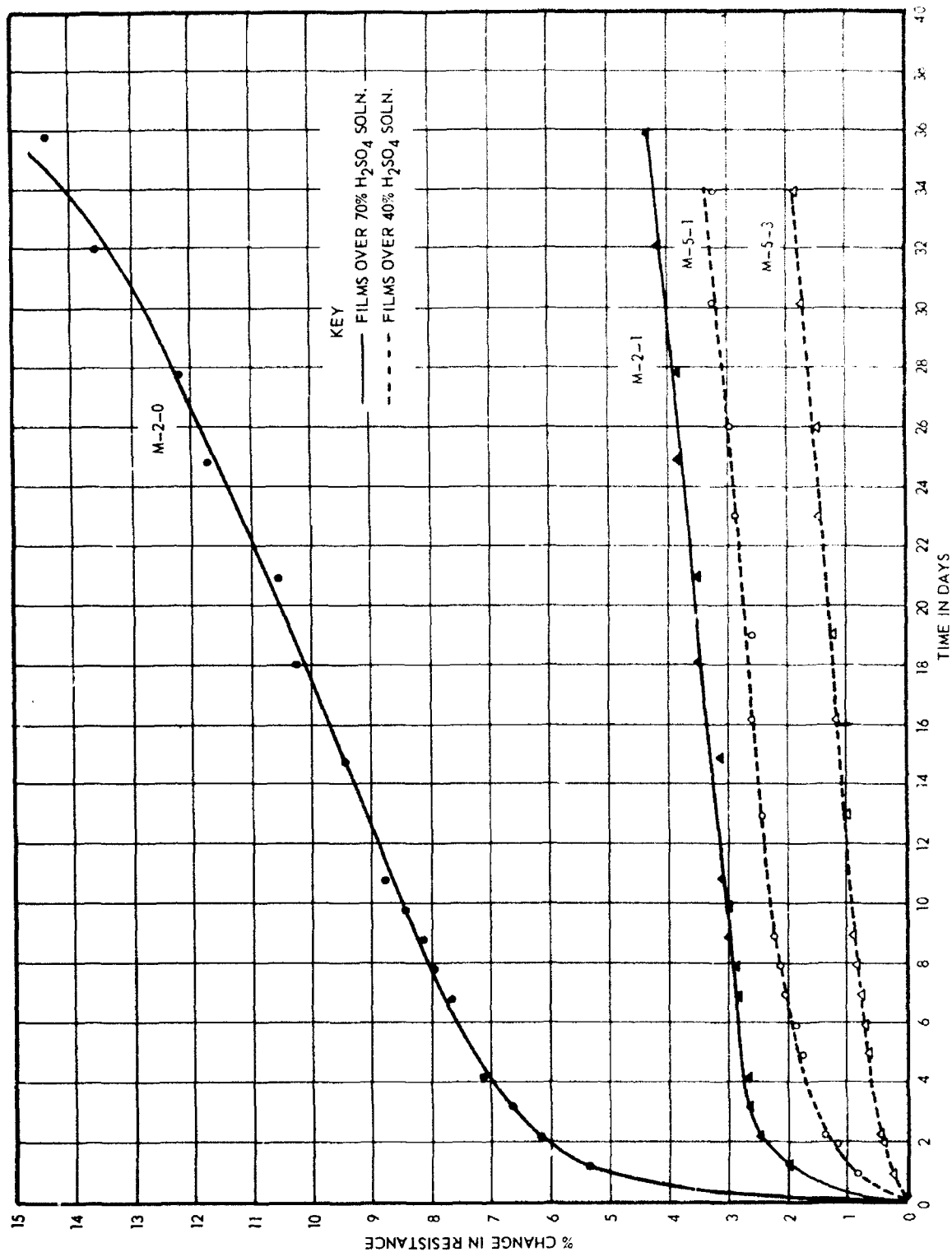


Figure 12. Plot of Resistance versus Time for Frictionally Applied Manganese Film.

was monitored as before. The data obtained are shown in Figure 13. These are replotted on a percent basis in Figure 14. During the temperature cycle the iron film decreased in resistance from the 22.5 ohms to 17.2 ohms, a reduction to 76.5% of its original resistance even though the film was deposited on a hot substrate⁹. The highest temperature coefficient of resistance observed was on the cooling curve of the initial temperature cycle, $0.0064/^{\circ}\text{C}$. This is approximately 43.5% the coefficient of bulk iron over the higher temperature ranges.

On the second temperature cycle the film departed sharply from its original plot at about 150°C . It is apparent that direct oxidation became rapid at this temperature.

Figure 15 is a plot of the resistance versus temperature data for an iron film deposited on a cool substrate and temperature cycled in air. Normally the plot should reveal at some point an annealing action displayed by a low or negative slope for a portion of the plot. One would expect this to occur around 350°C for iron as found for nickel films in the cited report WADC TR 57-660 and so shown subsequently for nickel in Figure 16, curve No. 1. However, Figure 15 shows only an upward slope which appears to increase in rate at about 200°C . This is ascribed to oxidation. A nickel film heated in air revealed rapid corrosion at approximately 250°C as noted in Figure 16 and in the paper cited in the previous paragraph.

3. Manganese Films

Studies of the corrosion of manganese films were conducted by means of the apparatus and methods outlined in paragraph F, 1, preceding.

Manganese films were deposited on substrates of vycor, cycled in vacuo to 600°C and cooled. Changes in electrical resistances were monitored throughout the temperature cycle.

Figure 17 gives a typical plot of data obtained. Subsequently the film was temperature cycled in air and its resistance change versus temperature change was monitored. These data are shown in Figure 18.

A somewhat thicker film deposited on a hot substrate, 350°C , was temperature cycled in vacuo and it exhibited as shown in Figure 19 a somewhat smaller irreversible resistance change than did the film for which data are exhibited in Figure 17.

The data presented indicate that manganese undergoes chemical attack within the vacuum chamber during temperature cycling to 600°C . Since the film exhibits a relatively low or negative temperature coefficient of resistance in the initial stages of the measurement it is evident that the film is highly imperfect in structure or that it may be interspersed with a considerable amount of its own oxide or other compounds. The

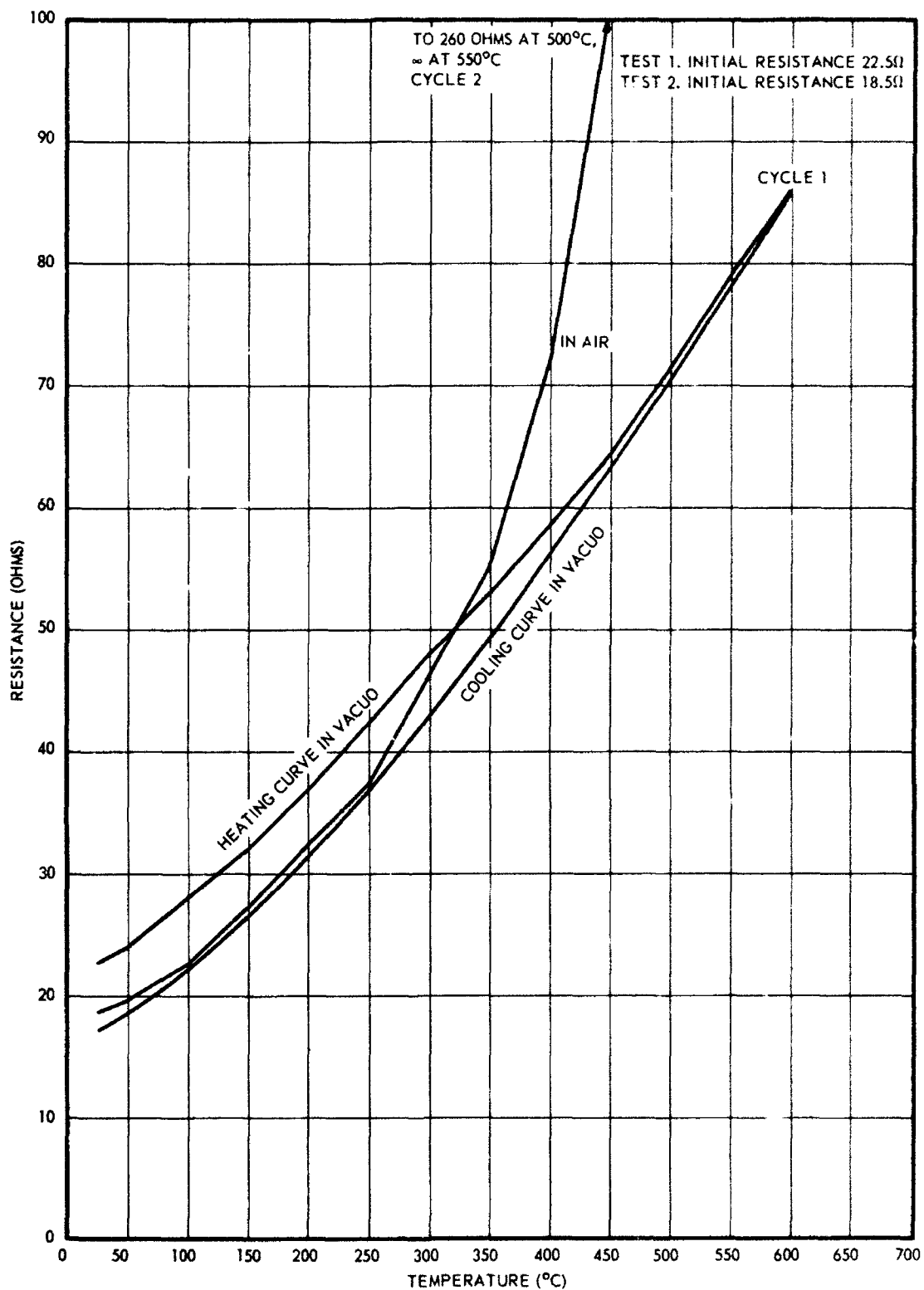


Figure 13. Plot of Actual Resistance versus Temperature Values for an Iron Film Deposited on Hot (400°C) Substrate and Heated First in vacuo and then in Air.

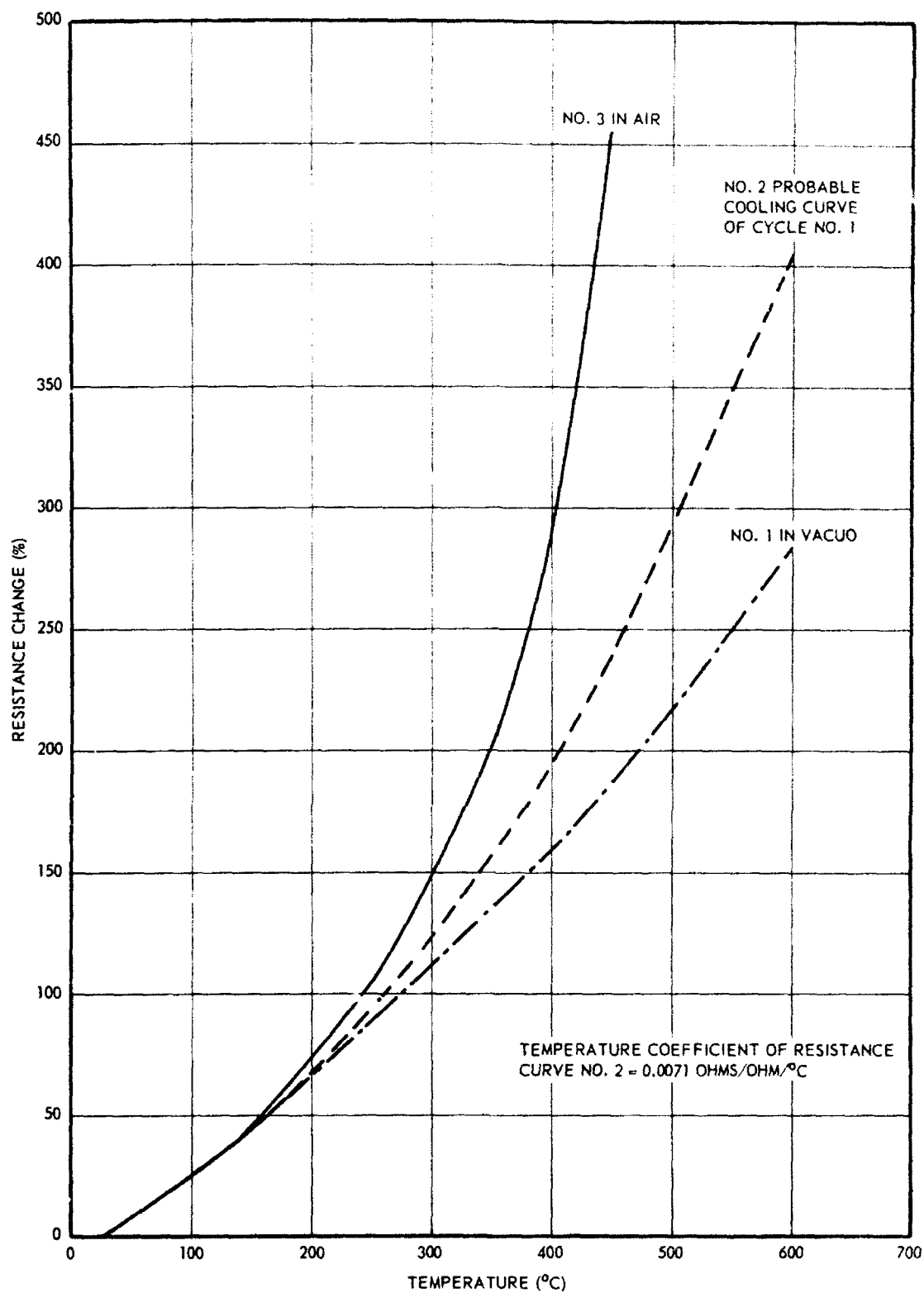


Figure 14. Percent Resistance Change versus Temperature Plots for an Iron Film Deposited on a Hot (400°C) Substrate and Heated First in vacuo and then in Air.

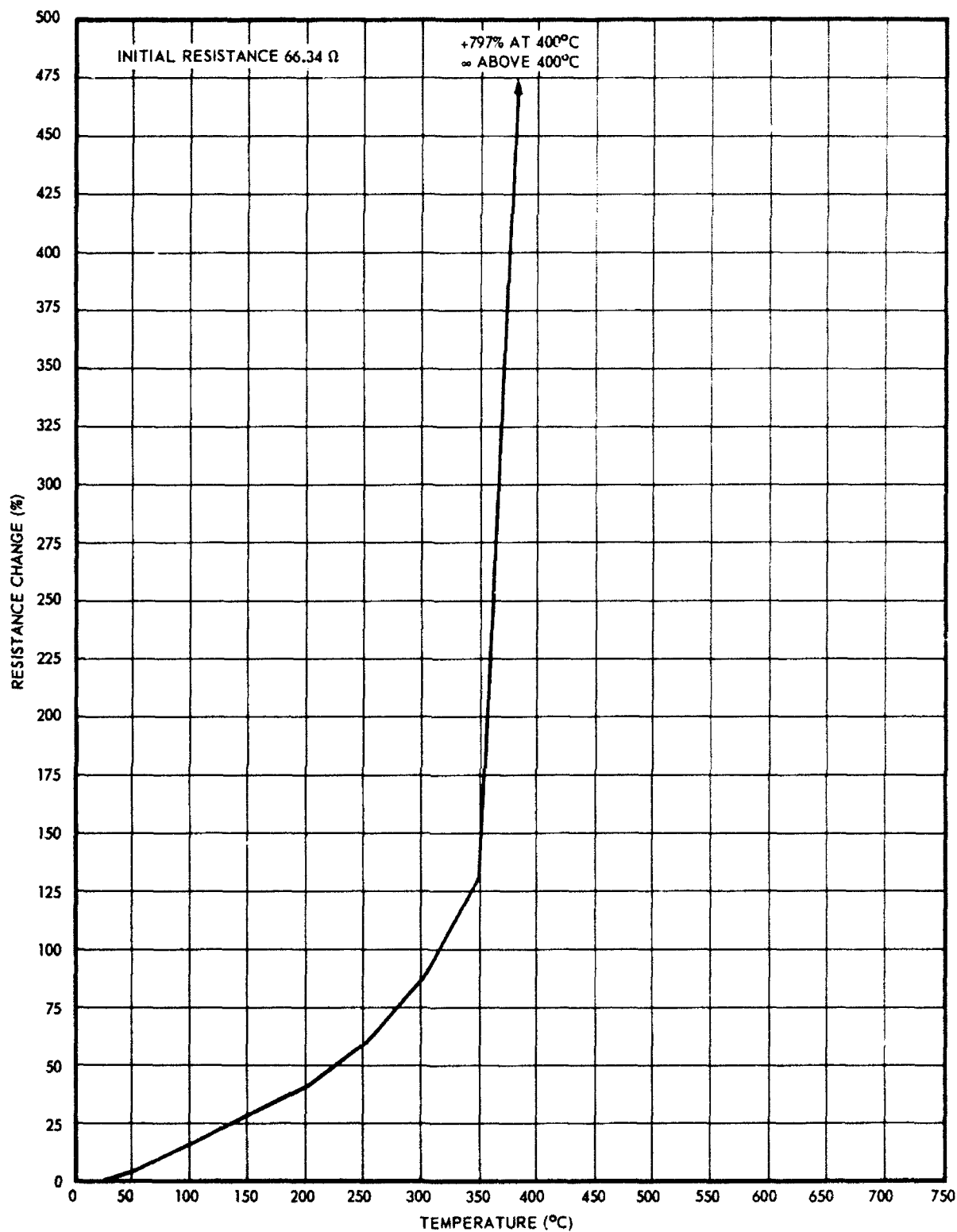


Figure 15. Percent Resistance Change versus Temperature Plot for Iron Film Deposited on a Cold Vycor Substrate and Heated in Air.

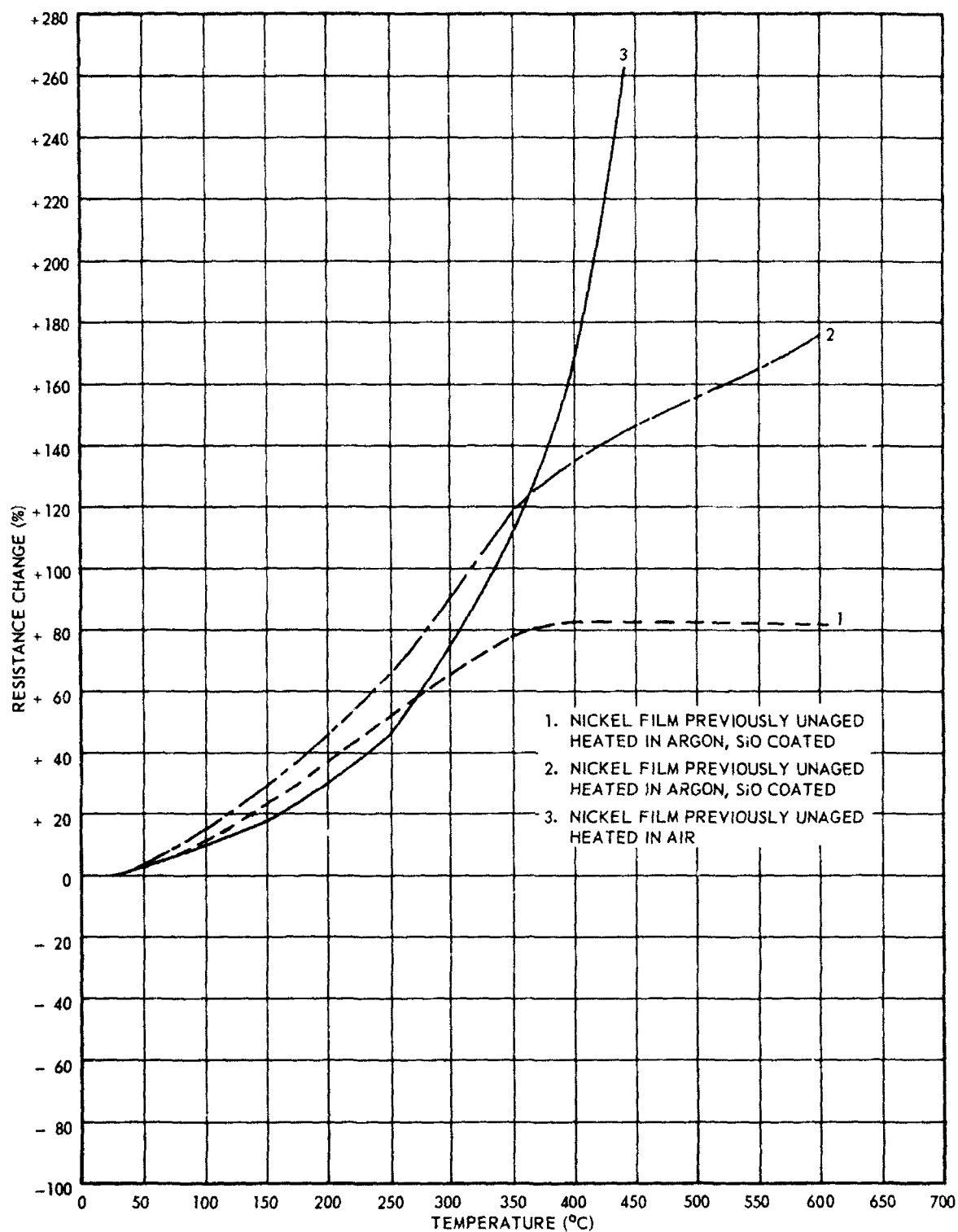


Figure 16. Percent Resistance Change versus Temperature Plots for Sputtered Nickel Films Deposited on Cold Substrates (One film was coated with silicon monoxide and heated in argon; the second was uncoated and heated in air, curve No. 3.)

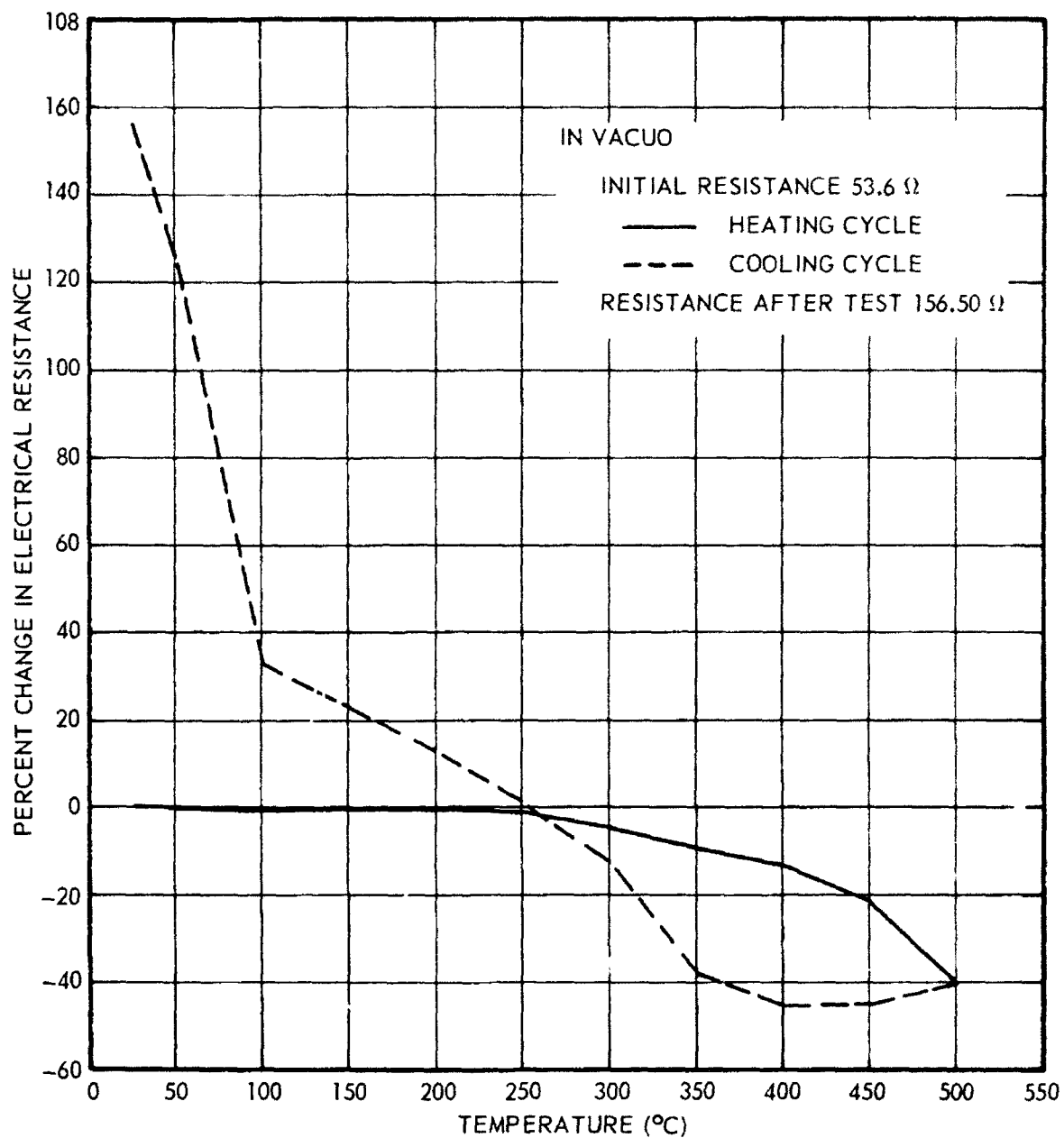


Figure 17. Plot of Electrical Resistance Data for Manganese Film
Temperature Cycled Through the Range 25°C to 600°C in vacuo.

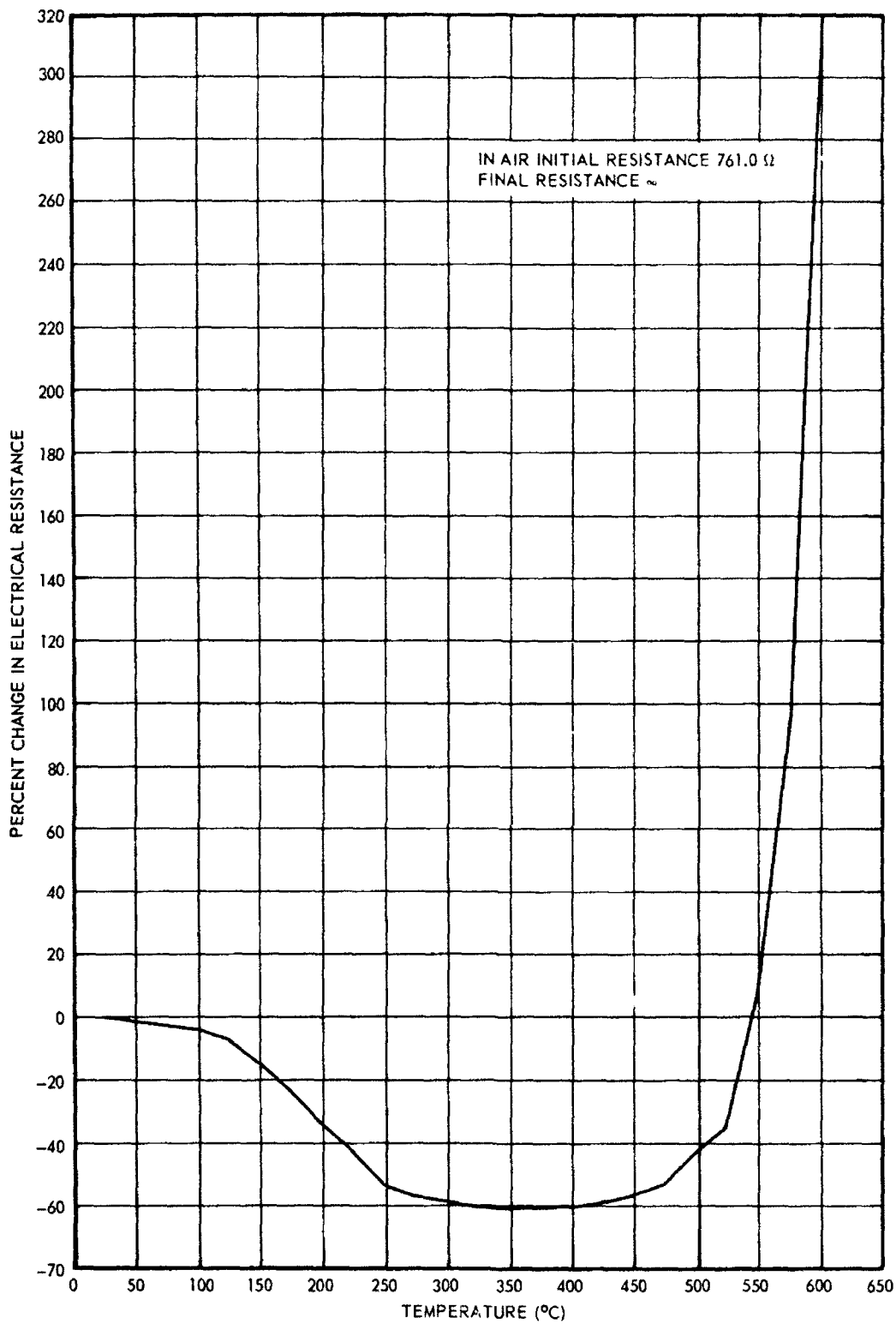


Figure 18. Plot of Electrical Resistance Data for a Manganese Film
Temperature Cycled Through the Range 25°C to 600°C in Air.

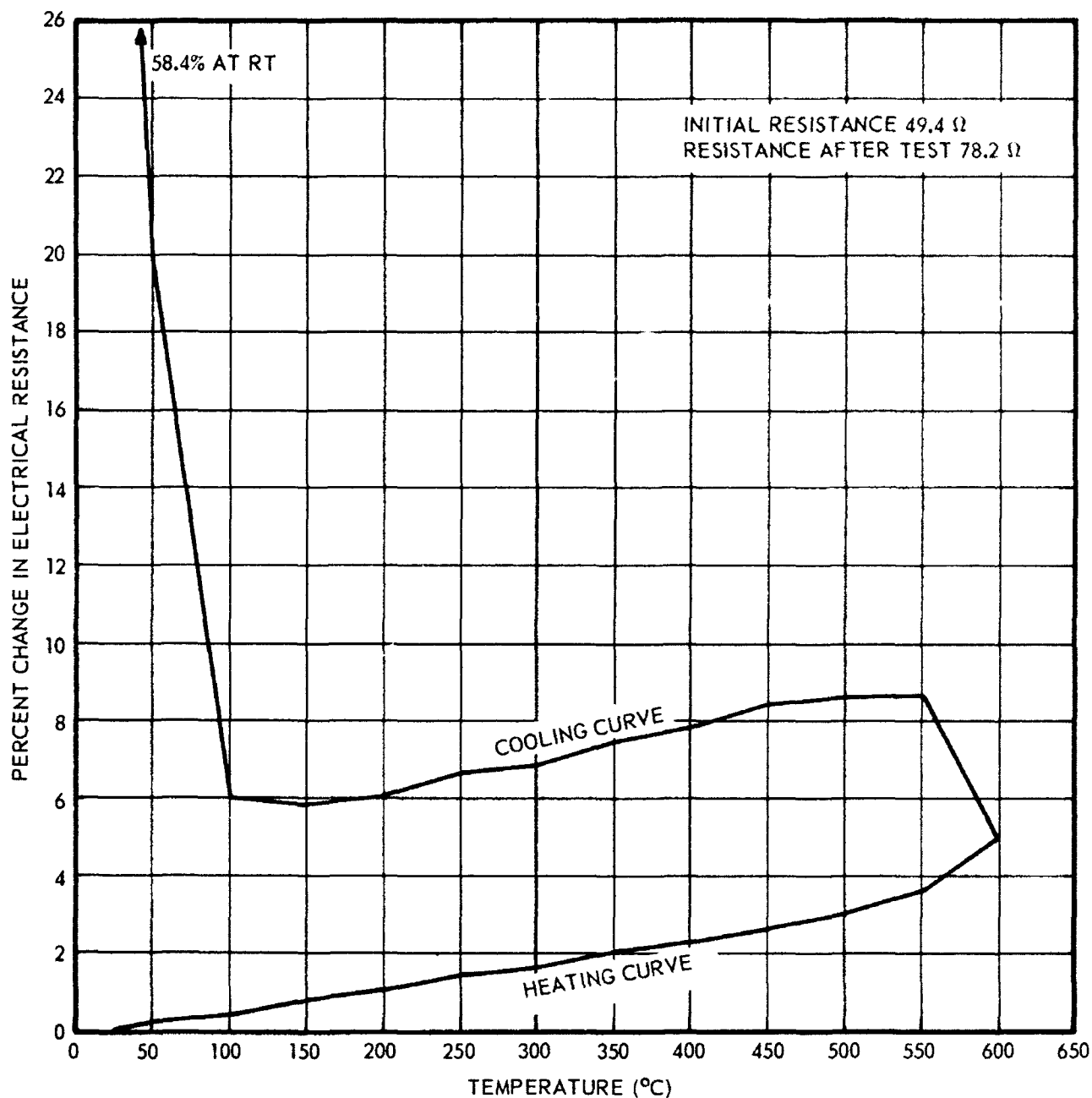


Figure 19. Plot of Electrical Resistance Data for Manganese Films Deposited on a Hot (350°C) Substrate and Temperature Cycled Through the Temperature Range 25°C to 600°C in vacuo.

high negative TCR exhibited in the cooling stage, especially at approximately 100°C, indicates that some previously unobserved phenomenon is occurring either in the film or in the connections to it. The complexity of the behavior prevents proper interpretation at this time; it indicates further that the corrosion of manganese films is more difficult to control than that of iron films and hence that manganese films are less desirable than iron films as indicators of corrosion.

4. Films of Other Metals

The oxidation temperatures of a number of other metals have been obtained in work previously outlined in Wright Air Development Center Technical Report 57-660 and in the paper cited in paragraph F, 1, preceding.

Examples of these are shown in Figures 20 and 21 for the metals tantalum and zirconium. In general, oxidation of films of some 15 semi-refractory and refractory metals examined occurred at or below 450°C with the exception of platinum, iridium, and chromium. Platinum showed no corrosion at 600°C and iridium only a small amount. Chromium exhibited corrosion at about 550°C. A remarkable characteristic of chromium is revealed in Figure 22. A film temperature cycled in air 600°C for eight cycles underwent successive increases in resistance at approximately 550°C. However, the temperature coefficient of resistance underwent virtually no change. It appears that the chromium must have oxidized gradually by a diffusion process through the oxide layer. This resulted in attritional corrosion without appreciable grain boundary penetration. Hence, the temperature coefficient of resistance remained virtually the same regardless of the thinning of the film by successive oxidation.

By use of this same method of the study of temperature coefficients of resistance of metal films one may examine the relative protective value of overcoating the films. Figure 23 displays the data obtained while cycling a tungsten film in air. It was possible to cycle this film three times in air to 600°C with only very small changes in electrical resistance, less than one percent during the period. Normally tungsten films have exhibited definite increases in corrosion at approximately 350°C.

5. Summary

The method of examining the temperature coefficient of resistance of a metal film in vacuo and in air reveals basic information concerning the corrosion behavior of metal films. This information is transferable to interpretation of the behavior of bulk metals. A similar study utilizing protective overcoating materials for the films reveals the relative compatibility and protective value of the overcoating materials and techniques. Hence, this method appears to be one which will give useful information about high temperature corrosion of metals and their protection from oxidation.

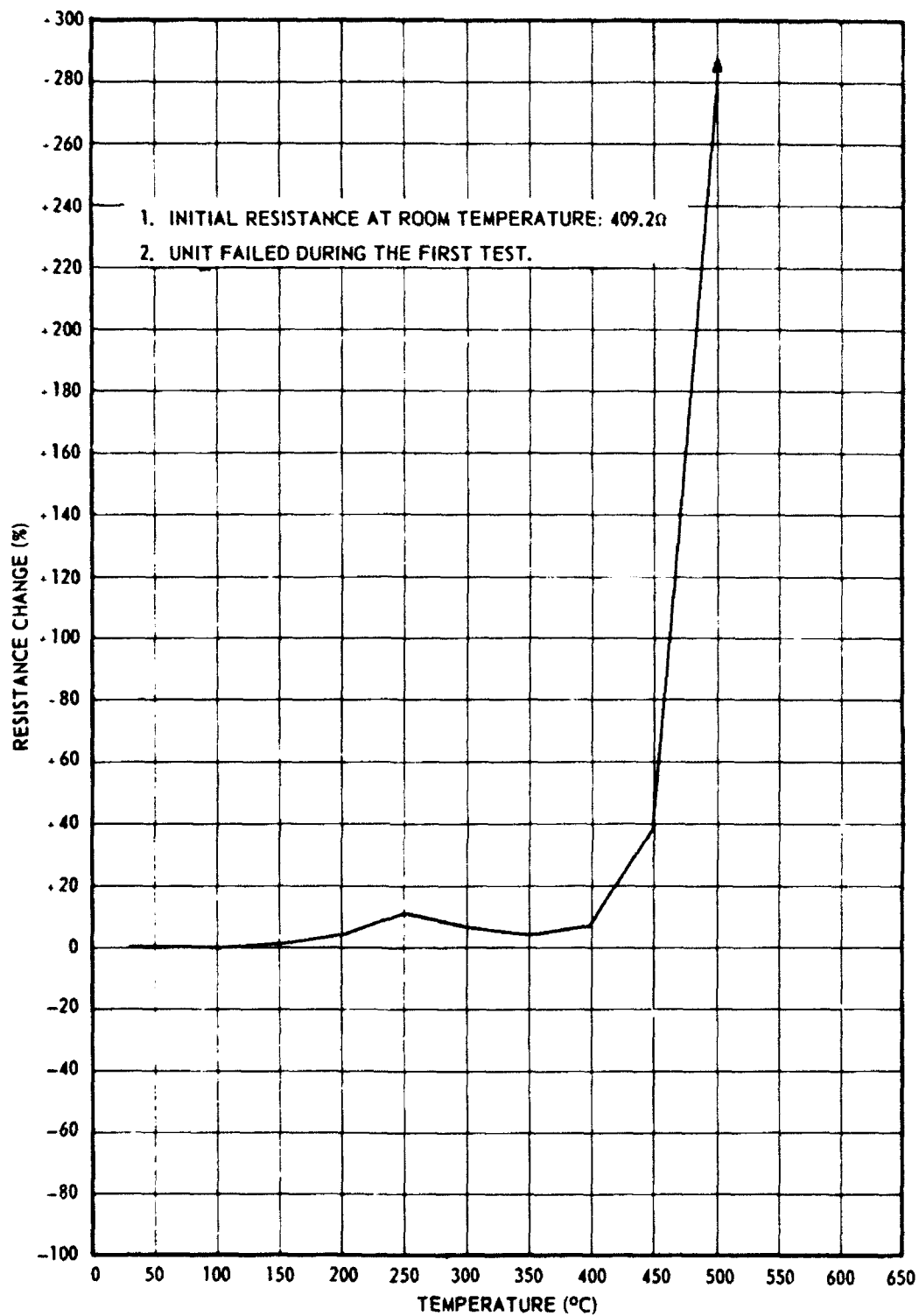


Figure 20. Temperature Coefficient of Resistance Data for a Tantalum Film Temperature Cycled in Air Revealing Rapid Onset of Corrosion at 400°C .

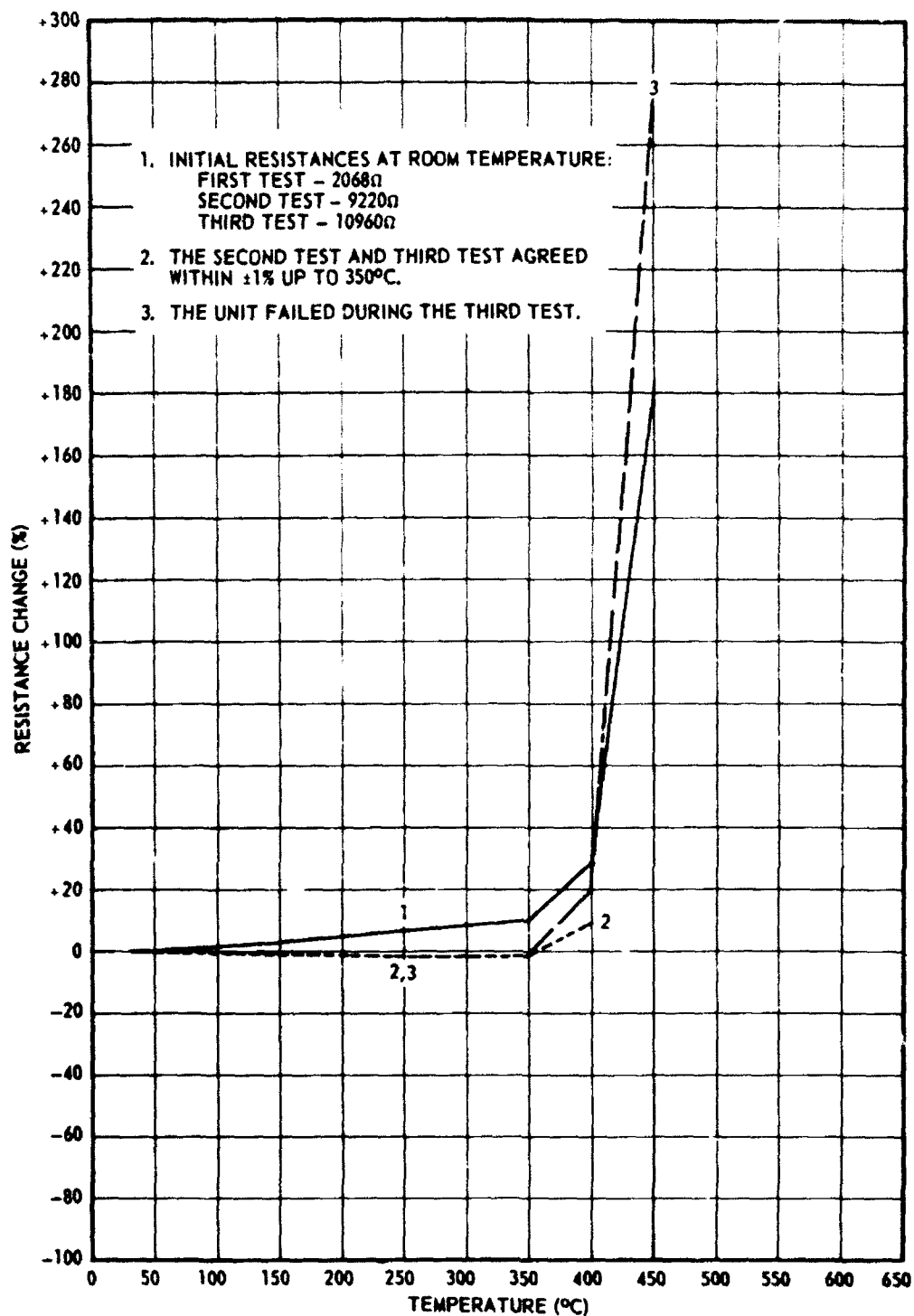


Figure 21. Temperature Coefficient of Resistance Data for a Zirconium Film Temperature Cycled in Air Revealing Rapid Onset of Corrosion at 350°C.

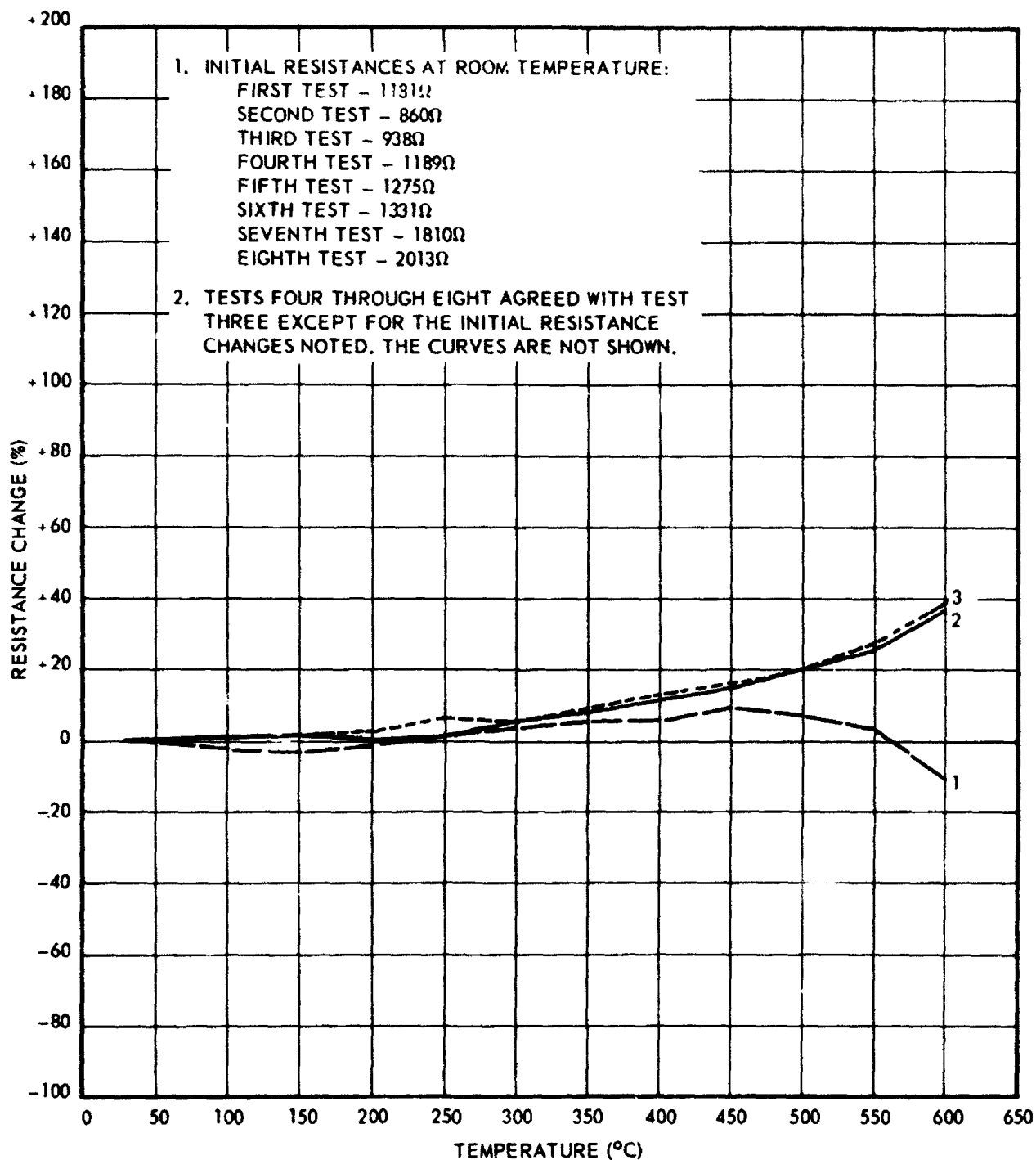


Figure 22. Temperature Coefficient of Resistance Data for a Chromium Film Temperature Cycled 8 Times in Air from 25°C to 600°C. (Note that although the resistance changed irreversibly above 550°C, the TCR below this value changed inappreciably on successive cycles.)

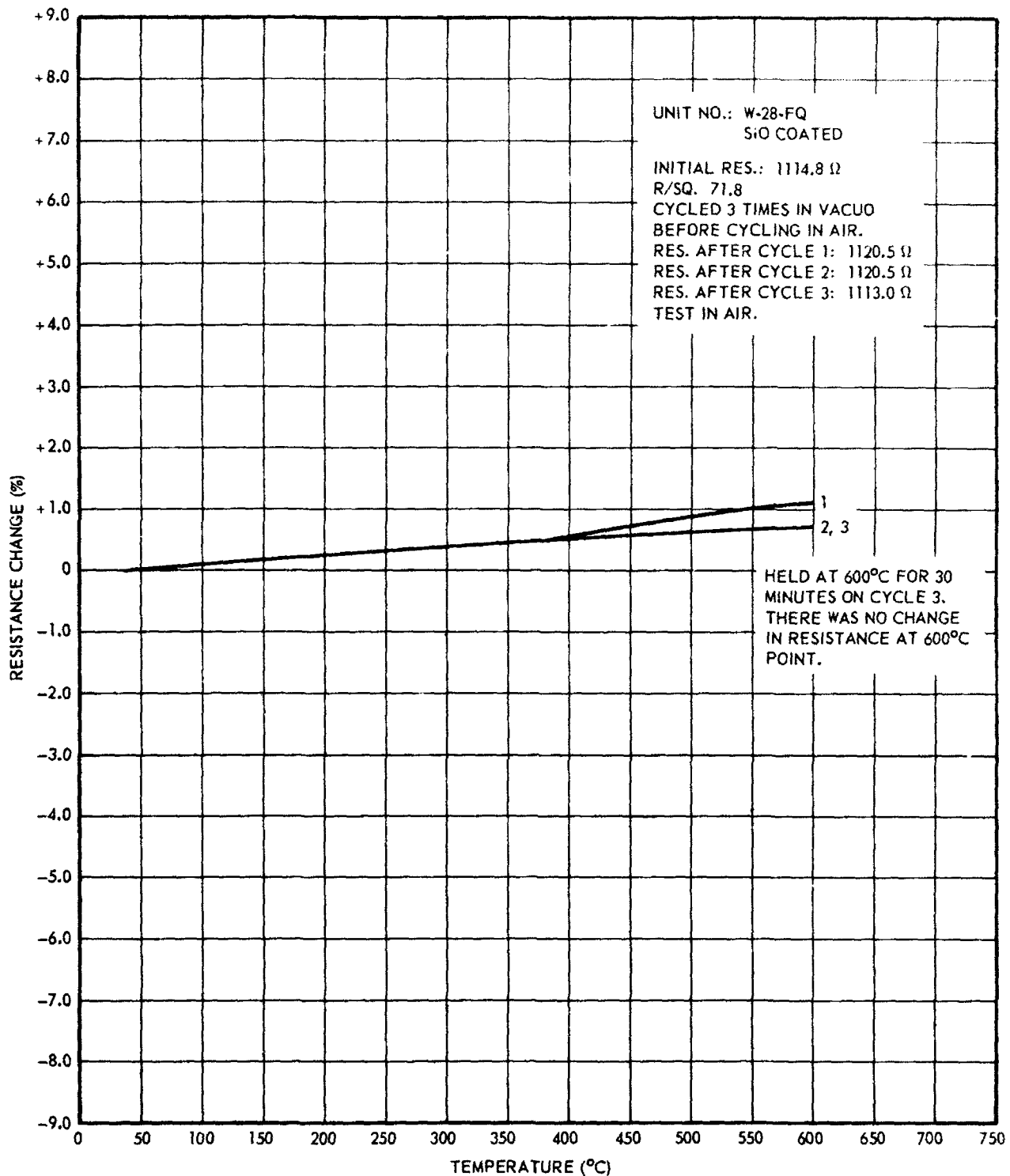


Figure 23. Temperature Coefficient of Resistance Data for a Tungsten Film, Overcoated with Silicon Monoxide, and Temperature Cycled in Air Three Cycles.

G. Corrosion of Bulk Steel Strips

Sixty-three specimens of rolled steel strip, a tool steel of about one percent carbon and Rockwell C Hardness in the range 52-55, were exposed in chambers in groups of three per chamber. The specimens were exposed in their received state after they were cleaned of all grease or other deposits by dipping in acetone or carbon tetrachloride and subsequently rinsing with isopropyl alcohol. Both sides of the specimens were inspected periodically for corrosion. The specimens exhibited small spots of corrosion in one to three days in the chambers at 25°C and 70 percent relative humidity. Very few specimens exhibited area damage greater than 3 to 5 percent in 60 days. Data collected are shown in Table VI.

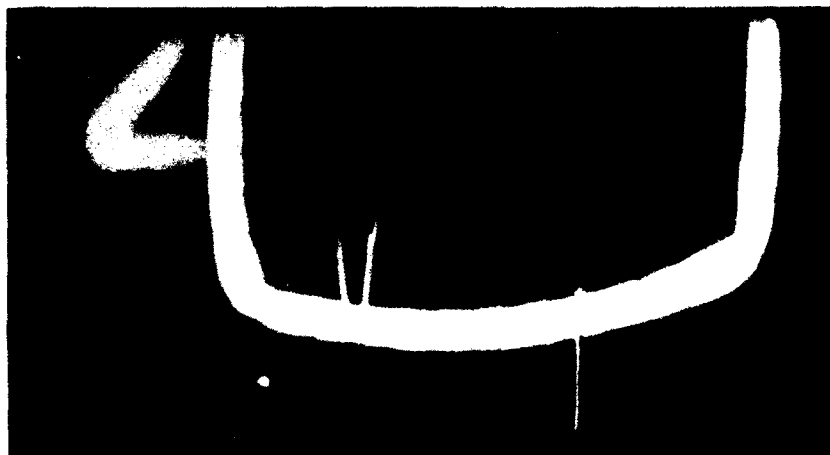
A few specimens exhibited 100 percent area damage overnight. These were prepared and inserted in the chambers at the same time that some iron films placed in the chambers exhibited similarly rapid corrosion. It is evident that these bulk specimens as well as the iron films were sensitized by some unknown chemical fume entering the laboratory during their preparation and installation in the humidity chamber. The correlation of the performance of the films and the bulk specimens, after inadvertent sensitization, revealed the great importance of handling techniques in fabricating corrosion indicators and the similar importance of preventing inadvertent sensitization of metal articles prior to packaging.

H. Other Experiments

1. Motion Picture Studies of Evaporating Metal

With regard to the selection of filament materials for preparation of bimetal films by simultaneous evaporation, motion picture studies of evaporating metal were made. A Fastex motion picture camera was set up and focused on a filament loaded with suspended metal hairpins. The arrangement consisted of a 4-inch glass cross with a plate glass window covering one end and the filament centrally located. The camera thus viewed the filament without distortion by intervening curved glass walls. At 500 frames per second the melting and flow of the evaporating metal over the the filament material could be discerned.

Iron wire "hairpins" suspended over a wire of stranded tungsten were observed to rotate about the filament in the electromagnetic field as the current passed through the filament. Evaporation began at the head of the hairpin and the respective legs of the hairpin appeared to sublime by shrinking into an invisible pool in direct contact with the filament. Copper and gold, on the other hand, flowed over the filament rather extensively. Typical behaviors are observed in Figures 24 and 25. Note



(A)



(B)

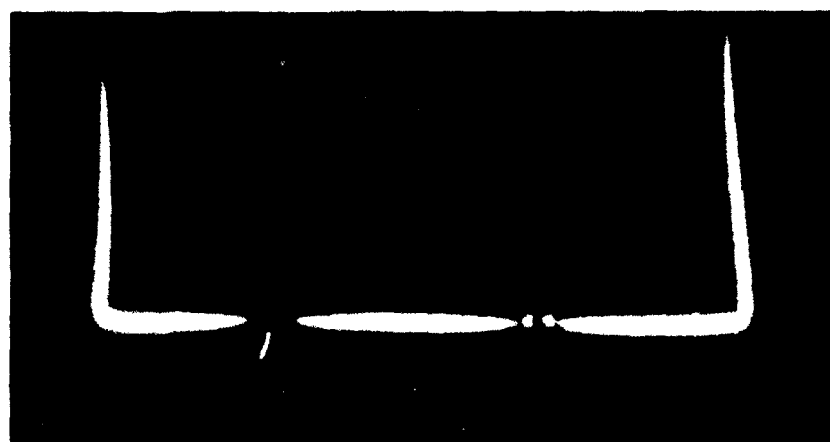


(C)

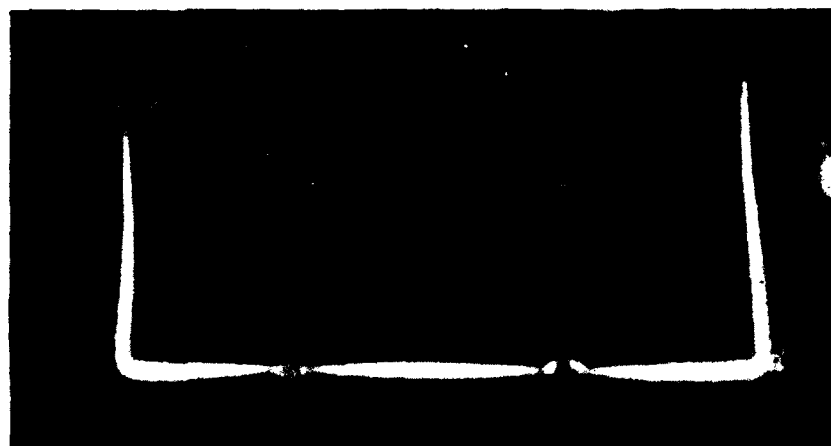
Figure 24. Successive Views of Iron Hairpins Evaporating from a Tungsten Filament.



(A)



(B)



(C)

Figure 25. Successive Views of Gold Hairpins Evaporating from a Tantalum Ribbon Filament.

that the sublimating iron* did not appear to cool the filament whereas the metals liquifying before evaporation did. From these studies it was determined that filaments of tungsten were the more suitable for the evaporation of iron because the alloy of iron with tungsten has a higher melting point than its alloy with tantalum. Tantalum is more suitable for the evaporation of gold or copper because it is wet better than tungsten by these metals.

The sections of movie film were attached to each other and edited into a short movie depicting the evaporation of the metals in a vacuum of 2×10^{-5} mm of mercury.

2. The Corrosometer

A corrosometer, developed by the Crest Instrument Company of Santa Fe Springs, California, for continuously monitoring small resistance changes in probes consisting of thin metal strips immersed in a corrosive environment, was obtained in August 1959. A study was made of this instrument and its adaptation to research on the corrosion of thin metal films.

Metal film specimens were prepared for test with this instrument by simultaneous evaporation of iron and copper. The film was divided in order to form two resistors of similar structure. One half of the specimen was protected with a coating of glyptal and the other half was left unprotected. Figure 26 shows a typical specimen.

Tests of a few specimens of this nature revealed high sensitivity of the corrosion rate to such actions as breathing on the specimen or even bringing one's hands near it. Records made over periods of more than 48 hours revealed unusual dips or changes in corrosion rate that appeared erratic as though the indication was affected by an unknown parameter related to temperature or voltage supply to the instrument. No satisfactory interpretation of these data was immediately realized and an investigation to clarify them was undertaken.

- - - - -

* An x-ray examination of the filament revealed that an iron-tungsten intermetallic compound was formed. During this action heat is liberated in the same order of magnitude as the heat of fusion of iron. All of the iron does not vaporize immediately; some remains as an iron-tungsten compound. Gold and copper, on the other hand, do not form intermetallic compounds with tungsten; the heat of fusion of these metals, therefore, causes the temperature of the filament to reduce to the melting point of gold or copper until the power input and heat conduction into the molten metal is sufficient to increase the temperature of the filament area covered by the molten metal.

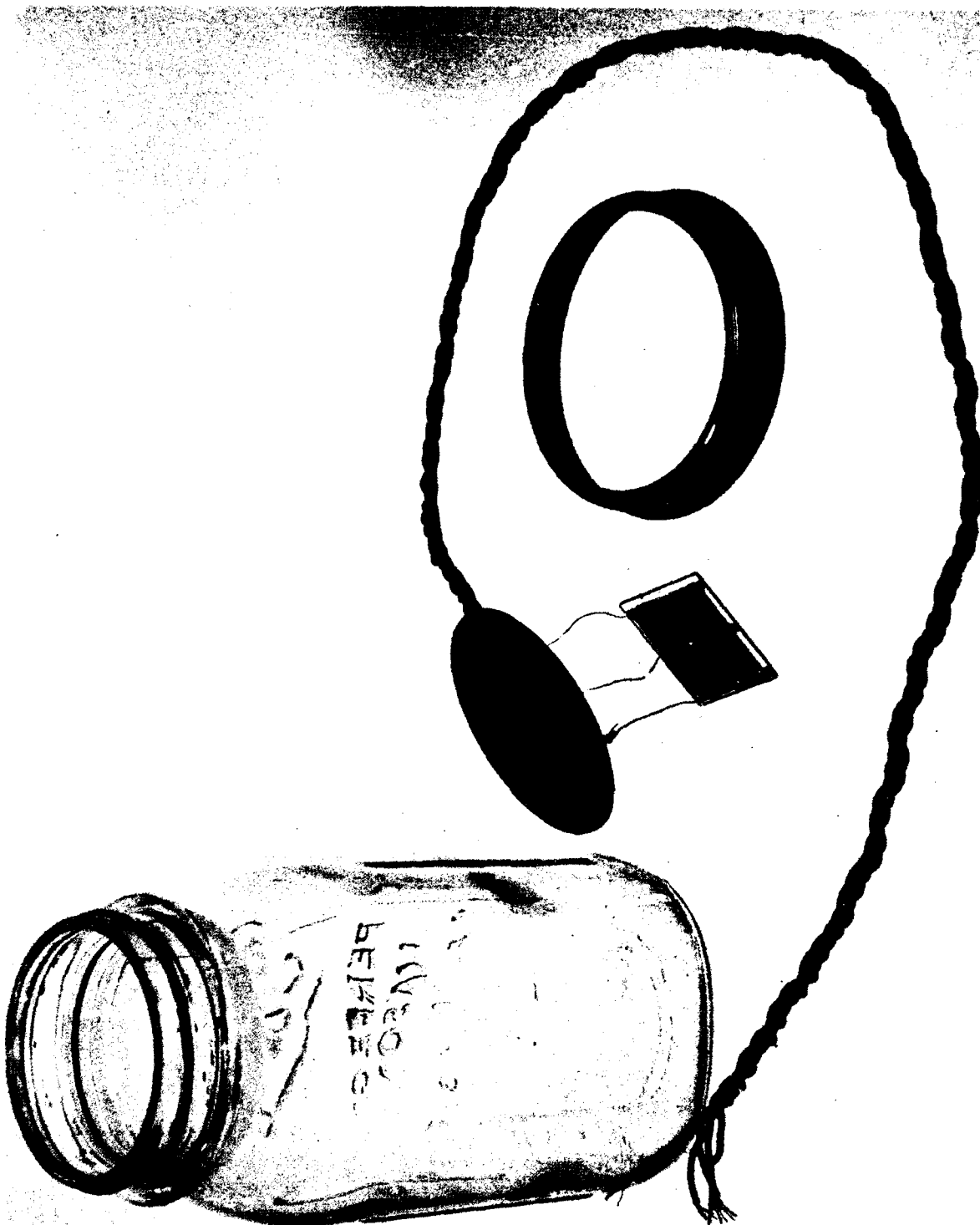


Figure 26. Typical Film Probe used with Corrosometer.

A check of the operation of the corrosometer revealed that the pick-off potentiometer was defective. A replacement furnished (at no additional cost) by the manufacturer was installed and proved satisfactory.

A new film probe like the one in Figure 26 was constructed and connected to the instrument. Initial measurements appeared to be erratic and a further check was made for an explanation of this behavior.

Several precautionary measures were found to be necessary for effective operation of the corrosometer. The effects of stray magnetic fields are nullified by tightly twisting all leads; and the effects of changes in temperature due to radiation effects on the glass and metal surfaces of the film can be reduced to a negligible influence by wrapping copper foil about the constant humidity jars. All connections to the metal film specimen must be carefully soldered. The leads should not be moved during a measurement.

It was found that when the pickoff potentiometer wiper travels past the end of the resistance element, the input circuit to the recorder opens momentarily, and the recorder pen may be expected to swing rapidly back and forth across the chart. A simple low-pass filter, a 500-ohm resistor in series with the signal path and a 250-microfarad capacitor shunting the recorder input eliminated this difficulty. The response time of the corrosometer is long compared to the filter, so the records were unimpaired by the presence of the filter.

Calibration measurements were made to determine the departure from linearity of the corrosometer indication. Figure 27 is a plot of the calibration. It can be seen that a $\Delta R/R$ range of ten percent corresponds to approximately a one-percent departure from linearity. Changing the reference resistor from 10 to 1000 ohms did not affect the calibration curve and use of either external or internal bridge supply voltage also did not affect the results.

When the precautions outlined above were strictly observed, the corrosometer was found to be a satisfactory instrument for recording corrosion rates of thin metal film specimens. These measurements are subject, of course, to the error of non-linear indication when $\Delta R/R$ is high; but the error can be corrected with the calibration curve of Figure 27.

Unfortunately, the time remaining for examining film specimens, after the thorough electronic check-out of the corrosometer and the elimination of procedure variables, was so short as to allow only a few experiments to be conducted. A film made up as depicted in Figure 26 was allowed to run for 64 hours in a container maintained at 25°C and 70 per cent relative humidity. The section of the film used as a control element for the double Kelvin Bridge at the temperature of varying resistance was coated with glyptal. The satisfactory curve shown in Figure 28 was obtained. The points for the curve were taken from the strip-chart record of the corrosometer.

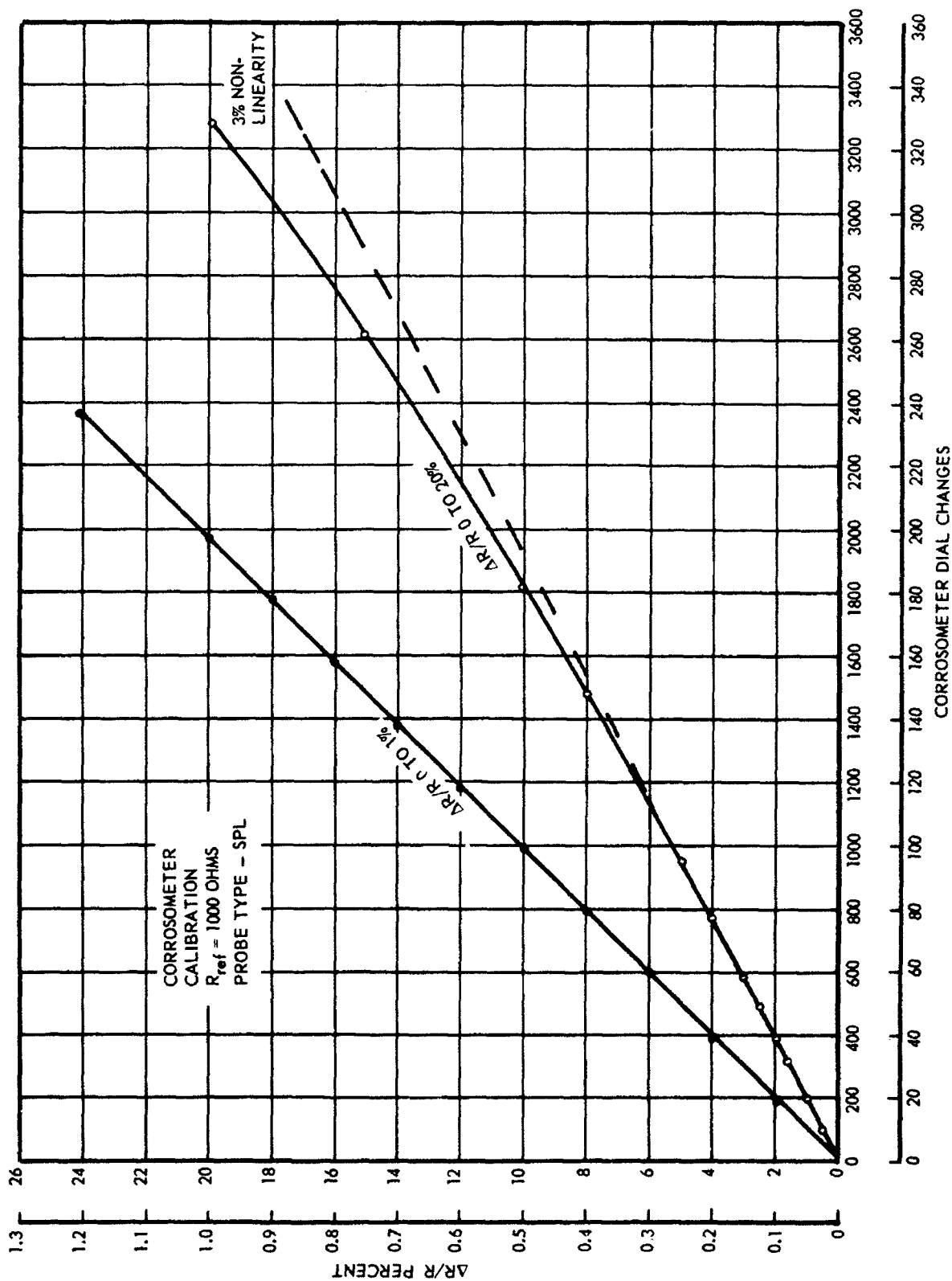


Figure 27. Corrosometer Calibration Data for Correction of Non Linearity of Indication when the Ratio $\Delta R/R$ Encountered is Large ($> 1\%$).

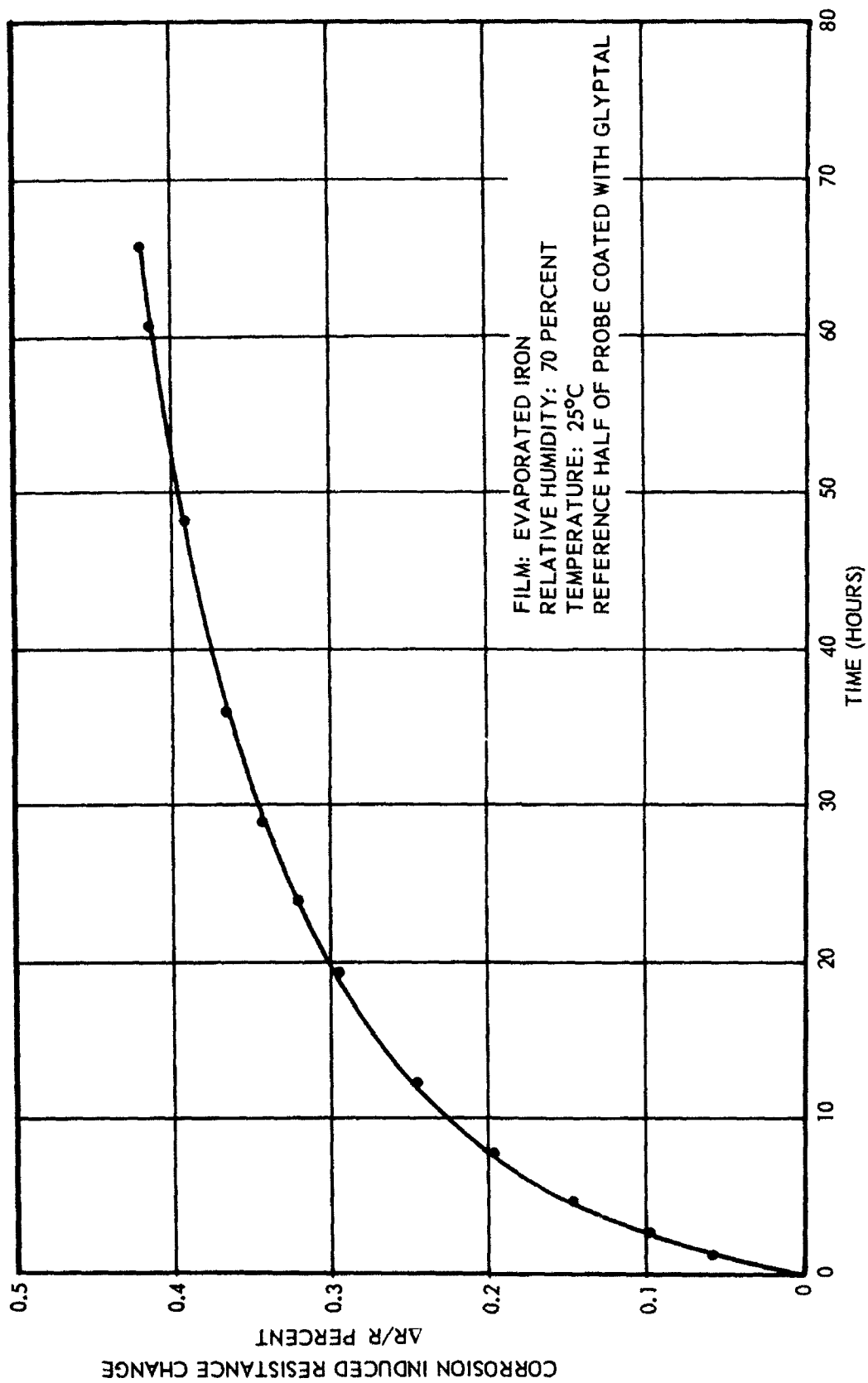


Figure 28. Data Extracted from Corrosometer Trace for Iron Film Exposed at 25°C and 70 Percent Relative Humidity. Reference Film Position Coated with Glyptal.

The corrosometer was used to compare the effectiveness of glyptal and lanolin as corrosion inhibitors. One half of an iron film specimen, such as that shown in Figure 26, was coated with glyptal; the other half was coated with lanolin. A record was then made of the relative change of resistance of one half with respect to the other half. The curve of Figure 29 records the results of the experiment.

The initial part of the curve of Figure 29 indicates the rate of corrosion under lanolin was slightly faster than under glyptal, but after about four hours, the trend reversed. During the next 36 hours, corrosion was faster under glyptal than under lanolin.

At the 18-hour point an attempt was made to rinse away the lanolin by immersing that half of the probe a number of times in xylene. Fresh solvent was used for each rinse, and the excess lanolin could be seen to dissolve quite rapidly. Apparently, however, a corrosion inhibiting layer of lanolin remained.

At the 40-hour point, two drops of salt water were placed on the lanolin coated half of the probe. The rapid corrosion which resulted is apparent in Figure 29.

At the 43-hour point, the probe was rinsed with tap water so that the salt induced corrosion was halted. The corrosion rates on the two halves of the probe were then observed to be nearly equal for the remainder of the experiment.

The preliminary data collected revealed the corrosometer to be a highly sensitive indicator of corrosion of the film elements made. Although insufficient data were obtained to completely evaluate the corrosometer the evidence obtained indicated that it would prove a useful accessory to studies of corrosion made over a suitable period of time. Further investigation is needed, however, to find a coating which completely inhibits corrosion on that half of the specimen which serves as a reference resistor. The curve of Figure 29 shows that corrosion under glyptal may be nearly as rapid as on an unprotected film; and the actual corrosion rate would then be considerably faster than the curve of Figure 28 indicates.

As a parallel result of this work it appears that the corrosometer may be a useful tool in studying the corrosion protective or inhibiting effects of thin films of organic or inorganic substances overlying a metal film. In truth, this could be its most important contribution as it would allow comparisons of the relative protective values of various substances for underlying films in atmospheres known to be highly corrosive in nature. A rapid evaluation of the protective nature of organic or inorganic finishes could well be a result.

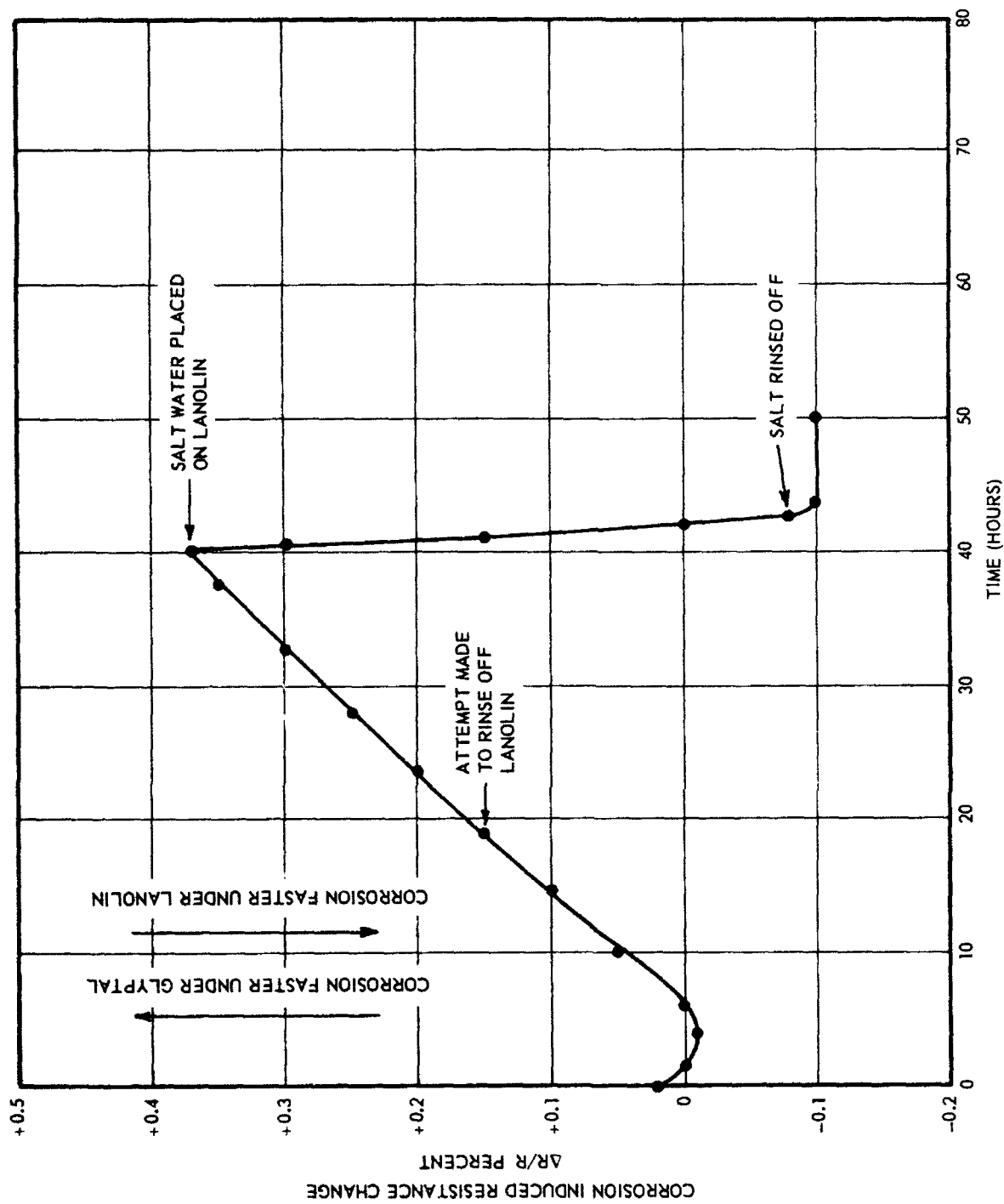


Figure 29. Data from Corrosometer Trace Showing Comparison of Glyptal and Lanolin Used as Protective Coatings over an Evaporated Iron Film.

SECTION IV

DISCUSSION

The experiments presented have revealed the primary factors affecting the corrosion rates of thin metal films and the difficulties in the control of each one of these in such a manner as to prepare a film corrosion indicator with a predictable and useful calibration. Whereas films of virtually zero corrosion at 25°C and 70 percent relative humidity in periods of over 60 days were readily prepared, to meter back into these a corrosion nucleating condition of a known and useful degree was most difficult and never truly achieved.

It is true that iron films were sensitized chemically by salts or vapors to give corrosion rates that were triggered by relative humidity conditions of 35 to 40 percent at 25°C; however, the influence of the salts was so strong as to overpower all the lesser factors contributing to the corrosion of the unsensitized film. Furthermore, no evidence has been determined in these experiments, or presented elsewhere, that corrosion rate scatter will not still be large with sensitized films where accurate time discrimination is made. It is true that the relatively rapid corrosion rates resulting for sensitized films at 25°C and 70 percent relative humidity have compressed time so that obvious and visually apparent corrosion may occur in a few hours instead of in a few days. However, it is also true that as the corrosion rate is reduced, corrosion scatter will likely increase because of the greater relative influence of the control parameters previously mentioned.

The factors that presently appear of importance in the corrosion rates of the basic film are:

- (1) The cleanliness of the substrate;
- (2) The temperature of the substrate during deposition;
- (3) The maximum temperature to which the substrate is raised subsequent to deposition and before exposure;
- (4) The purity of the metal film;
- (5) The smoothness of the substrate surface;
- (6) The thickness of the film;
- (7) The internal stress within the metal film - related to the method of deposit, pressure of deposit, rate of deposit, and temperature of deposit of the metal film;
- (8) The grain size and grain orientation of the metal film;

- (9) The handling of the film after removal of the film from the vacuum chamber and its storage before use; and
- (10) The presence of more electronegative metals in contact with the film (or dispersed in it; see (4)).

The effects of these factors except (8) have been pointed out in the experiments performed and (8) has been touched on indirectly by studies of films evaporated at several pressures and by sputtering. Films formed at pressures greater than 10^{-5} mm of Hg and by sputtering have smaller grain size and higher internal stress than films deposited by evaporation at a pressure of 2×10^{-5} mm of Hg or lower.

The effect of grain size appeared to be small although only a few experiments of this nature were conducted.

In general, the following statements may be made with pertinence primarily to iron films deposited on the respective glass substrates:

- (1) The cleaner the substrate the lower the corrosion rate of a film deposited subsequently upon it;
- (2) The higher the substrate temperature the lower the resultant corrosion rate;
- (3) The higher the temperature to which it is subsequently exposed in vacuo (not considering heating in air to any appreciable temperature) the lower the corrosion rate;
- (4) The greater the purity the lower the corrosion rate;
- (5) The lower the internal stress the lower the corrosion rate;
- (6) The smoother the surface the lower the corrosion rate;
- (7) The thicker the film the lower the corrosion rate;
- (8) The larger the grain size the lower the corrosion rate; (and probably the more uniform the orientation the lower the corrosion rate);
- (9) The less the handling and period of storage the lower the corrosion rate; and
- (10) The less electronegative the second metal the lower the corrosion rate.

Obviously the converse of each of these *maxims* is true and they are essentially applicable to all metals besides iron except where the recrystallization of the metal films may occur near or below room temperature. For these films the temperature effects would be different.

Certainly it is easy to see that with some ten parameters of known importance in corrosion rates of films corrosion rate scatter is an expected result.

Now the question arises as to whether films may be used as corrosion indicators at all - and the answer is yes. It has been shown that salt treated films do integrate, coarsely, conditions of temperature and relative humidity above about 35 to 40 percent although, obviously, once they have corroded such films only signify that an event has transpired. Likewise the rapid sensitization and corrosion of films by inadvertent fume sensitization, on occasion during handling, resulted in corrosion in 24 hours at 25°C and 70 percent relative humidity. Again the films signified that a corroding event other than temperature and humidity had transpired. Hence films would indicate the presence of such fumes in the laboratory.

Events of this type noted during the experiments were the operation of an FeCl_3 etching bath in a nearby laboratory, the opening of an HCl acid bottle in a room and nearby soldering with an acid flux. Hence, the unsensitized film records but does not identify such events, although conceivably corrosion products might be analyzed to furnish additional information.

Recently a report was made by Lodge, et al.¹², concerning studies of atmospheric pollution in the Cincinnati, Ohio, vicinity by thin metal films which showed correlation between observed corrosion rates of films and sensitizing pollution products over a period of some six months. The films in this case picked up the sensitizing agent and subsequently corroded at unreported conditions of temperature and humidity, although these could be obtained for the period from the U. S. Weather Bureau records. The higher rates were recorded in winter and the correlation was apparently with percentage of sensitizing agents in the air, primarily as the result of the presence of combustion products. Scatter of data was large; however, the evidence of pollution was definite.

It is apparent then that films can be used as indicators that corrosion events have transpired; it is also apparent that a series of films sensitized to trigger for certain events may be used to track the progress of certain types of corrosion phenomena. On the other hand, the probability of getting a single film to track corrosion progress as a calibrated indicator or integrator of total corrosion progress appears to be small.

Another matter of some significance to industry at large appears to be the implication that unintentional sensitizing of metal products to corrosion must frequently occur. For instance, only recently a stainless steel, type 304 plate was observed to corrode severely. Eventually it was discovered that a large soldering job, utilizing an acid flux, had been conducted nearby a few days previously.

On a second occasion hydrochloric acid was left in an open beaker for a few hours. The following day nearly every steel part in the room exhibited corrosion.

Attention to such details, proper desensitization of surfaces and subsequent protection of them by proper coatings appears to be a useful corrosion reducing method.

This study has reconfirmed the strong influence of some electrolytic phenomena in the support of corrosion; and, conversely, to point to the possibly grave importance of the electric conductivity or other electrical properties of greases, oils, paints or other finishes with the implication that high protective values must be closely related to high dielectric properties although undoubtedly other influence must exist as well.

Experiments with the corrosometer have indicated its possible use for the study of the protective values of organic and inorganic coatings with regard to metal surfaces. If this be true, and certainly there is good reason to believe it is, for the first time a rapid evaluation technique for such coatings is available. This feature alone appears worthy of definite and immediate further study.

A method of study of the corrosion of metals by use of temperature coefficient of resistance data for metal films over a large temperature range have been presented. This technique holds promise as an economical method of increasing knowledge of the corrosion and corrosion protection of refractory metals.

In conclusion, although the goal of a precisely calibrated film corrosion indicator has not been attained, indicators of corrosion events have been produced, and a method of monitoring corrosion progress by a series of corrosion-event indicators has been outlined. Furthermore, much basic information concerning corrosion phenomena has been presented; and new directions for profitable further research have been pointed out.

SECTION V

CONCLUSIONS

The corrosion rate of an iron film deposited on a glass substrate is affected by the cleaning history of the substrate and by the temperature of the substrate during and subsequent to deposition. In addition, the corrosion rate of the film is dependent on sensitization of the film subsequent to deposition, during handling, transfer or storage prior to use as a corrosion indicator. Other factors having effects on the corrosion rate are the relative smoothness of the surface of the film, the internal stress in it, and the thickness of the film.

The effects of these many factors, and the difficulties experienced in their precise control, result in film specimens exhibiting a large scatter in corrosion rates when exposed at 25°C and at relative humidities of 40 percent or above. If the films be intentionally sensitized by exposure to solutions of salt or of corrosive vapors, such as the fumes of hydrochloric acid, the films reveal very rapid corrosion rates (large percentages of area destruction in under 24 hours) at 25°C and at relative humidities of 40 percent or above. The effects of sensitization override the other parameters in the history of the films which normally control its corrosion rate and contribute to the large scatter observed.

Whereas the large scatter of corrosion rates prevents the true calibration of iron films as corrosion indicators which will denote on a standard curve a precise corrosion versus time position, these films do record corrosion events and integrate corrosive conditions of temperature and relative humidity with respect to time after sensitization.

The events recorded are the event of sensitization and the event of temperature and relative humidity increases, after film sensitization, above certain minimums such as 25°C and 40 percent relative humidity. Where statistically valid numbers of film indicators are employed the presence or absence of sensitizing fumes will be revealed by the films provided temperature and relative humidity conditions are above the minimums stated*. Likewise, once sensitized, the films will give a reasonable integration with respect to time of exposure to corrosive conditions of temperature and relative humidity above these limits.

The corrosion rates of films of other metals examined, magnesium, manganese and bimetal films of copper and iron, appeared to be controlled predominantly by the same general parameters of film history and handling as films of iron with the exception that films of specific metals are logically attacked to a greater or less degree by certain specific chemical species.

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* A relative humidity of 40 percent is sufficient for corrosion of a film to proceed but corrosion rates below temperatures of 25°C have not been examined.

The evidence of extensive corrosion effects resulting from sensitization both of thin films and bulk specimens supports the hypothesis that much corrosion of bulk metal materials may be the result of inadvertent sensitization of the metal articles during processing and storing, before packing and shipping. Proper care exercised during these phases should markedly reduce overall corrosion losses.

Plots of data relating to the measurement of the temperature coefficients of resistance of metal films furnish a method of examining the corrosion rates of metals at various temperatures and of measuring the protection of the metals provided by overcoating films of suitable materials.

SECTION VI

FUTURE PROGRAM

The studies reported have revealed many of the basic factors related to the corrosion rates of thin metal films and the correlation of the film behavior with that of bulk metal. Moreover, studies of the temperature coefficient of resistance plots of films of various metals have indicated temperatures at which film oxidation has become relatively rapid. Hence, a rapid and economic means of studying the corrosion behavior of expensive and/or refractory metals has been presented. Likewise studies of the corrosion protection of metals by the thin film method are feasible; comparisons of the relative protective values of various film substances for metals or metal films by means of the corrosometer appear possible.

It is recommended that work on studies of the corrosion and corrosion protection of the refractory metals be undertaken by thin film techniques, and that the corrosometer be evaluated as an instrument for studying the value of overcoating organic or inorganic films in protecting metal films or bulk metals.

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TABLE I

CORROSION RATES OF IRON FILMS DEPOSITED BY VACUUM EVAPORATION ON GLASS SUBSTRATES

Average Percent Resistance Increase or Area Destruction of Ten Iron Films on Glass Substrates as Functions of Cleaning Procedure and Time of Exposure in an Environment at 25°C and 70 Percent Relative Humidity

Specimen Identification	Cleaning Procedure	Exposure Time in Days							Comments
		1	3	5	10	20	30	40	
141-150	Standard	1	1	2	2	2	2	2	7 out of 10 behaved this way * 6 out of 10 behaved this way *
151-160	Standard - less flaming	100							
171-180	Standard - less flaming	95							
191-200	Standard - less blotting	95							
201-210	Standard - less blotting	90							No appreciable corrosion in 140 days 6 out of 10 behaved this way * 6 out of 10 behaved this way **
161-170	Standard - no blotting or flaming	< 1							
181-190	Standard - no blotting or flaming	95							
211-220	Acid only	< 1							
221-230	Acid only	95							No appreciable corrosion in 140 days 6 out of 10 behaved this way * 6 out of 10 behaved this way **
131-140	Acid + flaming	< 1						< 2	
251-260	Acid + flaming	< 1							
231-240	Acid, heater, shutter	< 1							
241-250	Acid, heater, shutter	< 1							No appreciable corrosion in 140 days No appreciable corrosion in 140 days

* Others showed less percent resistance increase.

** Others showed more percent resistance increase.

TABLE I (Continued)

CORROSION DATA FOR IRON FILMS DEPOSITED BY VACUUM EVAPORATION ON GLASS SUBSTRATES

Average Percent Resistance Increase or Area Destruction of Groups of Ten Iron Films on Glass Substrates as Functions of Cleaning Procedure and Time of Exposure in an Air Environment at 25°C and 70 Percent Relative Humidity

Specimen Identifi- cation	Cleaning Procedure	Exposure Time in Days								Comments
		1	3	5	10	20	30	40	60	
311-320	Acid	< 1	< 1	1	1	1	6	9	33	
321-330	Acid	< 1	< 1	< 1	< 1	3	11	13	37	
331-340	Acid	< 1	< 1	1	< 2	3	6	9	25	
341-350	Acid	< 1	< 1	< 1	< 1	1	< 2	3	10	
351-360	Acid	< 1	< 1	< 1	< 1	1	3	5	12	7 out of 10;
361-370	Acid	< 1	< 1	< 1	< 1	< 1	3	7	18	3 destroyed
371-380	Acid	< 1	< 1	< 1	< 1	< 1	< 1	1	3	
381-390	Acid	< 1	< 2	8	12	18	19	19	22	4 out of 10
		30	43	60	60	60	60	60	68	3 out of 10
		92	93	93	93	94	94	94	95	3 out of 10
391-400	Acid	76	95	98	99	--	--	--	--	Off test after 10 days
401-410	Acid	94	98	98	99	--	--	--	--	Off test after 10 days
411-420	Acid	< 1	8	14	30	--	--	--	--	2 out of 10
		17	42	65	65	--	--	--	--	2 out of 10
		83	95	98	99	--	--	--	--	6 out of 10
421-430	Acid	74	85	94	95	--	--	--	--	Off test after 10 days
281-290	Acid + H ₂ O + Blot	0	0	< 1	< 1	< 1	< 1	1	2	1 out of 10
291-300	Acid + H ₂ O + Blot	15	30	--	--	--	--	--	--	3 out of 10
		2	3	4	5	5	8	8	8	6 out of 10
		95	--	--	--	--	--	--	--	
301-310	Acid + Flaming	< 1	< 1	< 1	< 1	< 1	1	4	7	

TABLE II

CORROSION DATA FOR IRON FILMS PREPARED AFTER REVISION OF CLEANING AND STORAGE PROCEDURE

Average Percent Resistance Increase at 25°C, 70 Percent Relative Humidity

Code	No. of Films	Substrates	Total No. of Films	Exposure Time in Days								Comments
				1	3	5	10	20	30	40		
Fe-0	4	12	Soft glass, 25°C	1.3	3.3	3.5	4.4	5.1	6.5	6.5	Fairly uniform	
Fe-1	4	Soft glass, 25°C	1.3	3.4	3.5	5.6	5.8	6.8	6.7	Fairly uniform		
Fe-2	4	Soft glass, 25°C	3.0	4.6	5.1	6.1	6.8	8.0	8.0	1 high, 1 low		
T-Fe-0	4	Soft glass, 25°C, Tapered films	3-5 (ave) (4.2)	5-9 (ave) (6.9)	6-12 (ave) (8.6)	7-18 (ave) (11.6)	8-21 (ave) (13.5)	--	--	1 high		
T-Fe-1	4	" "	2-10 (ave) (4.2)	3-26 (ave) (6.9)	5-32 (ave) (8.6)	6-58 (ave) (11.6)	6-77 (ave) (13.5)	--	--	1 very high		
S-Fe-0	4	24	Soft glass, 25°C, Films scratched longitudinally	0.8	2.8	4.0	5.3	6.2	6.4	6.8	Fairly uniform	
S-Fe-1	4	" "	0.8	2.8	4.1	5.1	5.8	6.4	7.2	Fairly uniform		
S-Fe-2	4	" "	0.9	3.4	4.6	5.7	7.0	7.4	7.8	Thinner films, 1 high		
S-Fe-3	4	" "	1.0	9.4	11.8	13.9	16.3	--	--	1 high		
S-Fe-4	4	" "	--	3.6	4.9	6.0	7.3	--	--	1 high		
SB-Fe-0	4	16	Soft glass, 25°C, Sandblasted	7.7	10.0	10.9	13.1	15.6	17.4	--	1 high	
SB-Fe-1	4	" "	4.9	6.0	6.6	8.6	10.0	10.6	--	1 high		
SB-Fe-2	4	" "	6.5	8.4	9.2	11.6	13.8	14.8	--	1 high		
SB-Fe-3	4	" "	6.5	8.7	9.7	14.6	17.8	19.0	--	1 high		
HT-Fe-0	4	12	Pyrex, 25°C, Postheated 455° for 18 min.	1.1	1.5	1.4	2.1	--	--	--	Fairly uniform	
HT-Fe-1	4	" "	0.7	1.0	1.2	1.5	--	--	--	--	Fairly uniform	
HT-Fe-2	4	" "	0.4	0.5	0.6	0.9	--	--	--	--	Fairly uniform	

CORROSION RATES OF IRON FILMS DEPOSITED BY VACUUM EVAPORATION ON GLASS SUBSTRATES PRECOATED WITH SELECTED SALTS

Average Percent Area Destruction of Groups of Ten Films of Iron on Glass Substrates Precoated with a Salt as a Function of Time of Exposure in an Environment at 25°C and a Specified Level of Relative Humidity

Specimen Identification	Cleaning Procedure	Exposure Time in Days							Salts	Relative Humidity	Comments (No. out of 10)	
		1	3	5	10	20	30	40				60
261-270	Acid + Spray + Bake		3	3	5	5	7	7	7	NaCl	70%	4
271-280	--		9	9	18	20	28	28	28			4
	--		40	50	50	60	60	60	60			2
	--		20	20	23	23	25	30	35	NaCl	70%	2
	--		84	90	92	92	92	92	93			8
441-450*	"		100	--	--	--	--	--	--	NH ₄ Cl	70%	10
451-460	"		< 1	< 1	< 1	< 1	< 1	--	--	NH ₄ Cl	30%	10
461-470	"		< 1	< 1	< 1	< 1	< 1	--	--	NH ₄ Cl	35%	10
471-480	"		< 1	--	45	60	--	--	--	NH ₄ Cl	40%	10
481-490	"		100	--	--	--	--	--	--	NH ₄ Cl	40%	10

Average Percent Resistance Change as a Function of Treatment and Exposure Time in an Environment of 25°C and 30 Percent Relative Humidity

111-120	Acid, heater, O shutter + NaCl, 1% spray 60 sec.	0	0	0	0	< 1	< 3	< 3
121-130	" " " 1% spray 30 sec.	< 1	< 1	< 1	< 4	9	12	21 25

*Substrates for films 441-490 cleaned by modified acid cleaning procedure.

TABLE IV

ELECTRICAL RESISTANCE MEASUREMENTS OF SIMULTANEOUSLY
DEPOSITED IRON-COPPER FILMS EXPOSED AT 25°C AND
70 PERCENT RELATIVE HUMIDITY

Electrical Resistance Measurements in Ohms

Film Number	431	432	433	434	435	436	437	438	439	440
Days										
0	11.4	13.3	10.9	18.3	9.60	10.9	8.31	6.48	17.0	13.5
1	12.1	14.7	12.5	22.6	9.95	11.9	9.26	6.57	17.2	13.8
2	--	--	--	--	--	--	--	--	--	--
3	--	--	--	--	--	--	--	--	--	--
4	12.3	14.7	19.1	65.6	15.8	19.5	100	6.59	17.5	14.0
5	12.3	14.7	20.8	73.3	16.4	20.7	10.2	6.57	17.5	15.5
6	12.3	14.8	22.5	80.6	17.1	21.8	10.5	6.63	17.6	16.9
7	12.3	14.8	24.0	87.1	17.6	22.9	10.8	6.68	17.7	17.4
8	12.5	15.0	25.9	95.6	18.4	24.4	11.2	6.80	17.8	18.6
9	--	--	--	--	--	--	--	--	--	--
10	--	--	--	--	--	--	--	--	--	--
15	12.5	15.1	38.2	156	22.0	33.6	13.3	6.90	19.3	25.2
20	12.6	15.3	43.2	191	24.1	39.1	14.5	7.07	21.0	27.8
25	12.7	15.5	45.2	226	26.2	45.7	15.1	7.26	22.8	29.2
30	12.7	15.5	46.9	250	27.7	51.5	16.9	7.41	24.2	29.8
35	12.9	15.9	49.5	281	29.9	61.8	18.5	7.68	26.9	30.7
40	13.1	16.1	52.1	307	31.3	70.4	19.7	7.91	29.1	31.4
45	12.7	15.9	55.4	344	32.3	80.2	20.7	7.76	31.0	31.6
50	12.8	16.0	58.1	377	33.1	86.6	21.6	7.88	32.4	32.0
55	12.8	17.1	61.4	403	34.9	94.6	23.4	8.83	34.7	33.2
60	12.9	16.3	62.0	418	34.7	100	23.5	8.16	34.8	32.5

TABLE V

CORROSION DATA FOR BIMETAL FILMS OF IRON AND COPPER
(25°C, 70 Percent Relative Humidity)

Simultaneously Evaporated onto Hot Substrates (450°C)

Percent Increase in Electrical Resistance

Film No.	Days on Test						Remarks
	<u>1</u>	<u>2</u>	<u>5</u>	<u>10</u>	<u>20</u>	<u>85</u>	
CI-0-0	0	0	< 1	1	2	4	
CI-0-1	0	< 1	< 1	2	2	2	
CI-0-2	0	< 1	1	< 2	< 3	84	
CI-0-3	0	0	1	< 2	< 3	23	
CI-I-0	6	8	12	14	17	47	Watermarked
CI-I-1	0	< 1	1	1	1	4	
CI-I-2	0	0	0	< 1	< 2	8	
CI-I-3	0	0	< 1	1	1	4	
CI-2-0	0	< 1	< 2	< 2	< 2	5	
CI-2-1	0	0	0	< 1	2	4	
CI-2-2	0	0	< 1	< 1	1	7	
CI-2-3	0	< 1	< 1	< 1	1	5	
CI-3-0	0	0	< 1	< 1	1	2	
CI-3-1	0	0	0	< 1	1	5	
CI-3-2	0	0	0	< 1	< 1	10	
CI-3-3	0	0	0	< 1	< 1	13	

SUCCESSIVELY DEPOSITED LAYERS OF COPPER PLUS IRON

CI-4-0	0	0	0	0	0	7	Post heated to about 500°C
CI-4-1	0	0	0	0	0	2	Post heated to about 500°C
CI-4-2	0	0	0	0	0	11	Post heated to about 500°C
CI-4-3	0	0	0	0	< 1	32	Post heated to about 500°C
CI-5-0	3	5	14	14	14	56	Post heated to about 500°C, watermarked
CI-5-1	2	2	2	4	4	11	Post heated to about 500°C, watermarked
CI-5-2	0	0	0	0	0	2	Post heated to about 500°C, watermarked
CI-5-3	0	0	0	--	0	27	Post heated to about 500°C, watermarked

CORROSION DATA FOR FILMS OF IRON AND IRON OXIDE

OI-1-0	3	4	6	8	10
OI-1-1	5	7	10	14	16

TABLE VI
CORROSION DATA FOR BULK STEEL SPECIMENS

Exposed at 25°C and 70 Percent Relative Humidity

Jar No.	Date Test Began	% Corrosion Observed *										Comments
		1	2	5	10	20	40	60	140			
22	2-3-59	0	0	< 1	1	1	< 2	< 2	2	1 specimen only 2 sp Erratic c 1 specimen only 2 sp 1 specimen only 2 sp All speci		
23	2-4-59	0	< 1	< 1	< 1	1	< 2	< 2	< 3			
24	2-6-59	< 1	< 1	< 1	< 1	< 1	< 1	1	1			
25	2-11-59	0	< 1	< 1	1	1	1	2	< 3			
26	?	< 1	< 1	1	< 2	2	2	2	--			
28	2-20-59	< 1	< 1	< 1	1	1	< 2	< 2	--			
29	2-24-59	< 1	< 1	1	< 2	< 2	< 2	< 2	--			
30	2-24-59	< 1	< 1	2	2	2	2	2	--			
31	2-26-59	< 1	< 1	< 1	< 1	< 1	1	1	--			
32	3-10-59	< 1	< 1	< 1	1	1	1	< 2	--			
33	3-11-59	< 1	< 1	< 1	< 1	< 2	< 2	3	--			
34	3-12-59	< 1	< 1	< 2	< 3	< 3	< 3	< 3	--			
35	3-12-59	< 1	< 1	< 3	5	5	5	5	--			
36	3-17-59	0	< 1	1	1	1	1	1	--			
37	3-18-59	< 3	< 3	< 3	< 3	4	5	5	--			
38	3-20-59	1	< 2	< 3	< 3	< 3	< 3	< 3	--			
39	3-20-59	< 2	3	6	6	7	7	7	--			
40	3-23-59	3	7	10	20	--	--	--	--			
41	3-24-59	3	4	4	4	--	--	--	--			
42	3-25-59	~ 10	~ 10	~ 10	~ 12	--	--	--	--			
43	3-27-59	~ 25	~ 25	~ 40	~ 50	--	--	--	--			
44	4-16-59	~ 25	< 40	< 50	< 50	~ 50	< 60	< 60	--			
45	4-23-59	100	--	--	--	--	--	--	--			

* The inside surface usually exhibited appreciably more corrosion than the side turned toward the glass container. Tests were based on average area destruction of three specimens.