

FILM FORMATION ON PRECIOUS METAL SURFACES
IN THE PRESENCE OF EPOXY RESINS

by
Lawrence J. Kyle

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in partial fulfillment for the degree of

MASTER OF SCIENCE
in
Chemical Engineering

APPROVED:

Dr. N. F. Murphy, Chairman

Dr. J. P. Wightman

Dr. A. L. Fricke

October, 1968

Blacksburg, Virginia

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
Chemistry of Epoxy Resins	3
Resin Intermediates	4
Resin Cure	7
Curing Agents and Hardeners	8
Thermal Degradation	9
Outgassing of Plastic	10
Contaminants on Surface	11
Proposed Mechanisms of Film Formation	12
Static Polymer	12
Frictional Polymer	14
Electron Bombardment	15
Film Testing Techniques	15
Contact Resistance Probe	15
Ellipsometric and Radiotracer Methods	16
Surface Wettability	16
Gravimetric Technique	16
Friction Device	16

	Page
III. EXPERIMENTAL	18
Purpose of Investigation	18
Plan of Investigation	18
Materials	20
Apparatus	23
Method of Procedure	27
Preparation of Metal Samples	27
Epoxy Preparation	28
Exposure of Samples	32
Examination for Film	32
analysis of Outgasses	32
Results of Investigation	33
Haze Formation	33
Mass Spectrometer	34
Basis of Comparison	34
IV. DISCUSSION	71
Discussion of Procedure	71
Experimental Precision	71
Sensitivity of Testing	72
Discussion of Results of the Investigation	72
Formation of Haze	72
Mechanism of Film Formation	73

	Page
Frequency of Sample Observations . .	73
Mass Spectrometer Results	74
Effect of Curing Conditions and Epoxy Compositions	75
Effect of Exposure Temperature . . .	76
Effect of Metal Composition	77
Prevention of Film Formation	77
Recommendations	79
Limitations	81
V. CONCLUSIONS	84
VI. SUMMARY	85
VII. BIBLIOGRAPHY	87
VIII. ACKNOWLEDGMENTS	92
IX. VITA	93

LIST OF TABLES

Table		Page
I.	Dow D.E.N. 438 Epoxy Novolac Resin	21
II.	General Cleaning Procedure for Metal Samples	29
III.	Epoxy Curing Procedure	31
IV.	Weight Change of Pure Gold Samples	35
V.	Weight Change of Pure Silver Samples . . .	36
VI.	Weight Change of Pure Copper Samples . . .	37
VII.	Weight Change of 88% Gold-Copper Alloy Samples	38
VIII.	Weight Change of 75% Gold-Copper Alloy Samples	39
IX.	Weight Change of 75% Gold-Silver Alloy Samples	40
X.	Weight Change of 92% Gold-Copper Electroplated Samples	41
XI.	Weight Change of 87% Gold-Copper Electroplated Samples	42
XII.	Weight Change of 85% Gold-Copper Electroplated Samples	43
XIII.	Weight Change of 80% Gold-Copper Electroplated Samples	44
XIV.	Rate of Film Formation on Metal Samples Stored with Epoxy "A"	63
XV.	Rate of Film Formation on Metal Samples Stored with Epoxy "B"	64
XVI.	Maximum Weight Increase of Metal Samples Stored with Epoxy Samples	78

LIST OF FIGURES

Figure		Page
1.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 30 °C	45
2.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 30 °C	46
3.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 60 °C	47
4.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 60 °C	48
5.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 90 °C	49
6.	Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 90 °C	50
7.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 30 °C	51
8.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 30 °C	52
9.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 60 °C	53
10.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 60 °C	54
11.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 90 °C	55

Figure		Page
12.	Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 90 °C	56
13.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 30 °C	57
14.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 30 °C	58
15.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 60 °C	59
16.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 60 °C	60
17.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 90 °C	61
18.	Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 90 °C	62
19.	Effect of Temperature Upon Rate of Weight Gain for Pure Metal Samples Stored with Plastic Preparation "A" . . .	65
20.	Effect of Temperature Upon Rate of Weight Gain for Pure Metal Samples Stored with Plastic Preparation "B" . . .	66
21.	Effect of Temperature Upon Rate of Weight Gain for Gold Alloy Samples Stored with Plastic Preparation "A" . . .	67
22.	Effect of Temperature Upon Rate of Weight Gain for Gold Alloy Samples Stored with Plastic Preparation "B" . . .	68

Figure		Page
23.	Effect of Temperature Upon Rate of Weight Gain for Electroplated Gold Alloy Samples Stored with Plastic Preparation "A"	69
24.	Effect of Temperature Upon Rate of Weight Gain for Electroplated Gold Alloy Samples Stored with Plastic Preparation "B"	70

I. INTRODUCTION

The technology of designing and building electronic equipment such as computers, televisions, telephones, and space vehicles, has developed rapidly during the past two decades. With this development, considerable technological emphasis has shifted from studies of the intrinsic properties of the materials used, to studies of the environments in which they must operate. The life and reliability of many electronic devices now appear to be more dependent on the contaminating influences of the impurities associated with the materials of construction than on the inherent behavior of the materials themselves.

One of the common materials of construction in electrical devices is epoxy. Epoxy meets satisfactorily all the requirements of a construction material such as low electrical conductivity, low thermal expansion, easy moldability, and low cost.

The increased use of noble metal contacts in recent years has led to the discovery of films formed on the surface of these metals at room temperature and pressure when in the presence of epoxy resins or exposed to air containing organic vapors. These films have not been

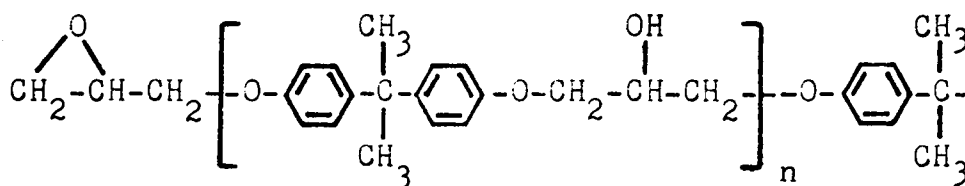
fully characterized or identified. No explanation of the mechanism of film formation, nor effects of noble metal and epoxy properties upon film formation has been verified.

The purpose of this study was to determine the effect of exposure conditions, resin composition, and resin treatment on film formation when the resin (epoxy novolac with 4-4' methylenedianiline as hardener) is exposed to pure gold, pure copper, pure silver, and gold alloys (with copper and with silver).

II. LITERATURE REVIEW

Chemistry of Epoxy Resins

Epoxy resins were first introduced in 1947⁽³⁷⁾ as the polycondensation product of epichlorohydrin and bisphenol A.



The name "epoxy" was derived from the fact that the resin molecule is terminated by epoxide rings.

Epoxy resins are thermosetting materials converted by curing agents (hardeners) and/or accelerators into tough, infusible solids. The resins are used primarily as castings, laminates, and adhesives because excellent strength, toughness, low shrinkage during cure, chemical resistance, and adhesion can be obtained. The greatest value of epoxy resins, however, is that all these good properties can be so combined that no one property need be sacrificed to achieve another.

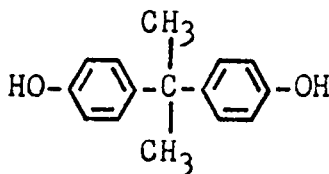
Epoxy resins obtain their strength and toughness from the cross linking with other molecules. The curing agent

(or hardener) acts as a catalyst causing epoxy molecules to bond directly to other epoxy molecules. The two types of reactions associated with the cross linking in epoxy resins are those with the terminal epoxy group and those of the secondary hydroxyl group in the repeating unit⁽³⁷⁾.

Functionality is a measure of the cross linking ability of a molecule and is equal to the number of positions in the molecule at which it can become joined to other molecules.

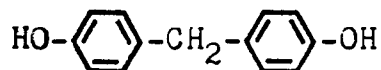
Resin Intermediates. The utility of the epoxy resins⁽³⁵⁾ depends to a great extent upon their functionality, since hardness, solvent resistance, and softening temperature in the final product are all increased by cross linking. By varying the basic compound many different combinations of properties can be obtained.

Bisphenol A, the first commercial epoxy,



has a varying functionality depending on the curing agent. This versatility has made bisphenol A almost an exclusive base for epoxy resins.

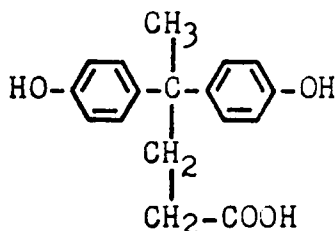
Bisphenol F,



gives more flexible epoxies than bisphenol A but they have a lower softening temperature.

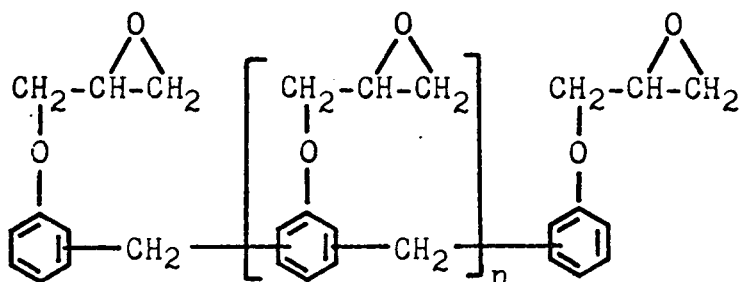
Tetrachlorobisphenol A may be used in place of bisphenol A to give epoxy resins which are flame retardant and possess good high temperature strength properties. They maintain their flexural strength and tensile strength to a greater degree as environmental temperature is increased, as compared to conventional resins.

Diphenolic acid,



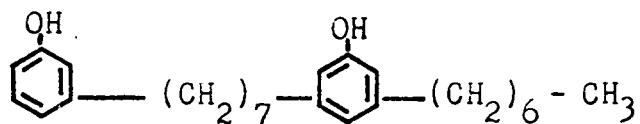
adds a carboxylic acid group to bisphenol A. The carboxyl increases functionality, thus improving softening temperature and solvent resistance. The carboxyl group can react with acids and amines to form esters and amines.

Novolacs ⁽⁴⁾.



The novolacs produce tightly cross linked cured systems with better elevated temperature performance, chemical resistance, and adhesion than the bisphenol A based resins. These resins can be cured at room temperature, and pressure because of their heat of reaction and do not generate undesirable reaction by-products. These resins do, however, have very high viscosities and this causes difficulty in maintaining uniform compositions during processing.

Cashew phenol,



derived from cashew nut oil, is reacted with epichlorohydrin to give an epoxide intermediate. This resin has high impact strength at ordinary temperatures, but has a low softening temperature.

Aliphatic diols and triols such as glycerine produce liquid epoxies of lower viscosity, which are easier able to impregnate and penetrate. They are less corrosion resistant, have a lower softening temperature than bisphenol A, and have residual chlorine which may be objectionable in some electronic applications.

Resin Cure. The cure of an epoxy resin is produced by the linking of one molecule of intermediate to another. Two types of linkage are possible: (1) directly to other epoxy intermediate molecules, with the aid of a catalyst; and (2) to a reactive hardener which combines with one or more additional molecules of resin⁽³⁵⁾.

The reaction of epoxides is very exothermic⁽³⁵⁾. Some hardening agents^(6,35) cause curing at room temperature because of the high heat of reaction. As heat is released and the temperature of the epoxy rises, the curing takes place at a faster rate. If the temperature of the cure is allowed to climb too high, the strength of the epoxy will be impaired. Best results come from a two-stage cure⁽³⁵⁾. In the first stage, monomer combines to form small clusters of polymer molecules. Then the temperature is raised, and in the second stage these clusters are joined together to form one big molecule.

The curing of an epoxy resin does not proceed smoothly and uniformly, but goes much faster wherever a start has been made. If the cure is incomplete, the uncured areas will tend to be bunched together. Anything that can be done to make the clusters more uniform in size will improve the final product. The use of a two-stage cure and the use of a curing agent with groups of differing reactivity are examples of ways that help.

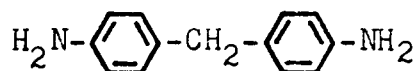
Curing Agents and Hardeners. Epoxy resins are cured by many types of materials, including polyamines, polyamides, polysulfides, urea- and phenol-formaldehydes, and acids or acid anhydrides.

Primary-Secondary Aliphatic Amines. These hardeners are chiefly ethylenediamine and higher members of its series. They are the most widely used of all curing agents for epoxies. They are fast-curing at room temperature, cheap, low in viscosity, readily miscible, and produce moderately tough castings. However, their fast action at room temperature causes a short pot life. Other drawbacks are that they are highly exothermic and can cause bubbling, are toxic, and have low softening temperatures.

Aromatic Primary Amines. These compounds require high temperatures to bring about cure. Some are solids

at ordinary temperatures, and must be heated to melt. These resins degrade after storage at high temperatures, but have a long pot life and high softening temperature. One of the commercially important⁽³⁵⁾ members of this group, MDA (4-4' methylenedianiline) was used for the work reported in this paper.

MDA, 4-4' methylenedianiline,



has a molecular weight of 198, has a recommended concentration range of 28 to 30 weight parts MDA per 100 parts epoxy, and a curing temperature range of 60 to 210 °C⁽¹⁷⁾.

In addition to high distortion point and excellent chemical resistance, the aromatic primary amines provide good electrical properties under conditions of high moisture.

Thermal Degradation. It is known that the thermal degradation of polymers is a radical-chain process^(23,31,34). Analysis of gaseous products have shown the presence of significant quantities of methane, carbon monoxide, propylene, water, formaldehyde, acetaldehyde, and acrolein. As the thermal degradation continues, liquid products of

comparatively low molecular weight distill off from the polymer^(10,33,34).

Neiman and associates propose that the terminal groups of the cured resin are very easily detached from the polymer. This radical isomerizes and then forms acrolein and hydroxyl. Neiman also proposes that the radical also splits into acetaldehyde radical and ethylene oxide which in turn isomerizes and degrades to carbon monoxide and a methyl radical. These radicals then take hydrogen atoms from the polymer and form acetaldehyde and methane molecules. Besides the removal of the terminal groups, the bonds between the carbon atoms in the aliphatic sections of the epoxide resin chains can also be disrupted. Volatile products of low molecular weight are formed in the process.

Outgassing of Plastic. Outgassing is the process by which the volatile material in a plastic escapes. A wide range of plastics and organic materials⁽¹⁰⁾ have shown outgassing at 160 °C from 0.012 per cent of the original plastic weight for Teflon to 17.2 per cent of the original plastic weight for Mylar tape. These outgasses are the volatile low molecular weight fractions, unreacted monomer, and degradation products.

Soldatos⁽³⁶⁾ has shown that the amount of outgassing characteristic to a particular polymer can be kept to a minimum by optimizing the curing cycle and the quantity of hardener added during polymerization. For his systems, cycloaliphatic epoxy resins, he observed considerable improvement by using an excess of stoichiometric hardener (115 per cent) and relatively high curing (80 to 110 °C) and post curing temperatures (160 to 200 °C).

Contaminants on Surfaces

The term "contamination" has come to have very diverse meanings when applied to surfaces. With the development of more sophisticated techniques for examining surfaces, there has come a greater concern with cleanliness on an atomic scale, so that adsorbed gases or trace amounts of oxides on metals, for example, can be considered as contaminants.

In the telephone industry, particularly, electrical contacts made of noble metals fail during usage and after storage. The early attempts to reduce contact failure were aimed at eliminating obvious surface contaminants^(9,10,28). These contaminants consisted mainly of dust and fingerprints from handling^(9,10). The dust

particles were analyzed⁽¹⁰⁾ and were found to contain all forms of clothing fibers, dead skin, pollen, insect scales, ashes, soot, earth, solder, insulation materials, and many other materials.

Not until in the 1940's had serious thought been given to the contaminating influences of the impurities associated with the materials of construction. In an attempt to increase contact reliability, contacts were enclosed in sealed containers for dust exclusion⁽²⁸⁾. This enclosing caused contacts to fail 20 times as fast as before encapsulation. The performance of contacts in the Bell Laboratories were also observed to deteriorate when the laboratory walls were painted⁽²⁸⁾. These circumstances led to extensive work which verified that contamination from the outgassing of organic materials of construction were the most important single cause for failures^(2,12,24,28,38).

Proposed Mechanisms of Film Formation

Static Polymer. Little is known of the path by which organic vapors are converted into contact deposits. Physical adsorption from the vapor state onto the contact surface is the most likely possibility^(4,15,20,26,29,30).

At the contact surface the molecular weight of the adsorbed material may build up by polymerization under the catalytic influence of the noble metal contact^(8,10,27). Thick films are conceivably grown by the diffusion of hydrocarbons through the film or organic contaminant to the polymer-metal interface, where a continuing catalytic reaction generates more polymer. Thus, the film grows from the metal surface⁽¹⁰⁾. Most of the isolated deposits seem obviously to be crystalline. The crystals look as though they have grown from the surface rather than as if deposited on the surface⁽¹⁰⁾.

The adsorption phenomena mechanism also explains the fact that different surfaces become contaminated at different rates and to different levels. Organic vapors that contaminate some surfaces do not contaminate others^(16,38). Organic contamination is not just a case of material "falling out" onto a surface but is a reaction (adsorption) on the surface with the contaminant⁽³⁸⁾.

The experiments of Chaikin⁽¹⁰⁾, which measured the organic contamination on metal surfaces by the use of a contact resistance probe, showed that generally, gold and silver are the metals less susceptible to contamination

when compared with gold alloys, palladium, and rhodium. Also, elevated temperatures (80 to 160 °C) decreased contamination in many cases. This is unexpected, for it would be thought that elevated temperatures would cause more outgassing and would, therefore, furnish more raw material for generation of polymer. Several explanations are possible⁽¹⁰⁾. They are: (1) low molecular weight polymer or degradation products revolatilize; and (2) the polymer-producing reaction is not favored by elevated temperatures.

Organic contaminations formed are very tightly bound to the metal surface. The only effective way found to remove these organic films is by altering or splitting the organic molecules. The most successful technique⁽⁷⁾ is by exposing the film to oxidizing conditions such as heating to 400 °C in air, boiling in hydrogen peroxide solution, or exposing to oxidizing acids.

Frictional Polymer. Disturbed metal surfaces are known to emit electrons which may effect the polymerization. It was proposed^(12,21) that rubbing might cause electron emission from the metal surfaces and that these electrons might then cause chemical changes in hydrocarbons in the vicinity. It is believed⁽¹⁶⁾ that frictional polymers are produced by some combination

of the effects of catalysis and of electron emission from the rubbed surface.

Electron Bombardment. In the presence of electron bombardment^(13,25), the mechanism of film formation is the free radical polymerization of the organic molecules adsorbed on the surface. The molecules are cross linked by the electron beam to form a solid polymer film. This mechanism favors lower temperatures because the lower the temperature, the longer the molecule will reside on the surface such that it can encounter an electron.

Film Testing Techniques

There are many varied techniques for measuring the extent of contamination which a sample has undergone. A few of these techniques are: the use of contact resistance probes^(3,8,10,11), friction devices⁽²⁴⁾, gravimetric techniques^(5,18), ellipsometric^(14,32), radiotracer⁽³²⁾, and surface wettability⁽³⁸⁾.

Contact Resistance Probe. A contact resistance probe is an instrument which can either nondestructively detect the presence of films on normally conductive surfaces, or destructively determine the mechanical and electrical properties of films. By measuring the voltage

drop (resistance) at the probe-contact junction, the thickness of the film can be determined.

Ellipsometric and Radiotracer Methods. Ellipsometric (polarization spectrometer) and radiochemical techniques correlate well in comparative measurements involving adsorption of organic compounds on polished metal surfaces. The linear thickness found ellipsometrically is a direct function of the surface concentration determined radiochemically to levels well below that of a monomolecular film.

Surface Wettability. In the surface wettability technique, the surface to be tested is sprayed with a fine mist of water and if the impinging drops spread on the surface, it is considered clean. If the water remains as droplets, the surface is considered dirty, or contaminated by organic material. By measuring the change in the contact angle of the droplets, the amount of contamination can be determined.

Gravimetric Technique. In the gravimetric technique, the quantity of film formed on a sample exposed to contamination is determined by measuring the weight gain of the sample.

Friction Device. With the friction device, a contact arm is oscillated back and forth on the surface

of the sample being tested. Current is usually passed through the contact but is not necessary. By measuring the weight gain of the sample tested, the amount of film formation is determined.

III. EXPERIMENTAL

This section contains the purpose of investigation, plan of experimentation, description of the materials and apparatus used, method of procedure for the investigation, and results of the investigation.

Purpose of Investigation

The purpose of this investigation was to follow up the work originally started by T. H. Forsyth. A more detailed study of the effects of exposure conditions, resin composition, and resin treatment on film formation was attempted when the resin (epoxy novolac with 4-4' methylenedianiline as hardener) was exposed to pure gold, pure copper, pure silver, and gold alloys (with copper and with silver).

Plan of Investigation

This problem was attacked in two major parts, the first being the manufacturing of the metal samples to be tested and the second being the aging of the metal samples in the presence of the epoxy resins.

The metal samples were first attempted to be made by electroforming. However, because of the inconsistency of the composition of the samples produced, other methods were sought. The pure metals (gold, copper, and silver) were purchased. The 75.0 per cent gold-copper alloy and gold-silver alloy were made by melting the pure metals together and then rolling to a thin foil. A limited number of electroplated samples were obtained by dissolving the plate from the base metals of existing samples.

Rods of epoxy novolac resin were prepared with 4-4' methylenedianiline at two polymerization and annealing temperatures and two hardeners to epoxy ratios. This was done in order to determine if resin composition and treatment would affect film formation.

The metal samples were carefully weighed on an analytical balance and stored with an epoxy sample in covered petri dishes, thus isolating the metal samples and plastic from the atmosphere and from other samples. The petri dishes were stored at several temperatures and at atmospheric pressure to determine the effect of ambient conditions upon film formation.

The metal samples were weighed at intervals to determine the increase in weight due to film formation on the sample surface.

Materials

The materials used in the investigation are described in this section.

Acetone. Technical grade. Obtained from Cardinal Products, Inc., Durham, N. C. Used to dry samples before weighing.

Copper. Sheet, 1/32 inch thick, 99.95% pure. Obtained from Blacksburg Lumber Co., Blacksburg, Va. Used as samples for part of study.

Drierite. Granular, 10-20 mesh. Obtained from W. A. Hammond Drierite Company, Xenia, Ohio. Used as desiccant to remove moisture from plastic samples.

Epoxy Novolac Resin. Semi-solid, externally catalyzed. See Table I for specifications. Manufactured by Dow Chemical Co., Midland, Mich. Used to form plastic rods for testing.

Ferrous Sulfate. Anhydrous, reagent grade, catalog I-147, lot 770015. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used as a reducing agent in the gold analysis.

Gold. Foil, 0.001 inch thickness, 99.95% pure. Obtained from A. J. Mackay, Inc., New York, N. Y. Used as samples for part of study.

TABLE I

Dow D.E.N. 438 Epoxy Novolac Resin

The specification properties of Dow D.E.N. 438 epoxy novolac resin are listed below:

Functionality	3.6
Specific gravity, 25/4 °C	1.20-1.24
Epoxy equivalent weight	175-182
Viscosity, 52 °C, cp	30,000-90,000
Viscosity, 100 °C, cp	135

Physical properties when Dow D.E.N. 438 epoxy novolac resin is hardened with 28 parts per hundred

4-4' methylenedianiline are listed below:

Gel time at 100 °C, min	8
Heat distortion temperature, °C	180-207
Flexural strength, psi	15,400
Compressive yield strength, psi	35,600
Tensile strength, psi	9,100
Dielectric constant at 25 °C, 60 cp	4.02
Dissipation factor at 25 °C, 60 cp	0.0074
Weight loss at 160 °C	
4 days exposure, %	0.26
21 days exposure, %	0.28

Dow Chemical Company, D.E.N. Epoxy Novolac Resins
Bulletin, Form No 170-143B (1967), The Dow Chemical
Company, Midland, Mich.

Hydrochloric Acid. Reagent grade, 36.5-38.0% HCl, specific gravity (60 °C) of 1.1854-1.1923, catalog A-144, lot 771742. Manufactured by Fisher Scientific Co., Fair Lawn, N. J. Used to make aqua regia for analysis and for cleaning samples.

4-4' Methylene dianiline. Reagent grade, crystalline solid, minimum freezing point 89.0 °C, minimum assay (diazo titration) 97.0%. Manufactured by Dow Chemical Co., Midland, Mich. Used as hardener in preparing plastic samples.

Methyl Ethyl Ketone. Reagent grade, concentrated, lot 773589. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used to swell and partially dissolve epoxy resins.

Nitric Acid. Reagent grade, 69.0-71.0% HNO₃, specific gravity (60 °C) 1.416-1.420, catalog A-200, lot 765413. Manufactured by Fisher Scientific Co., Fair Lawn, N. J. Used to make aqua regia for analysis and for cleaning samples.

Oakite. Cleaning agent. Obtained from Oakite Products, Inc., New York, N. Y. Used to remove oil and grease from metal samples and petri dishes.

Silver. Foil, 0.001 inch thickness, 99.9+% pure. Obtained from A. D. Mackay, Inc., New York, N. Y. Used as samples for part of study.

Sulfuric Acid. Reagent grade, 95.0-98.0% H_2SO_4 , specific gravity (60 °C) 1.8407-1.8437, catalog A-300, lot 776380. Manufactured by Fisher Scientific Co., Fair Lawn, N. J. Used in analysis of gold samples.

Water. Single distilled. Obtained by distillation of tap water in a tin-lined still. Used for cleaning and general purpose.

Apparatus

The apparatus used in the investigation are described in this section.

Balance. Mettler, type H, analytical balance, optical scale, 160 gm capacity, increments of 0.0001 gm, serial 263987. Obtained from E. H. Sargent & Co., Chicago, Ill. Used for weighing samples.

Cups. Paper Dixie cups, 3 oz. Manufactured by American Can Co., Green Bay, Wisc. Used as disposable mixing containers for epoxy resin.

Desiccator. Two, glass, 25 cm diameter, catalog 8-595-B. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used to remove water from plastic samples.

Desiccator. Vacuum, glass, 12.5 cm diameter, catalog 8-632-4. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used in removing air from samples during molding of epoxy.

Furnace. Hoskins electric furnace, type FD 204C, 110 v, 30.9 amp, serial 34928. Manufactured by Hoskins Manufacturing Company, Detroit, Mich. Used to melt gold, silver, and copper for making alloys.

General Laboratory Equipment. Beakers, graduated cylinders, erlenmeyer flasks, dewar flask, gooch crucibles, mortar and pestle, porcelain crucibles with lids, tongs, spatula, and glass stirring rod. Used for chemical analysis and general laboratory work.

Hot Plate. Temco-3, variable temperature control, 110 v, 60 cy, 660 w, model 2500. Obtained from Thermo-electric Manufacturing Company, Dubuque, Iowa. Used to heat cleaning solutions, acid cleaning baths, and chemical analysis solutions.

Mass Spectrometer. Hitachi Perkin-Elmer RMU-6E, double focusing mass spectrometer. Operated under the direction of the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Va. Used to determine the compositions of the outgasses from polymer samples.

Oven. Constant temperature, 110 v, 600 w, 5.5 amp, temperature range 35-180 °C, thermocouple controlled, catalog 1250, serial 100-2761. Manufactured by Precision Scientific Co., Chicago, Ill. Used to store samples at 60 °C.

Oven. Two, Fisher Isotemp, 115 v, 550 w, thermocouple controlled. Manufactured by Fisher Scientific Co., Fair Lawn, N. J. Used to store samples at 30 °C and 90 °C.

Oven. Vacuum, with gage reading to 30 inches vacuum, 115 v, 400 w, maximum temperature 175 °C, thermocouple controlled, catalog 31463, serial M-10. Manufactured by Precision Scientific Co., Chicago, Ill. Used as curing oven.

Petri Dish. One hundred and fifty, glass, 12.5 cm diameter, catalog 8-757-101B. Manufactured by Fisher Scientific Co., Fair Lawn, N. J. Used to store individual epoxy and metal samples.

Pins. Steel, straight. Obtained from Clinton Scovill Pin Co., Oakville, Conn. Used to prop metal samples up off the bottom of petri dish.

Pressure Gage. Dual purpose, maximum vacuum 30 in. Hg, maximum pressure 15 in. Hg, 1 inch graduations. Manufactured by Jas. P. March Corp., Chicago, Ill. Used to measure vacuum pulled on vacuum desiccator.

Pump. Vacuum, 600 rpm, capable of 0.0003 mm Hg vacuum. Manufactured by Fisher Scientific Co., Chicago, Ill. Used to produce vacuum for removal of dissolved air from resin.

Rolling Mill. Model TA 315, size 5 x 8 in., serial 35357. Manufactured by Stanat Manufacturing Co., Inc., Westbury, N. Y. Used to roll gold alloys to obtain thin foil.

Test Tubes. Small, pyrex, 10 x 75 mm, catalog 95050-A. Obtained from Corning Glass Works, Parkersburg, W. Va. Used as vessel for molding epoxy rods.

Test Tube Holder. Three, asbestos, capable of holding six test tubes. Manufactured in Chemical Engineering Shop, Virginia Polytechnic Institute, Blacksburg, Va. Used to hold test tubes in upright position while epoxy was being cured.

Thermometer. Mercury in glass, range from 0 to 50 °C in 0.2 °C graduations, catalog 33742-A. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used to measure temperature of 30 °C oven.

Thermometer. Two, mercury in glass, range from -20 to 110 °C in 1 °C graduations, catalog 19240-A. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used to measure temperature of 60 and 90 °C ovens.

Method of Procedure

The procedure used to carry out this investigation is described in detail in this section.

Preparation of Metal Samples. The pure metal samples (gold, silver, and copper) used in this investigation were purchased. The 75 per cent gold-copper alloy and gold-silver alloy samples were made by melting the pure metals together in a closed crucible and then rolling to a thin foil three mills thick by the use of a rolling mill machine. A few 88 per cent gold-copper alloy rings, used in an earlier work, were prepared by pretreating with boiling aqua regia for five minutes to remove the film which would be on the surface. Limited numbers of electroplated gold-copper alloy samples ranging in composition from 80 to 92 per cent gold were obtained by dissolving the plate from the base metal of existing samples by the use of 50 per cent nitric acid.

All metal samples were approximately 1/2 by one by 0.003 inch except for the 88 per cent gold-copper alloy rings which were in the shape of washers with inside and outside diameters of 1/8 inch and 1/4 inch, respectively.

All gold-copper alloys were analyzed by the method suggested by Foulke and Crane⁽¹⁹⁾. This method determines the metallic gold in a sample. By taking the ratio of the weight of the metallic gold in a sample to the total weight of the original sample, the composition is determined.

The gold-silver alloy samples were analyzed by the method of Swanger⁽²²⁾. This analysis measures both the silver content and the gold content analytically.

All metal samples with the exception of the pure silver ones were cleaned by a general cleaning procedure which is given in Table II. The pure silver samples were cleaned by a slightly modified procedure which uses a 12 per cent nitric acid wash in step four instead of the 50 per cent nitric acid wash as presented in the general procedure.

Epoxy Preparation. The epoxy samples used in this investigation were of two compositions. The first epoxy, which will be referred to as epoxy "A", had a weight composition of 27 parts of 4-4' methylenedianiline (MDA) per hundred parts of epoxy novolac. This composition was selected because it has the most desirable mechanical properties and is frequently used in the electronic industry.

The second epoxy, which will be referred to as epoxy "B", had a weight composition of 31-1/2 parts of 4-4' methylenedianiline (MDA) per hundred parts of epoxy novolac. This composition was selected because it has the most desirable chemical configuration⁽³⁶⁾, has excellent mechanical properties, and is highly recommended for industrial applications.

TABLE II

General Cleaning Procedure for Metal Samples^a

1. Wash with Oakite detergent solution
2. Rinse with tap water
3. Wash with acetone
4. Dip in warm 50 per cent HNO_3 for one minute
5. Rinse with distilled water
6. Boil in Oakite detergent solution
7. Boil in distilled water
8. Rinse in fresh acetone
9. Dry in 120 °C oven for one-half minute.

^aFor pure silver samples step 4 is changed to:

4. Dip in warm 12 per cent HNO_3 for two minutes.

The MDA in both cases was weighed on an analytical balance using an aluminum weighing dish as tare. The tare for the epoxy measurements was a paper cup. The epoxy in the paper cup was heated for 30 minutes in a 120 °C oven prior to mixing with the hardener. The MDA hardener, pulverized to a very fine powder, and epoxy were mixed in the paper cup by the use of a glass stirring rod until the hardener was dissolved. If the hardener had not dissolved by the end of five minutes, the sample was discarded.

While the plastic was still hot and fluid, it was placed in a vacuum desiccator and evacuated to three inches of mercury, absolute for five minutes to remove air bubbles and dissolved air. The epoxy then was removed from the vacuum chamber and poured from the paper cup into the preheated test tubes, which acted as the molds. The test tubes were then placed in an oven for further polymerization and curing. The curing schedules for epoxy "A" and epoxy "B" are given in Table III. The pressure at which all epoxy rods were prepared was atmospheric pressure.

Following the curing treatment, the glass test tubes were carefully broken away from the epoxy samples. A

TABLE III

Epoxy Curing Procedure

Curing Procedure for Epoxy "A"

1. Heat epoxy in 120 °C oven for 30 minutes
2. Add hardener (powdered), 27 parts per 100 parts epoxy
3. Hold at 120 °C for five minutes
4. Remove from oven and mix
5. Check for undissolved crystals; discard if any present
6. Evacuate to remove dissolved air
7. Pour in preheated test tube molds
8. Cure four hours at 65 °C
9. Post cure four hours at 125 °C.

Curing Procedure for Epoxy "B"

1. Heat epoxy in 120 °C oven for 30 minutes
2. Add hardener (powdered), 31.5 parts per 100 parts epoxy
3. Hold at 120 °C for five minutes
4. Remove from oven and mix
5. Check for undissolved crystals; discard if any present
6. Evacuate to remove dissolved air
7. Pour in preheated test tube molds
8. Cure two hours at 120 °C
9. Post cure four hours at 180 °C.

flat surface was put on each epoxy sample by sanding so that they would not roll about in the petri dishes.

Exposure of Samples. Immediately after preparation of the epoxy rods, each plastic sample was placed into a petri dish with a cleaned, weighed metal sample. The samples were stored at atmospheric pressure at either 30, 60, or 90 °C. Each epoxy sample was placed randomly in a petri dish but was not in contact with a metal sample. Each metal sample was propped up from the bottom of the petri dish by the use of steel pins. After 60 days exposure, the metal samples were placed facing the epoxy rods, one-half inch away. Shortly after this time half of the samples were taken off the pins and placed flat on the bottom of the petri dish.

Examination for Film. The metal samples were taken out of the ovens and weighed at successive intervals of about 15, 35, 60, 90, and 120 days. An analytical balance of ± 0.0001 gram sensitivity was used to observe the changes in weight of the metal samples.

Analysis of Outgasses. In an attempt to examine the composition of the volatile material lost by the outgassing from the epoxy rods, two samples of each epoxy "A" and epoxy "B" were crushed and placed in specially constructed containers for running on the

mass spectrometer. These samples were very carefully evacuated to one inch of mercury and then flushed with dry nitrogen several times before sealing. After sealing the samples, the containers were placed in a constant temperature oil bath at 120 °C. After holding the samples two weeks at this temperature, the outgasses from the samples were tested on the mass spectrometer. These vapors were injected into the mass spectrometer by using a sampling loop.

The components in the samples were determined by comparing the major peaks of the results with the "Mass Spectral Data"⁽¹⁾ listed for different compounds by the American Petroleum Institute Research Project 44.

Results of Investigation

Tables IV through XIII show the changes in weight of the metal samples after exposure to the epoxy rods for up to five months. The results tabulated were obtained by subtracting the original weight from the weight after the indicated exposure time.

Haze Formation. The effect of time upon haze formation is shown in Figures 1 through 18. These figures are plots of the data shown in Tables IV through XIII. The

figures point out four major characteristics. These characteristics are that weight gain (film formation) of the electroformed samples is greater than the weight gain of the other samples. The samples stored with epoxy "A" gain slightly more weight more quickly than those stored with epoxy "B". The weight gain increases significantly with the removal of the metal samples from the pin props and their placement on the bottom of the dishes. And, the samples stopped gaining weight after a certain level of film had been formed.

All of the metal samples stored without plastic at 30, 60, and 90 °C, as shown in Tables IV through XIII, had no gain in weight.

Mass Spectrometer. The mass spectrometer analysis made on the outgasses from the epoxy "A" and from the epoxy "B" showed the presence of several organic compounds. The major components of the gases were identified as toluene, carbon monoxide, propylene, water, acetaldehyde, acrolein, and trace amounts of several other compounds.

Basis of Comparison. The basis for experimental conclusions will be the rate of weight gain per unit area per day for each sample at each exposure temperature. The rate of weight gain is recorded in Tables XIV and XV, and plotted in Figures 19 through 24.

TABLE IV
Weight Change of Pure Gold Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.0	0.0	0.0	0.0	0.0	0.1
	2	0.1	0.0	0.0	0.1	0.0	0.0
	Blank ^a	-0.1	0.0	-0.1	---	---	---
35	1	0.0	0.0	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0
	Blank ^a	0.0	0.0	0.0	---	---	---
60	1	0.0	0.0	0.0	0.1	0.0	0.0
	2	0.0	0.0	0.1	0.1	0.0	0.0
	Blank ^a	0.0	0.0	0.0	---	---	---
90	1	0.1	0.0	0.0	0.0	0.1	0.1
	2	0.1	0.0	0.0	0.1	0.1	0.0
	Blank ^a	0.0	0.0	0.0	---	---	---
110	2 ^b			0.0	0.1	0.1	0.0
120	1	0.0	0.0	0.0	0.1	0.1	0.1
	2 ^b	0.1	0.0				
	Blank ^a	0.0	0.0	0.0	---	---	---
125	2 ^b			0.1	0.2	0.2	0.1
135	2 ^b	0.2	0.2				
140	1			0.0	0.1	0.1	0.1
	2 ^b			0.1	0.2	0.2	0.1
150	1	0.0	0.1				
	2 ^b	0.3	0.2				
	Blank ^a	0.0	0.0	0.0	---	---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE V
Weight Change of Pure Silver Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.1	0.0	-0.1	0.0	0.0	-0.1
	2	0.1	0.1	0.0	0.0	0.0	0.0
	Blank ^a	0.0	0.0	-0.1	---	---	---
35	1	0.1	0.1	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0
	Blank ^a	0.0	0.0	-0.1	---	---	---
60	1	0.1	0.0	0.0	0.0	0.0	0.0
	2	0.1	0.0	0.0	0.0	0.1	0.1
	Blank ^a	0.0	0.0	0.0	---	---	---
90	1	0.1	0.0	0.1	0.0	0.0	0.1
	2	0.1	0.0	0.0	0.0	0.1	0.1
	Blank ^a	0.0	0.0	0.0	---	---	---
110	2 ^b			0.0	0.0	0.1	0.1
120	1	0.2	0.1	0.1	0.0	0.0	0.1
	2 ^b	0.2	0.1				
	Blank ^a	0.0	0.0	0.0	---	---	---
125	2 ^b			0.3	0.2	0.3	0.3
135	2 ^b	0.3	0.3				
140	1			0.1	0.0	0.1	0.1
	2 ^b			0.3	0.2	0.3	0.4
150	1	0.2	0.1				
	2 ^b	0.3	0.3				
	Blank ^a	0.0	0.0	0.0	---	---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE VI
Weight Change of Pure Copper Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	-0.1	0.1	-0.1	0.0	0.0	0.0
	2	-0.1	0.0	-0.1	0.0	0.0	0.0
	Blank ^a	-0.1	0.0	0.0	---	---	---
35	1	0.0	0.1	-0.1	0.0	0.0	0.0
	2	-0.1	0.0	0.0	0.0	0.0	0.0
	Blank ^a	-0.1	0.0	0.0	---	---	---
60	1	0.0	0.0	0.0	0.0	0.0	0.1
	2	0.0	0.0	0.1	0.0	0.0	0.1
	Blank ^a	0.0	0.0	0.0	---	---	---
90	1	0.0	0.0	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.1	0.0	0.0	0.1
	Blank ^a	0.0	0.1	0.0	---	---	---
110	2 ^b			0.1	0.0	0.0	0.1
120	1	0.0	0.0	0.0	0.0	0.0	0.0
	2 ^b	0.0	0.0				
	Blank ^a	0.0	0.0	0.0	---	---	---
125	2 ^b			0.1	0.0	0.0	0.2
135	2 ^b	0.0	0.2				
140	1			0.1	0.0	0.0	0.1
	2 ^b			0.2	0.1	0.1	0.2
150	1	0.0	0.1				
	2 ^b	0.1	0.2				
	Blank ^a	0.0	0.0	0.1	---	---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE VII

Weight Change of 88% Gold-Copper Alloy Samples

Storage Time days	Sample No.	Epoxy "A"		
		Oven Temperature, °C		
		30	60	90
mg/sq in.				
15	1	0.0	0.0	0.0
	2	0.0	0.0	0.0
	Blank	0.0	0.0	0.0
35	1	0.0	0.0	0.2
	2	0.0	0.0	0.0
	Blank	0.0	0.0	0.0
60	1	0.0	0.0	0.0
	2	0.0	0.0	0.0
	Blank	0.0	0.0	0.0
75	2 ^a	0.0	0.0	0.0
90	1	0.0	0.0	0.2
	2 ^a	0.0	0.0	0.2
	Blank	0.0	0.0	0.0
105	1	0.0	0.0	0.2
	2 ^a	0.0	0.2	0.4

^aSamples taken off pins and placed flat on petri dish.

TABLE VIII

Weight Change of 75% Gold-Copper Alloy Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.1	0.1	0.0	0.0	0.1	0.0
	2	0.1	0.1	0.0	0.0	0.1	0.0
	Blank ^a	0.0	0.0	0.0	---	---	---
35	1	0.2	0.1	0.0	0.1	0.2	0.0
	2	0.2	0.1	0.0	0.0	0.1	0.1
	Blank ^a	0.0	0.1	0.1	---	---	---
60	1	0.2	0.1	0.0	0.0	0.1	0.0
	2 ^b	0.2	0.1	0.0	0.0	0.1	0.0
	Blank ^a	0.0	0.0	0.0	---	---	---
75	2 ^b	0.2	0.1	0.0	0.0	0.1	0.1
90	1	0.2	0.1	0.0	0.0	0.1	0.1
	2 ^b	0.2	0.2	0.1	0.1	0.2	0.2
	Blank ^a	0.0	0.0	0.0	---	---	---
105	1 ^b	0.2	0.1	0.0	0.0	0.1	0.1
	2 ^b	0.2	0.2	0.1	0.1	0.2	0.2
	Blank ^a	0.0	0.0	0.0	---	---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE IX

Weight Change of 75% Gold-Silver Alloy Samples

Storage Time	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
days		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.0	0.1	0.0	0.0	0.1	0.0
	2	0.1	0.0	0.1	0.0	0.1	0.1
	Blank ^a	0.0	0.0	0.0	---	---	---
35	1	0.0	0.1	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0
	Blank ^a	0.0	0.1	0.0	---	---	---
60	1	0.0	0.1	0.0	0.0	0.0	0.0
	2	0.1	0.0	0.0	0.1	0.0	0.1
	Blank ^a	0.0	0.0	0.0	---	---	---
75	2 ^b	0.1	0.0	0.0	0.1	0.0	0.1
90	1	0.0	0.1	0.0	0.0	0.0	0.1
	2 ^b	0.1	0.1	0.1	0.2	0.1	0.2
	Blank ^a	0.0	0.0	0.0	---	---	---
105	1	0.0	0.1	0.0	0.0	0.1	0.1
	2 ^b	0.1	0.2	0.1	0.2	0.1	0.2
	Blank ^a	0.0	0.0	0.0	---	---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE X
Weight Change of 92% Gold-Copper
Electroplated Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1 Blank ^a	0.1	0.0	0.1	0.0	0.1	0.1
			0.0	0.0		---	---
35	1 Blank ^a	0.1	0.0	0.1	0.0	0.0	0.1
			0.0	0.0		---	---
60	1 ^b Blank ^a	0.1	0.0	0.1	0.0	0.1	0.1
			0.0	0.0		---	---
75	1 ^b	0.1	0.1	0.1	0.0	0.1	0.1
90	1 ^b Blank ^a	0.2	0.2	0.2	0.1	0.2	0.2
			0.0	0.0		---	---
105	1 ^b Blank ^a	0.2	0.2	0.2	0.2	0.2	0.2
			0.0	0.0		---	---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE XI
Weight Change of 87% Gold-Copper
Electroplated Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.1	0.0	0.0	0.0	0.0	0.0
	Blank ^a	0.0	0.0		---	---	
35	1	0.1	0.0	0.0	0.1	0.1	0.0
	Blank ^a	0.0	0.0		---	---	
60	1 ^b	0.1	0.0	0.0	0.1	0.0	0.0
	Blank ^a	0.0	0.0		---	---	
75	1 ^b	0.2	0.2	0.1	0.2	0.2	0.2
	Blank ^a	0.0	0.0		---	---	
90	1 ^b	0.2	0.2	0.1	0.2	0.2	0.2
	Blank ^a	0.0	0.0		---	---	
105	1 ^b	0.2	0.2	0.2	0.2	0.2	0.2
	Blank ^a	0.0	0.0		---	---	

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

TABLE XII
Weight Change of 85% Gold-Copper
Electroplated Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.1	0.0	0.1	0.0	0.0	0.0
35	1	0.0	0.0	0.1	0.0	0.0	0.0
60	1 ^a	0.1	0.0	0.1	0.0	0.0	0.0
75	1 ^a	0.2	0.2	0.1	0.1	0.2	0.1
90	1 ^a	0.2	0.2	0.2	0.1	0.2	0.2
105	1 ^a	0.3	0.2	0.2	0.2	0.2	0.2

^aSamples taken off pins and placed flat on petri dish.

TABLE XIII
Weight Change of 80% Gold-Copper
Electroplated Samples

Storage Time days	Sample No.	Epoxy "A"			Epoxy "B"		
		Oven Temperature, °C			Oven Temperature, °C		
		30	60	90	30	60	90
		mg/sq in.			mg/sq in.		
15	1	0.0	0.1	0.1	0.1	0.1	0.0
	Blank ^a	0.0		0.0	---		---
35	1	0.1	0.1	0.1	0.1	0.1	0.0
	Blank ^a	0.0		0.0	---		---
60	1 ^b	0.0	0.1	0.1	0.1	0.1	0.0
	Blank ^a	0.0		0.0	---		---
75	1 ^b	0.1	0.2	0.2	0.3	0.2	0.1
90	1 ^b	0.2	0.3	0.3	0.3	0.3	0.2
	Blank ^a	0.0		0.0	---		---
105	1 ^b	0.3	0.3	0.3	0.3	0.3	0.2
	Blank ^a	0.0		0.0	---		---

^aBlanks the same for both epoxy "A" and epoxy "B".

^bSamples taken off pins and placed flat on petri dish.

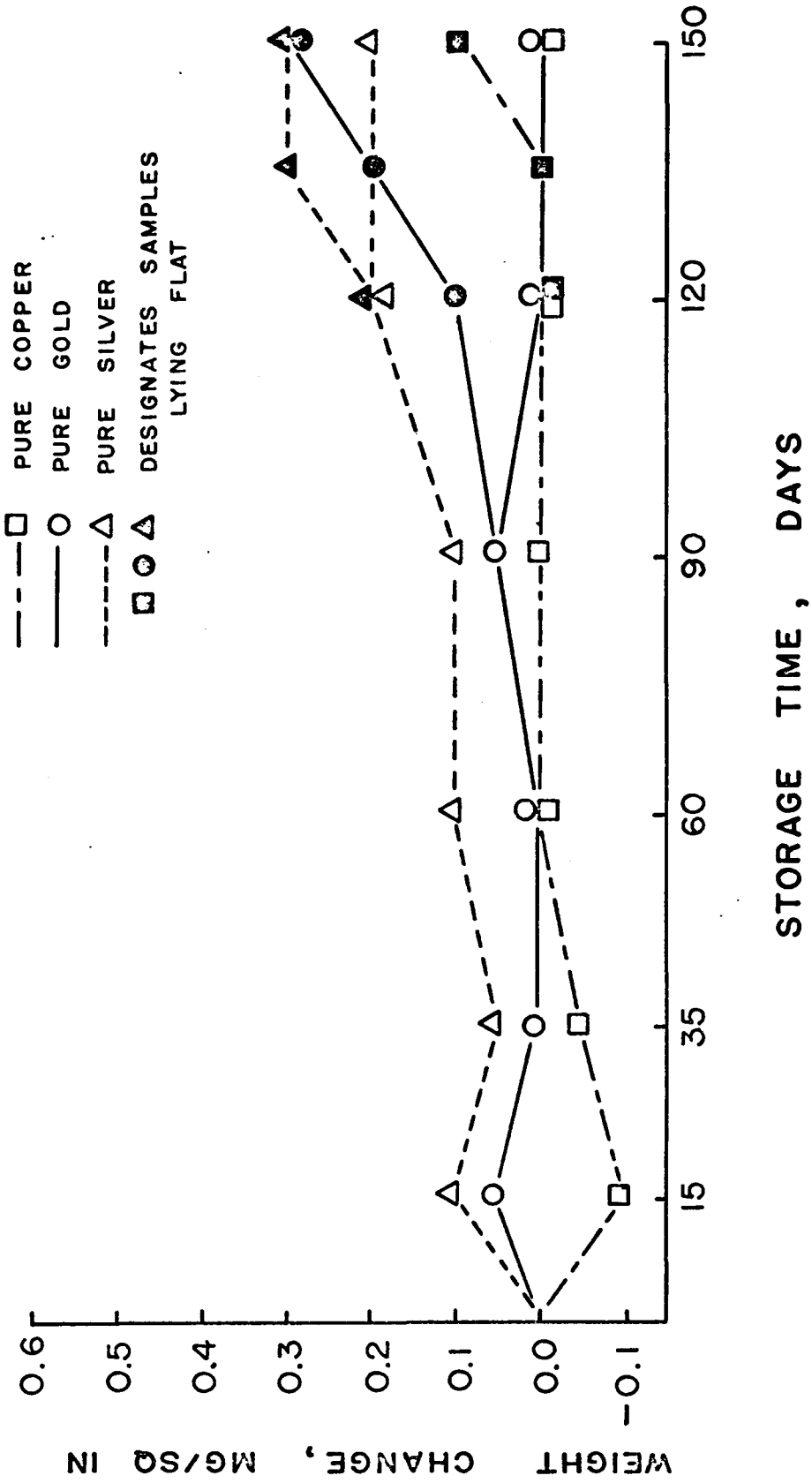


Figure 1. Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 30 °C

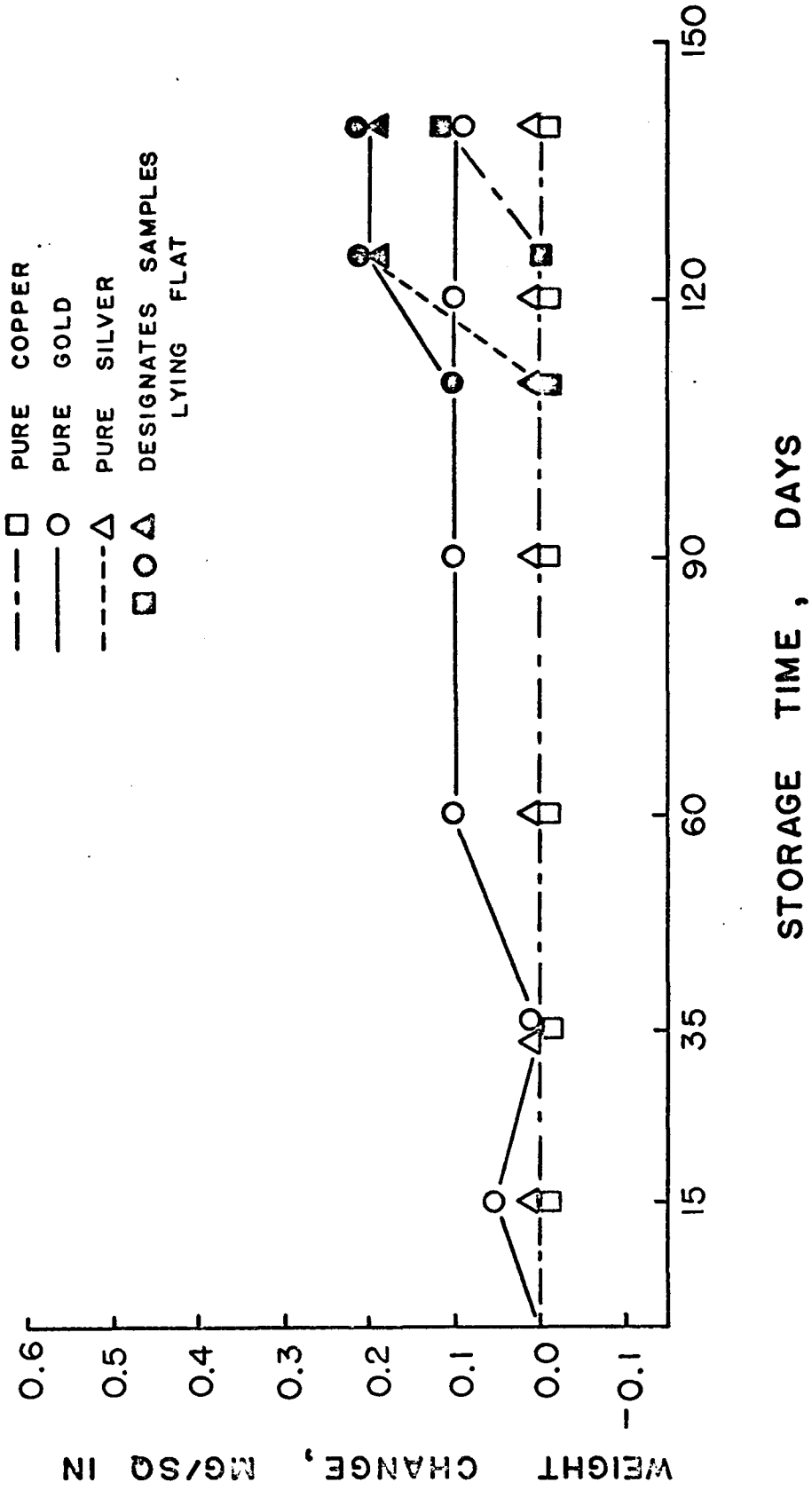


Figure 2. Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 30 °C

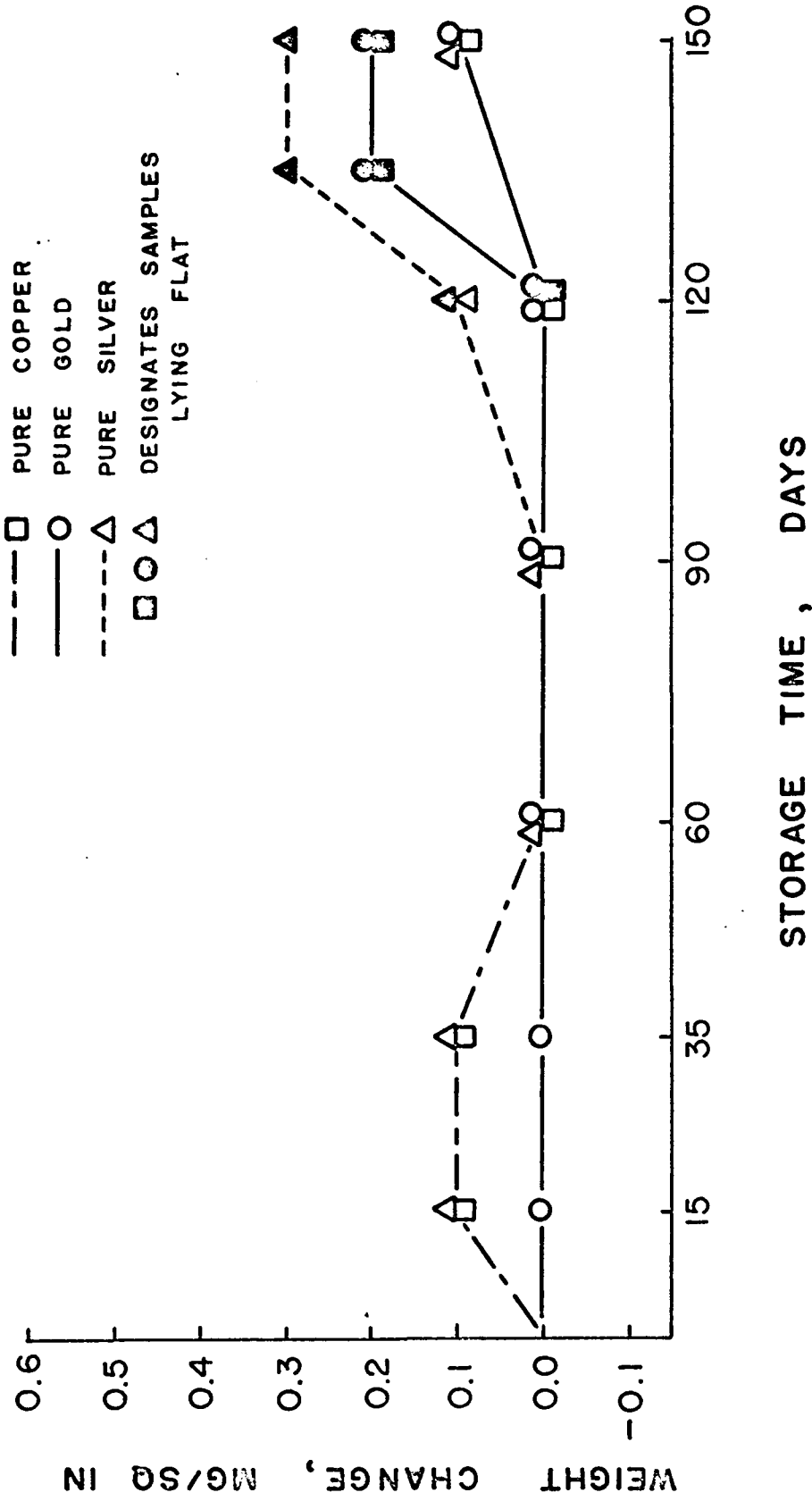


Figure 3. Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 60 °C

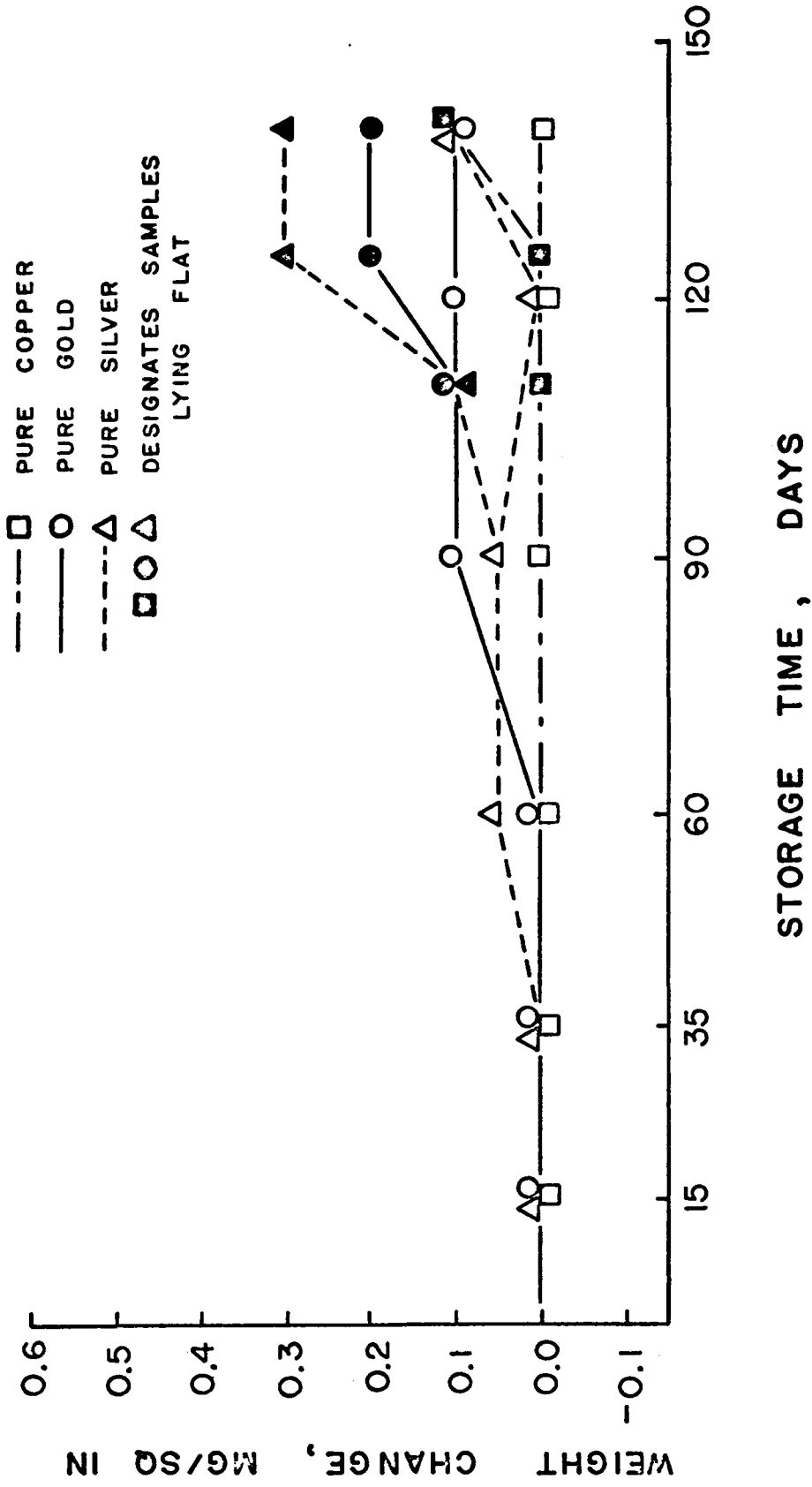


Figure 4. Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 60 °C

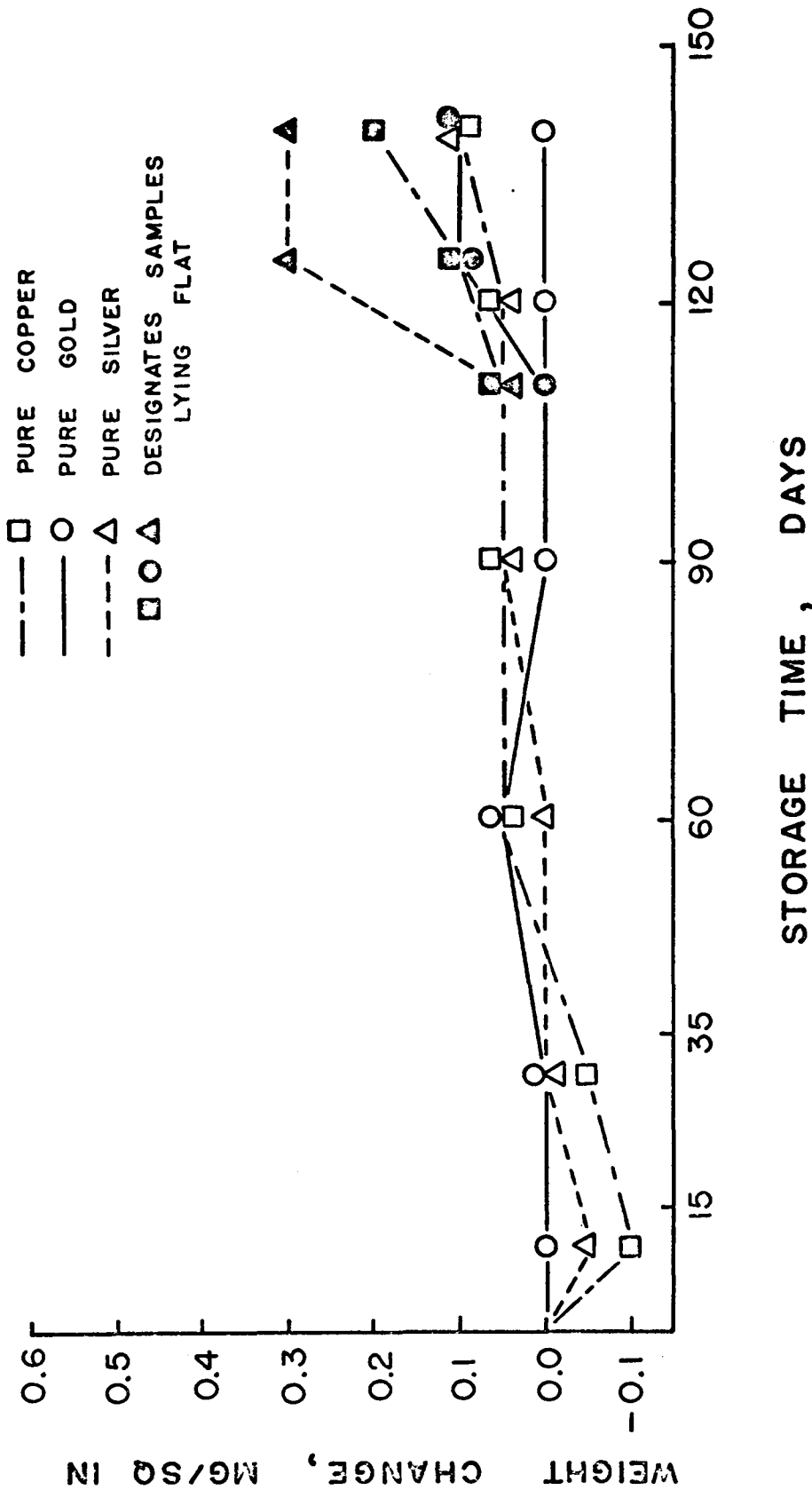


Figure 5. Weight Change of Pure Metal Samples Stored with Plastic Preparation "A" at 90 °C

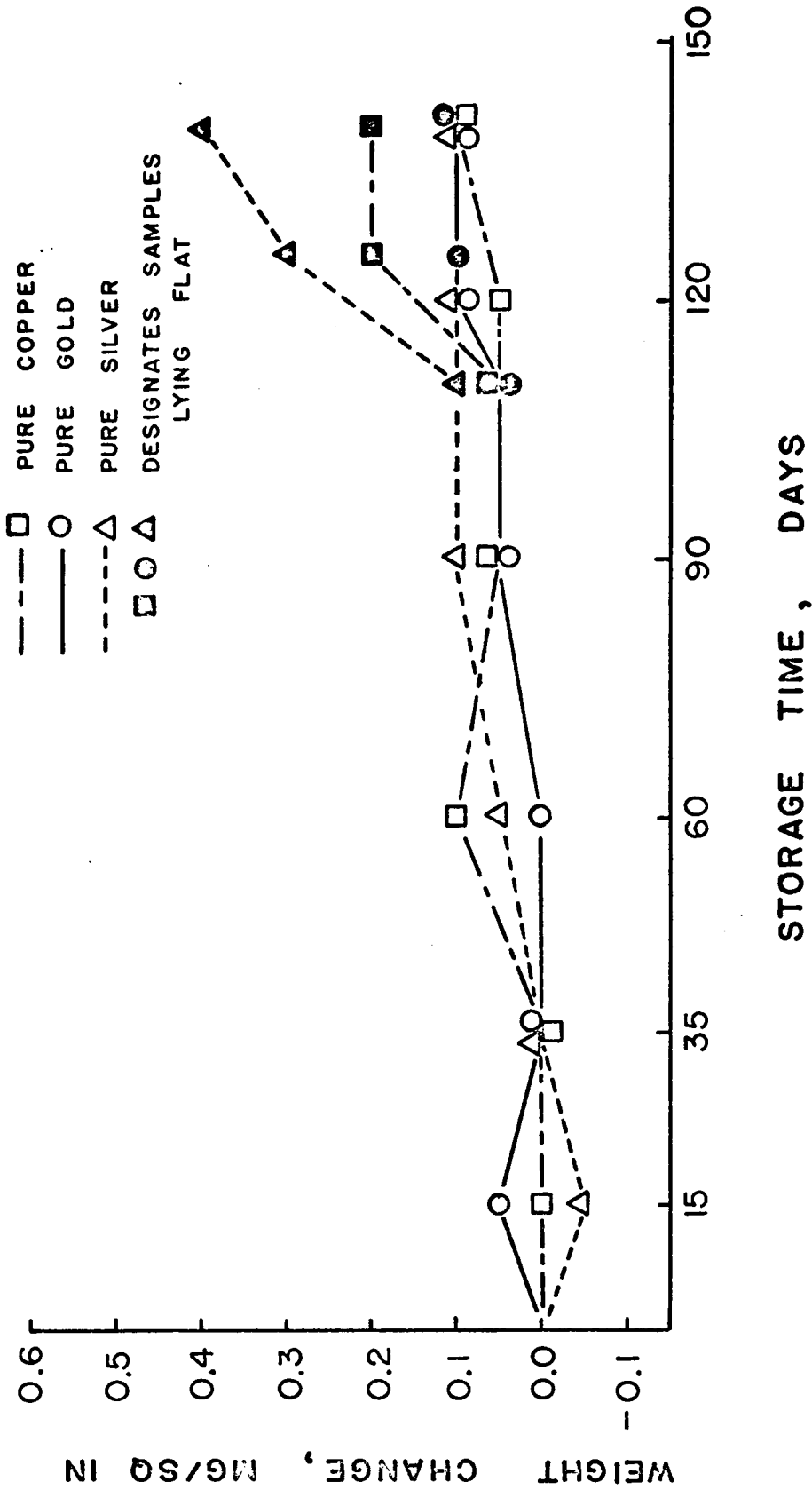


Figure 6. Weight Change of Pure Metal Samples Stored with Plastic Preparation "B" at 90 °C

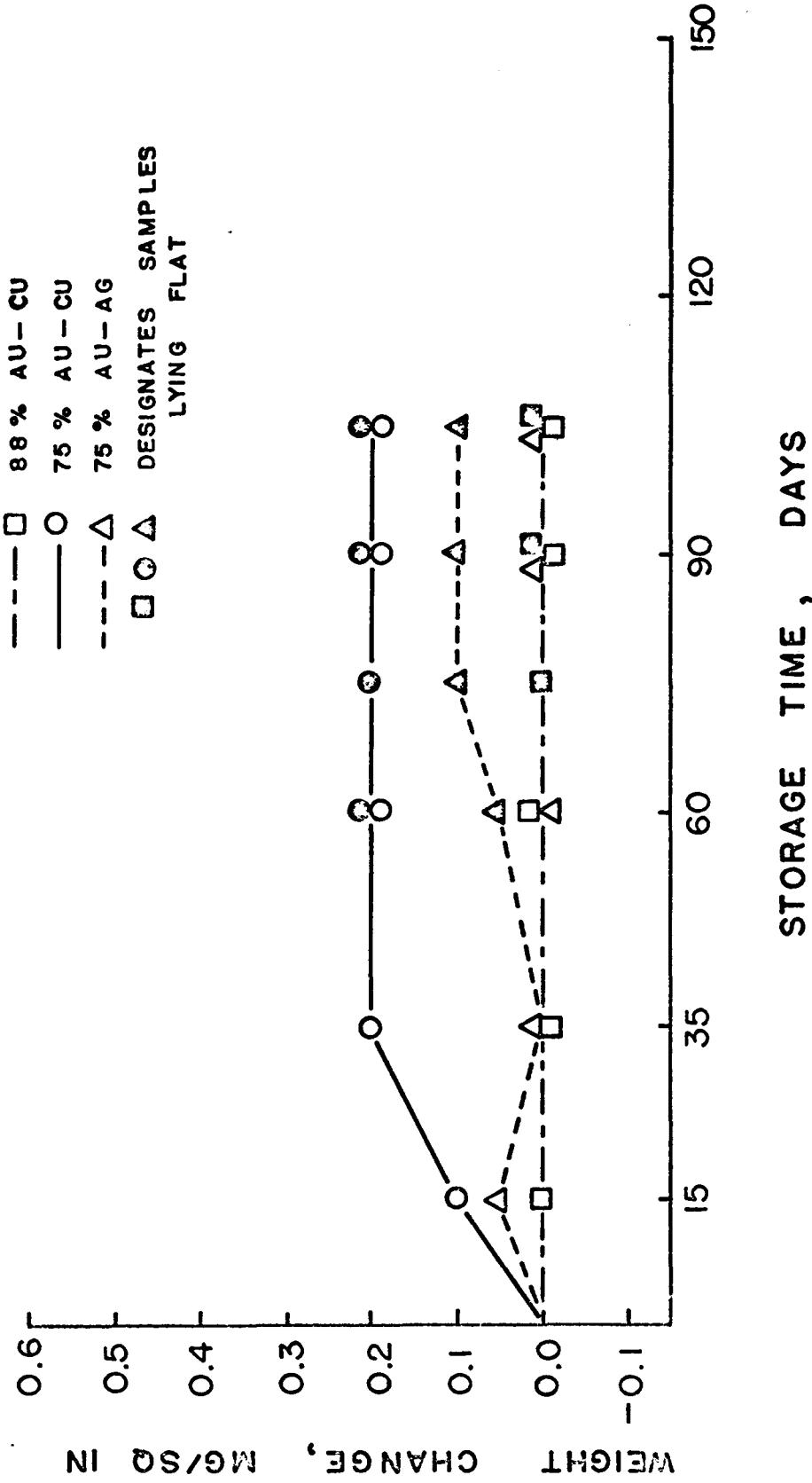


Figure 7. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 30 °C

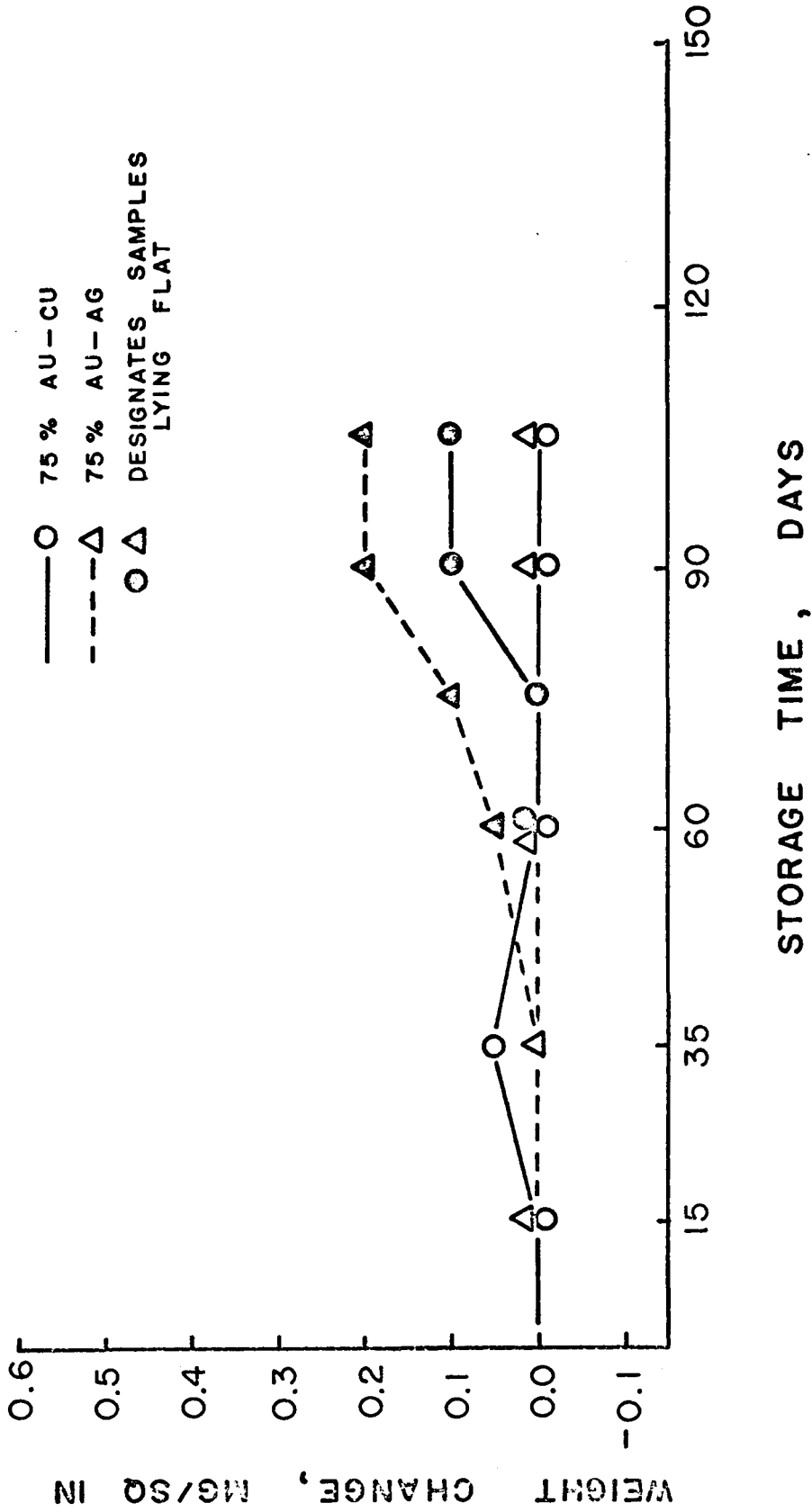


Figure 8. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 30 °C

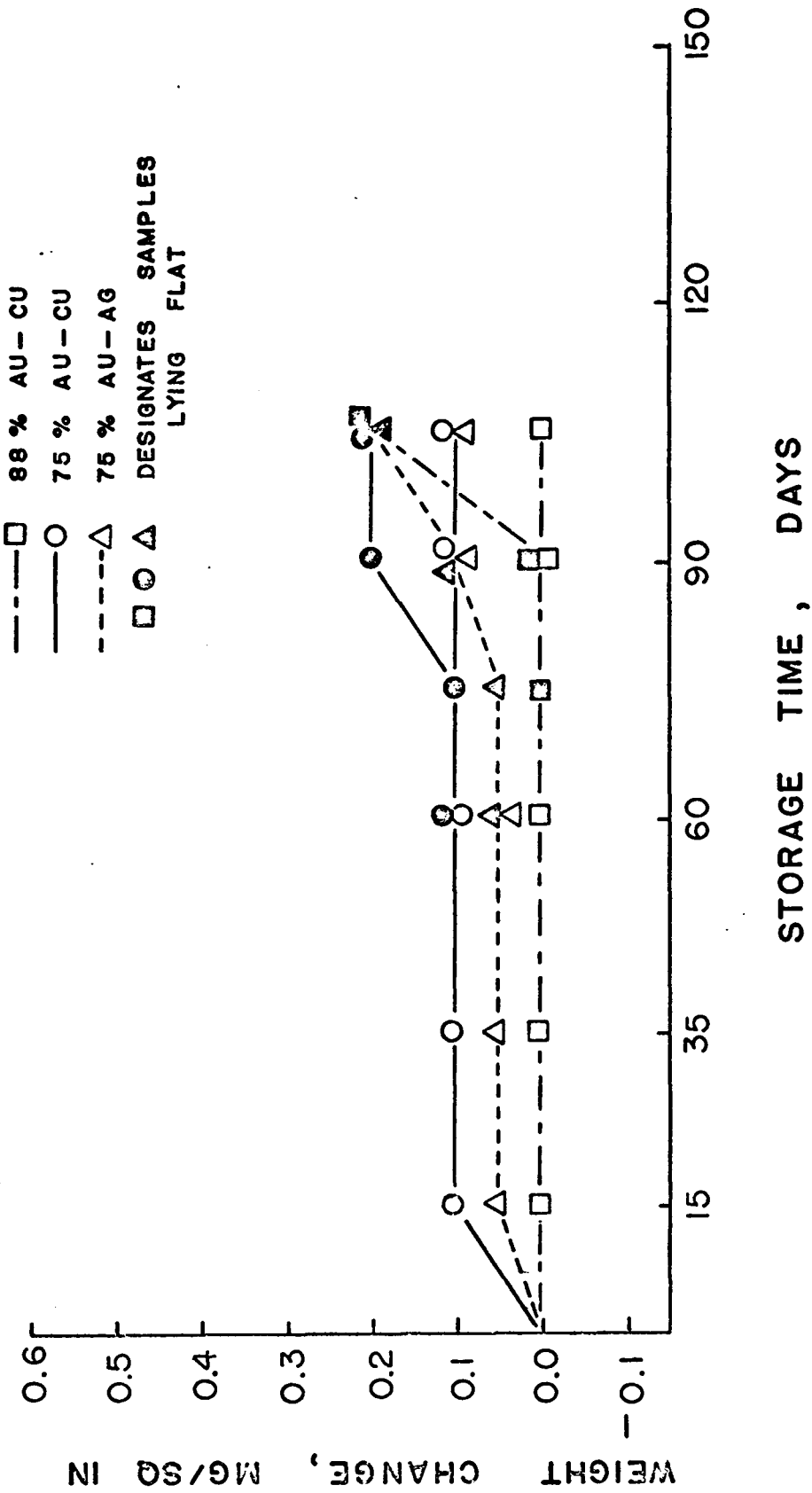


Figure 9. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 60 °C

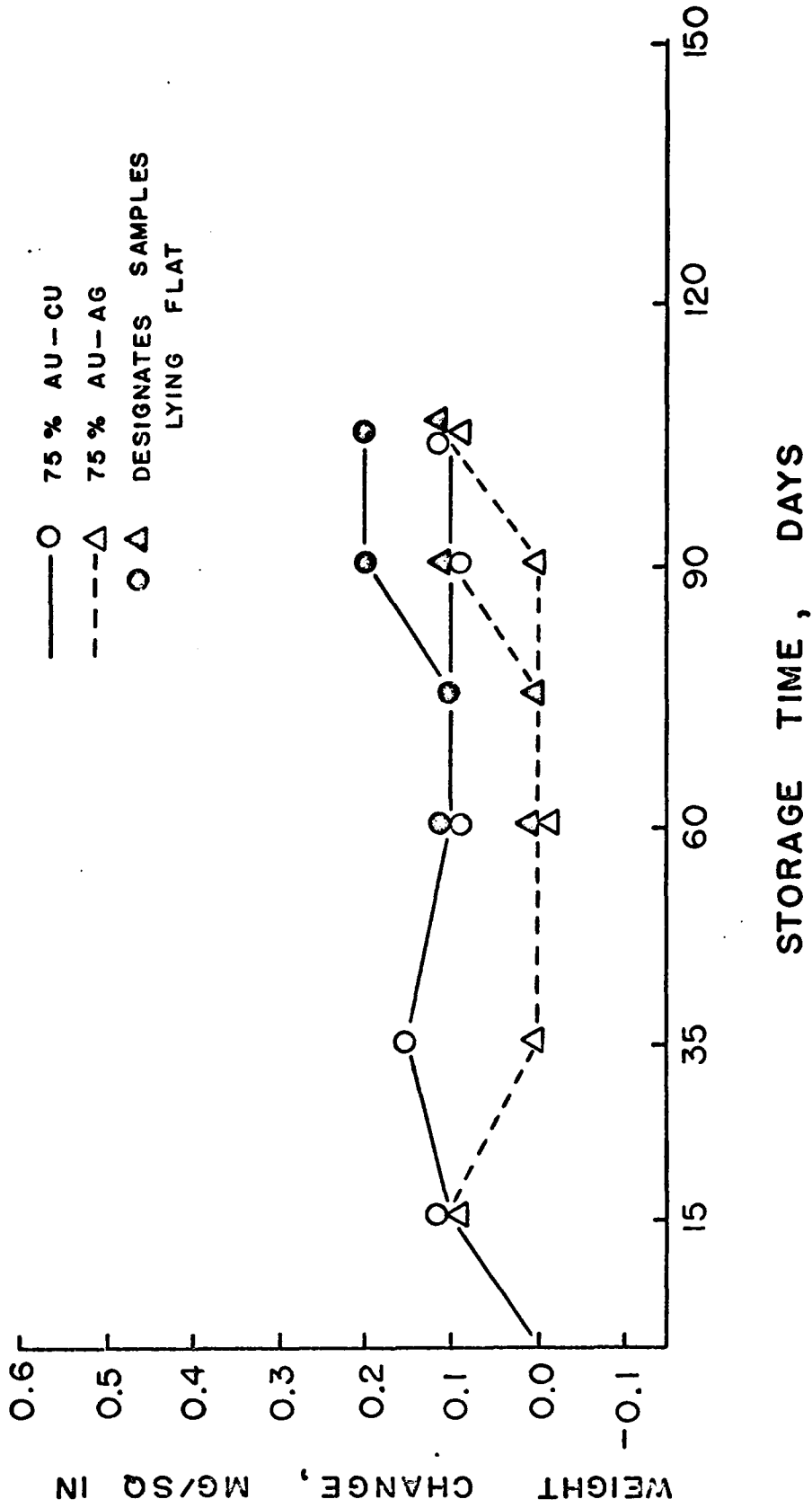


Figure 10. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 60 °C

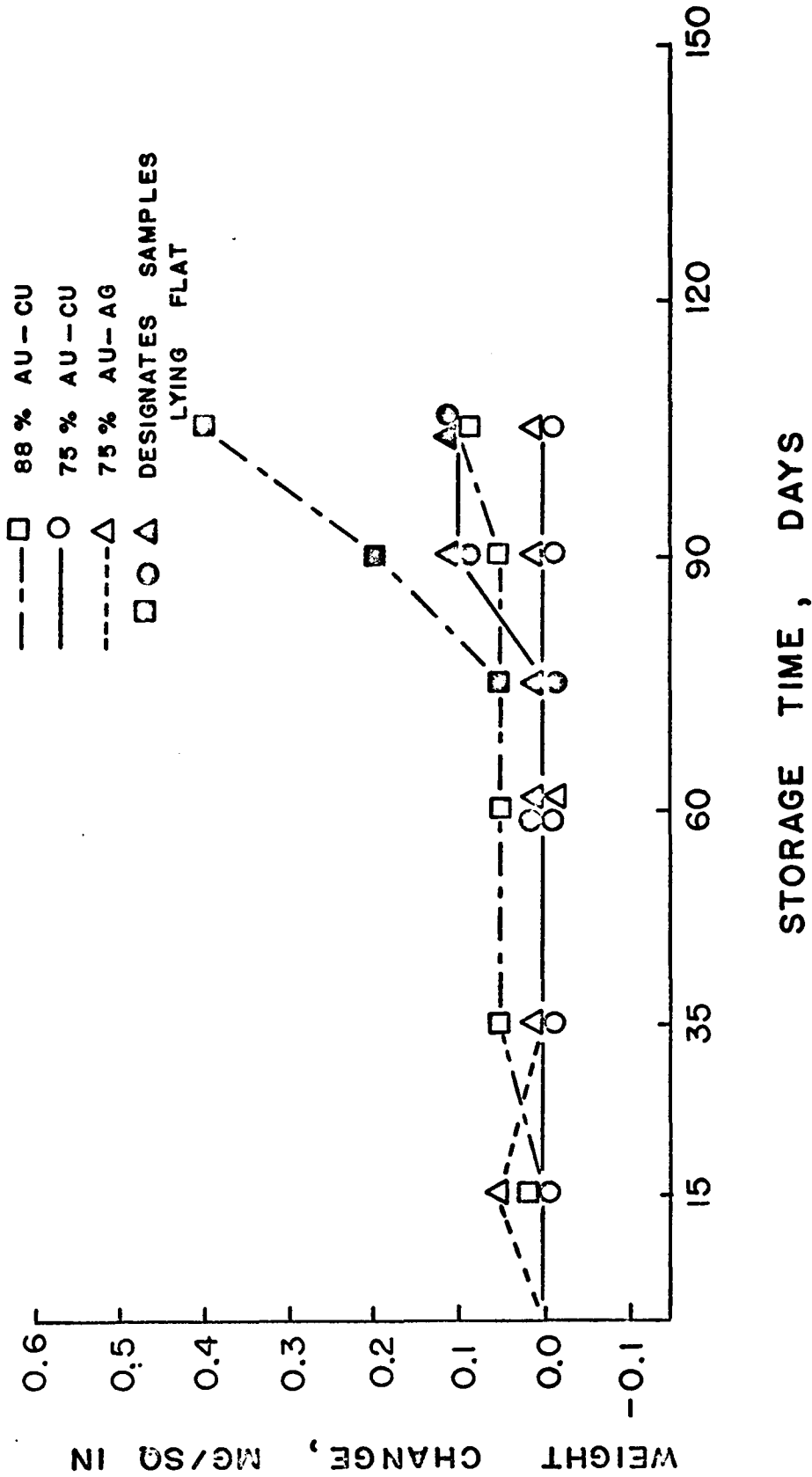


Figure 11. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "A" at 90 °C

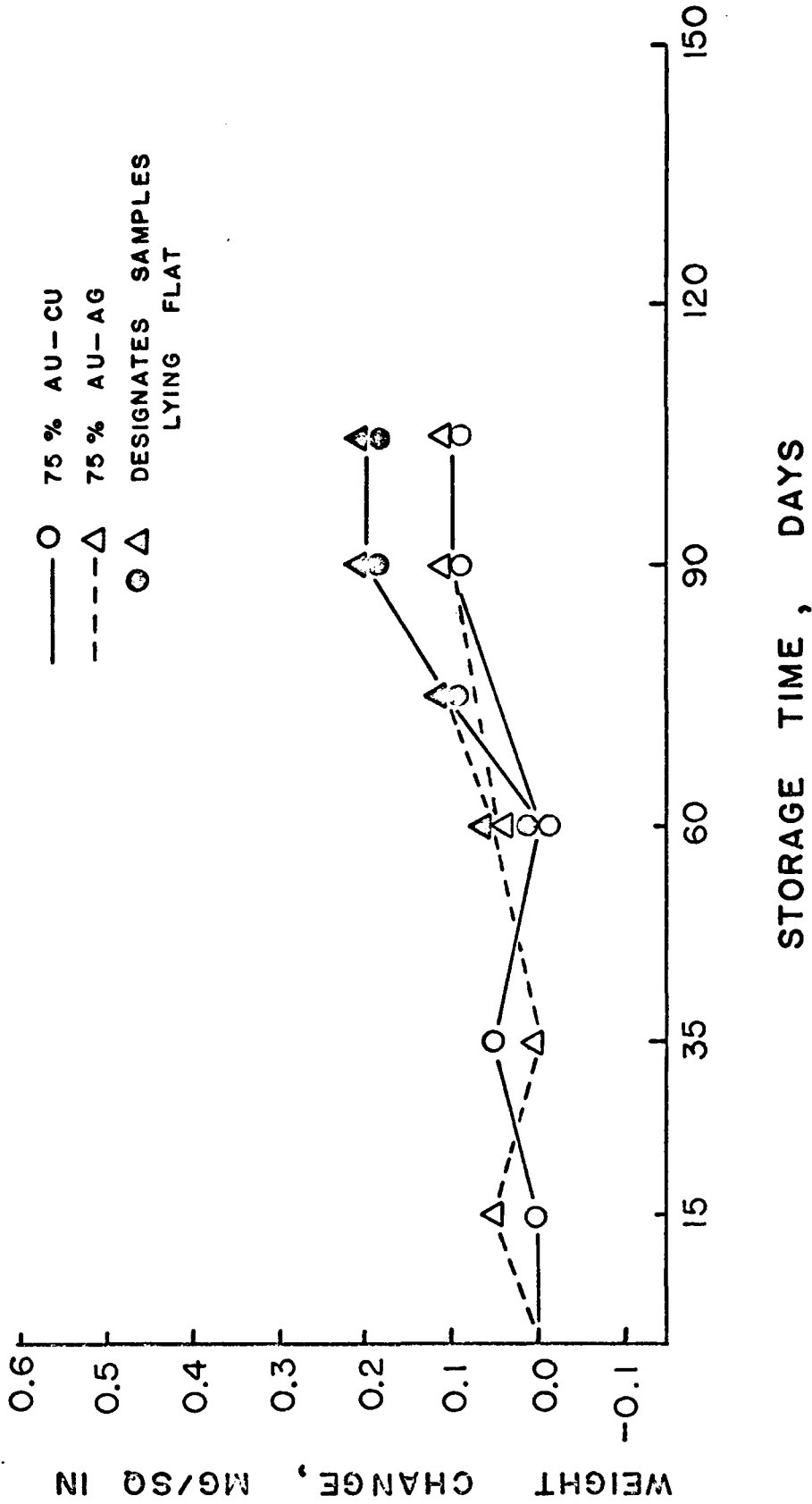


Figure 12. Weight Change of Gold Alloy Samples Stored with Plastic Preparation "B" at 90 °C

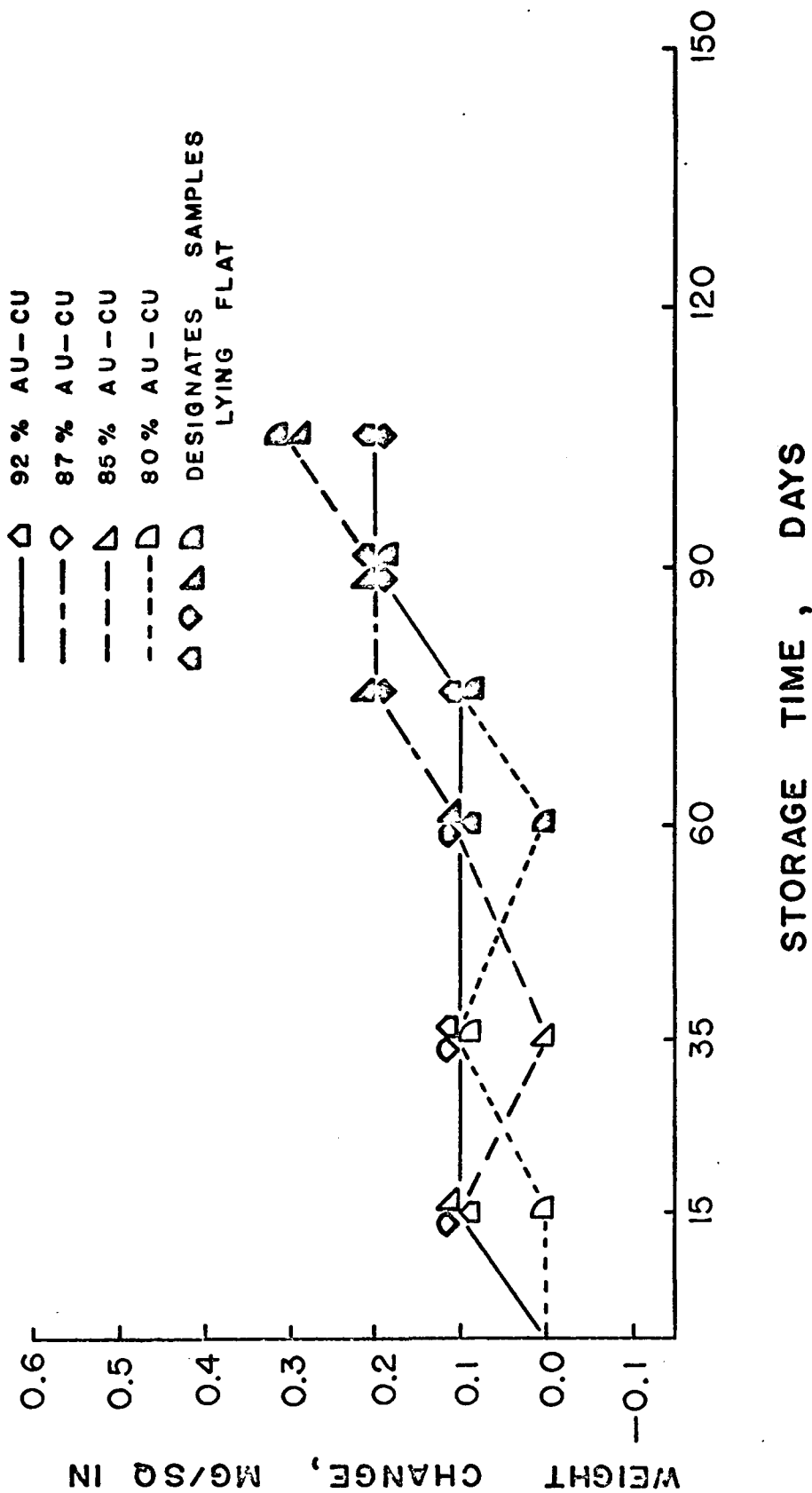


Figure 13. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 30 °C

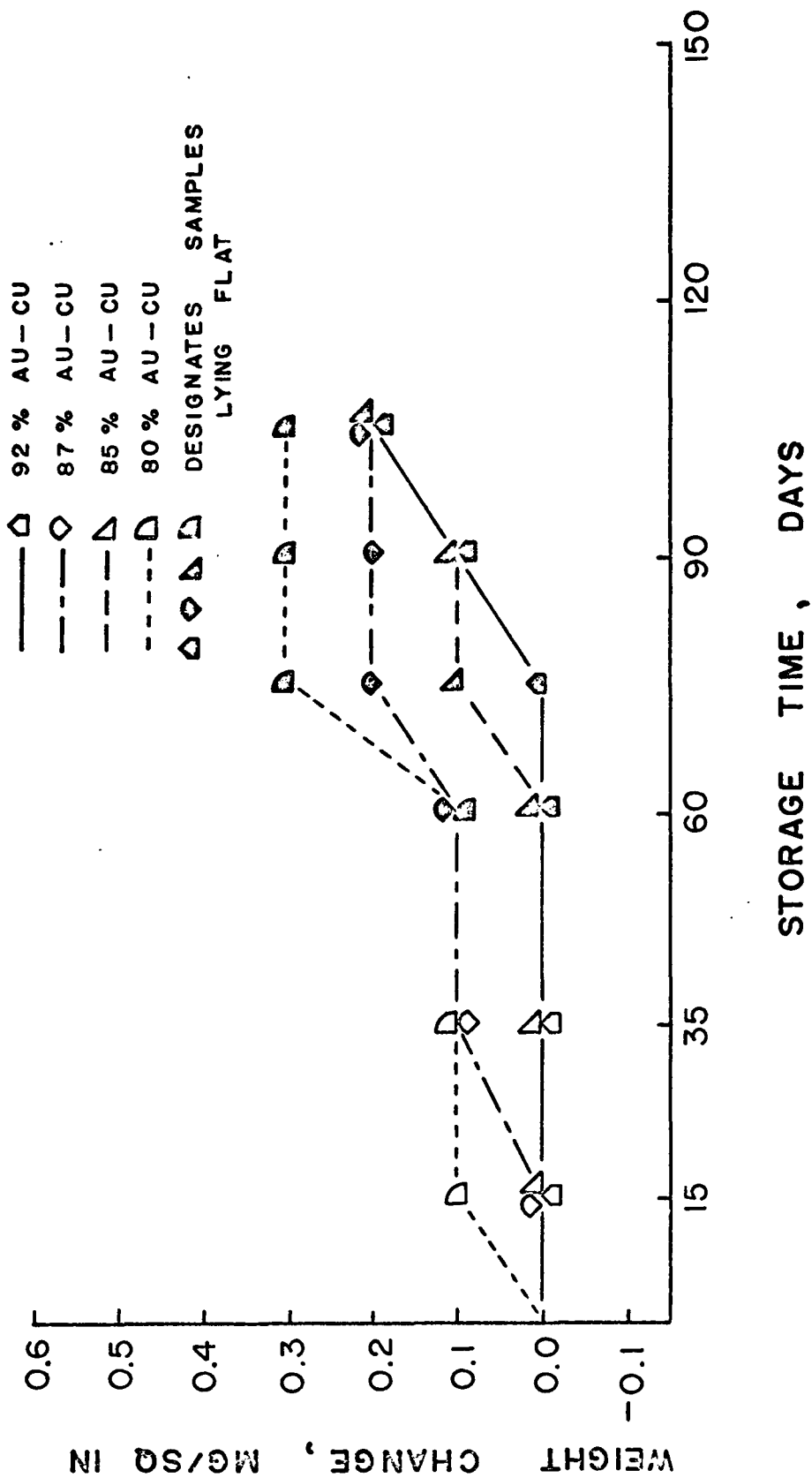
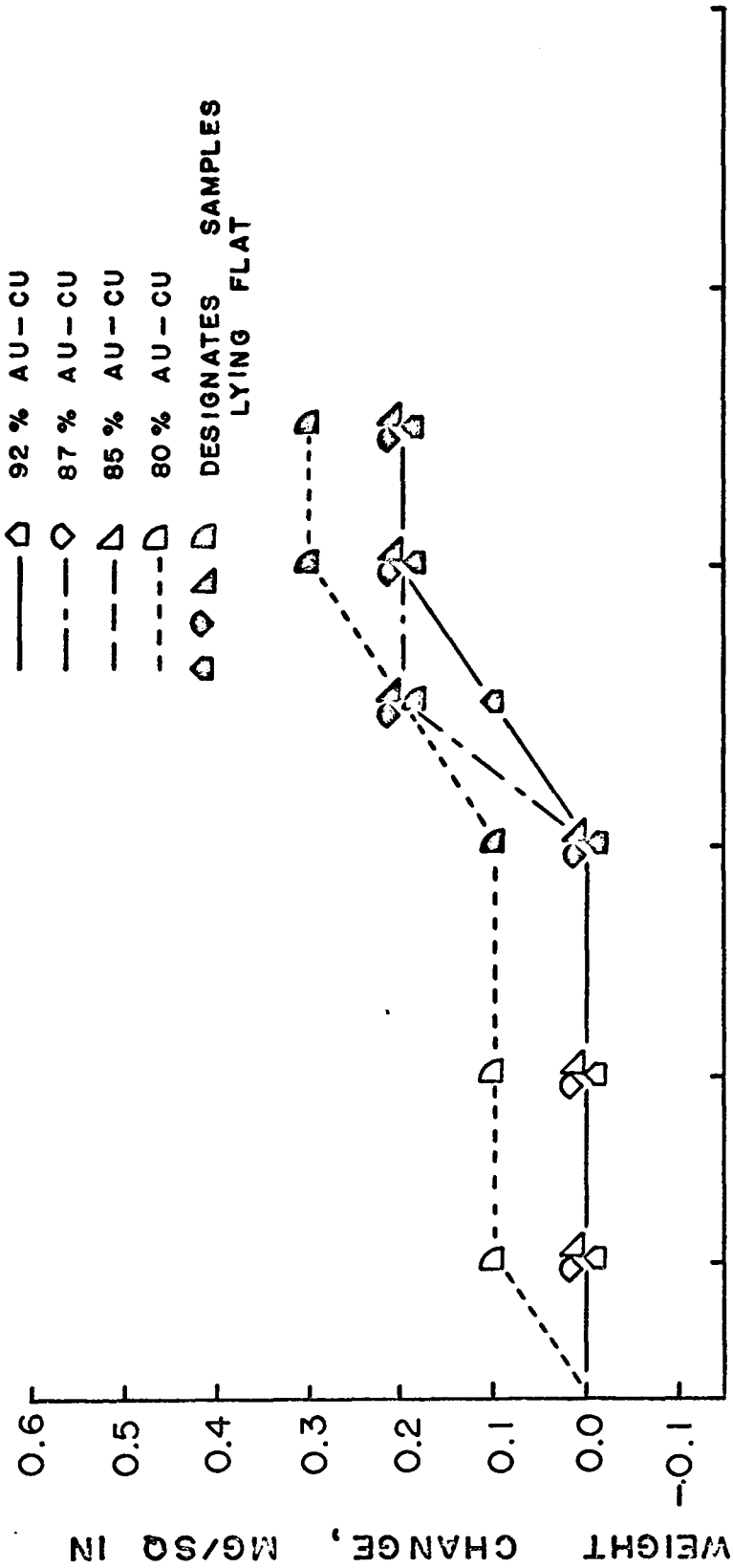


Figure 14. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 30 °C



STORAGE TIME, DAYS

Figure 15. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 60 °C

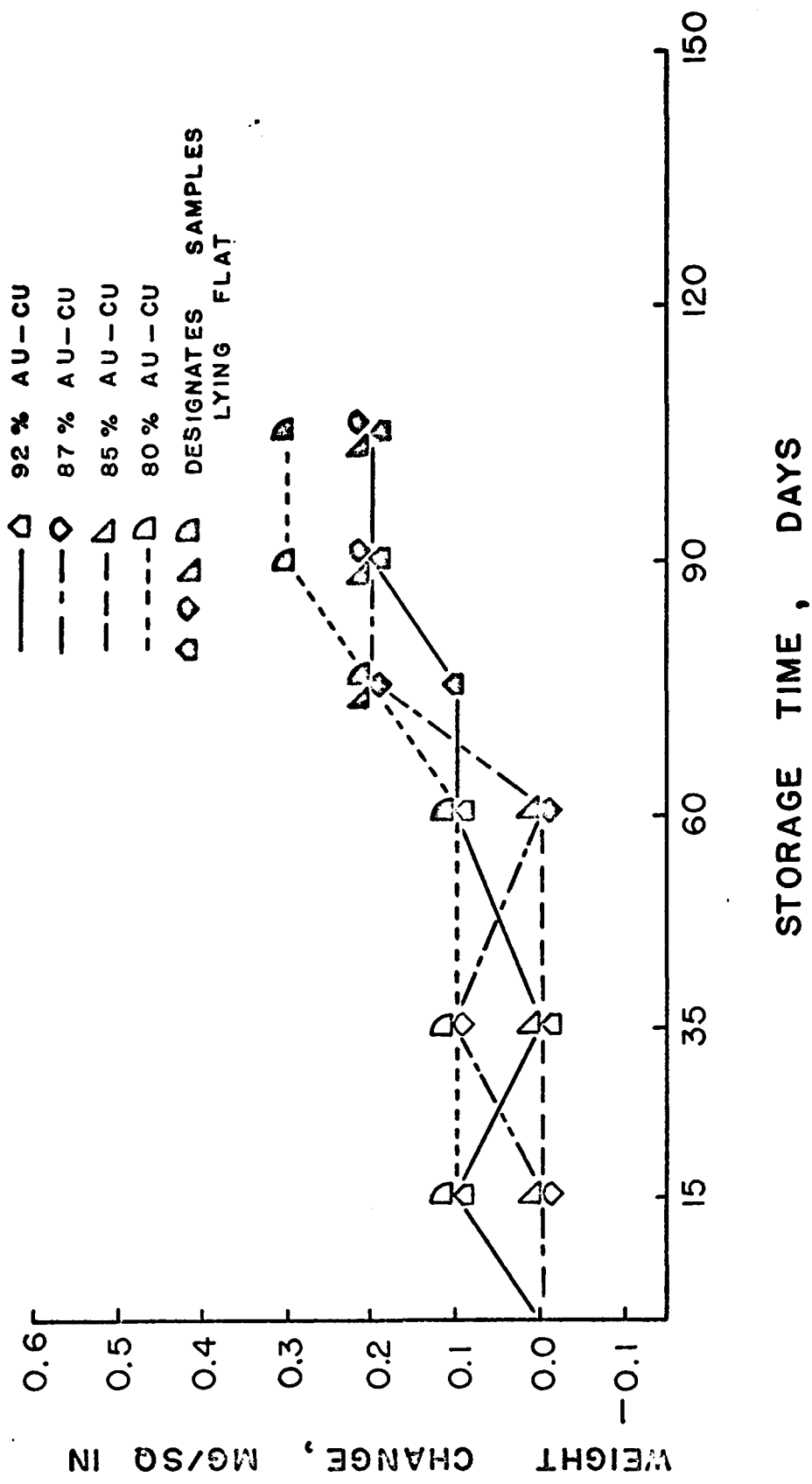


Figure 16. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 60 °C

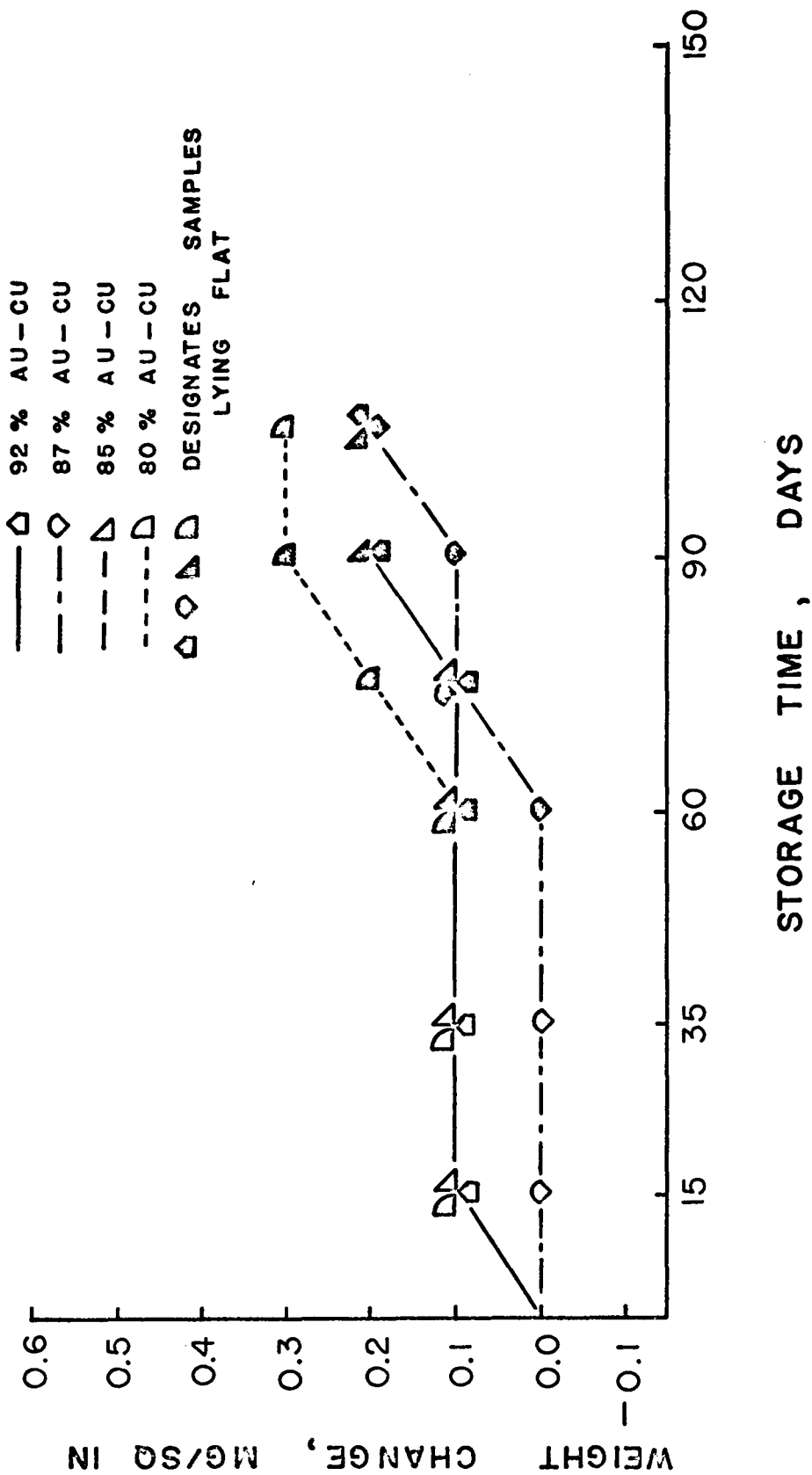


Figure 17. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "A" at 90 °C

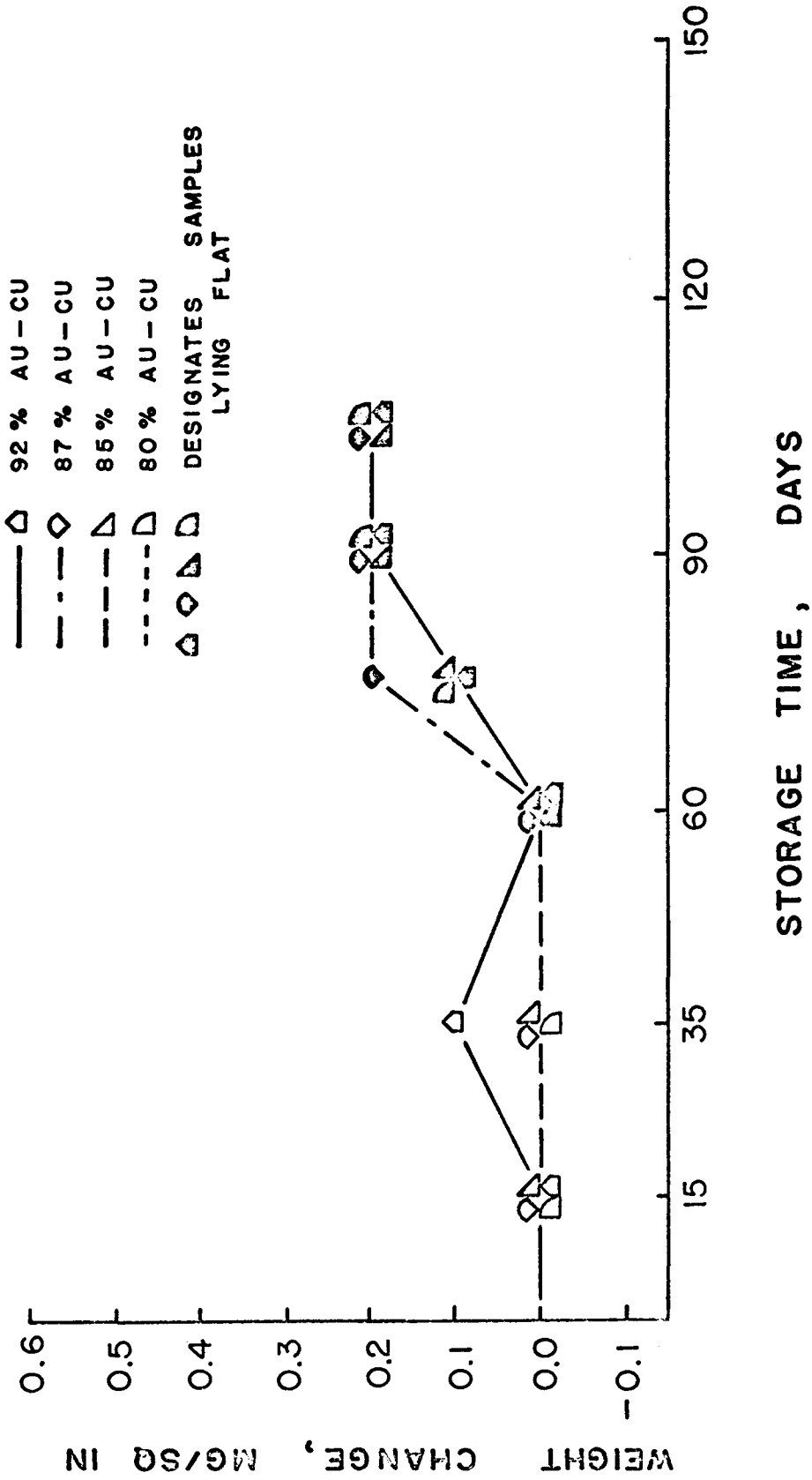


Figure 18. Weight Change of Electroplated Gold Alloy Samples Stored with Plastic Preparation "B" at 90 °C

TABLE XIV

Rate of Film Formation on Metal Samples Stored with Epoxy "A"

Metal Sample	Samples Propped Up		Samples Lying Flat	
	Oven Temperature, °C 30	60	Oven Temperature, °C 30	60
	$\times 10^3$ mg/sq in.-day			
Pure gold	0.55	0.67	0.83	0.83
Pure silver	1.3	0.84	0.71	0.71
Pure copper	0.0	0.67	0.71	0.71
88% Gold-copper alloy	0.0	0.0	0.95	0.95
75% Gold-copper alloy	5.7	6.6	0.0	0.0
75% Gold-silver alloy	0.0	1.1	0.0	0.0
92% Gold-copper electroplated	2.9	0.0	2.9	2.9
87% Gold-copper electroplated	2.9	0.0	0.0	0.0
85% Gold-copper electroplated	2.9	0.0	2.9	2.9
80% Gold-copper electroplated	2.9	2.9	2.9	2.9

$\times 10^3$ mg/sq in.-day

TABLE XV

Rate of Film Formation on Metal Samples Stored with Epoxy "B"

Metal Sample	Samples Propped Up		Samples Lying Flat	
	Oven Temperature, °C 30 60 90		Oven Temperature, °C 30 60 90	
	x 10 ³ mg/sq in.-day		x 10 ³ mg/sq in.-day	
Pure gold	1.7	1.1	0.84	2.9
Pure silver	0.0	0.7	1.1	7.1
Pure copper	0.0	0.0	0.7	2.0
88% Gold-copper alloy	Not measured		Not measured	
75% Gold-copper alloy	0.0	1.7	1.1	1.8
75% Gold-silver alloy	0.0	0.95	1.1	3.6
92% Gold-copper electroplated	0.0	0.0	2.8	2.8
87% Gold-copper electroplated	2.8	2.8	0.0	2.5
85% Gold-copper electroplated	0.0	0.0	0.0	2.8
80% Gold-copper electroplated	2.8	2.8	0.0	5.0
				3.6
				2.8

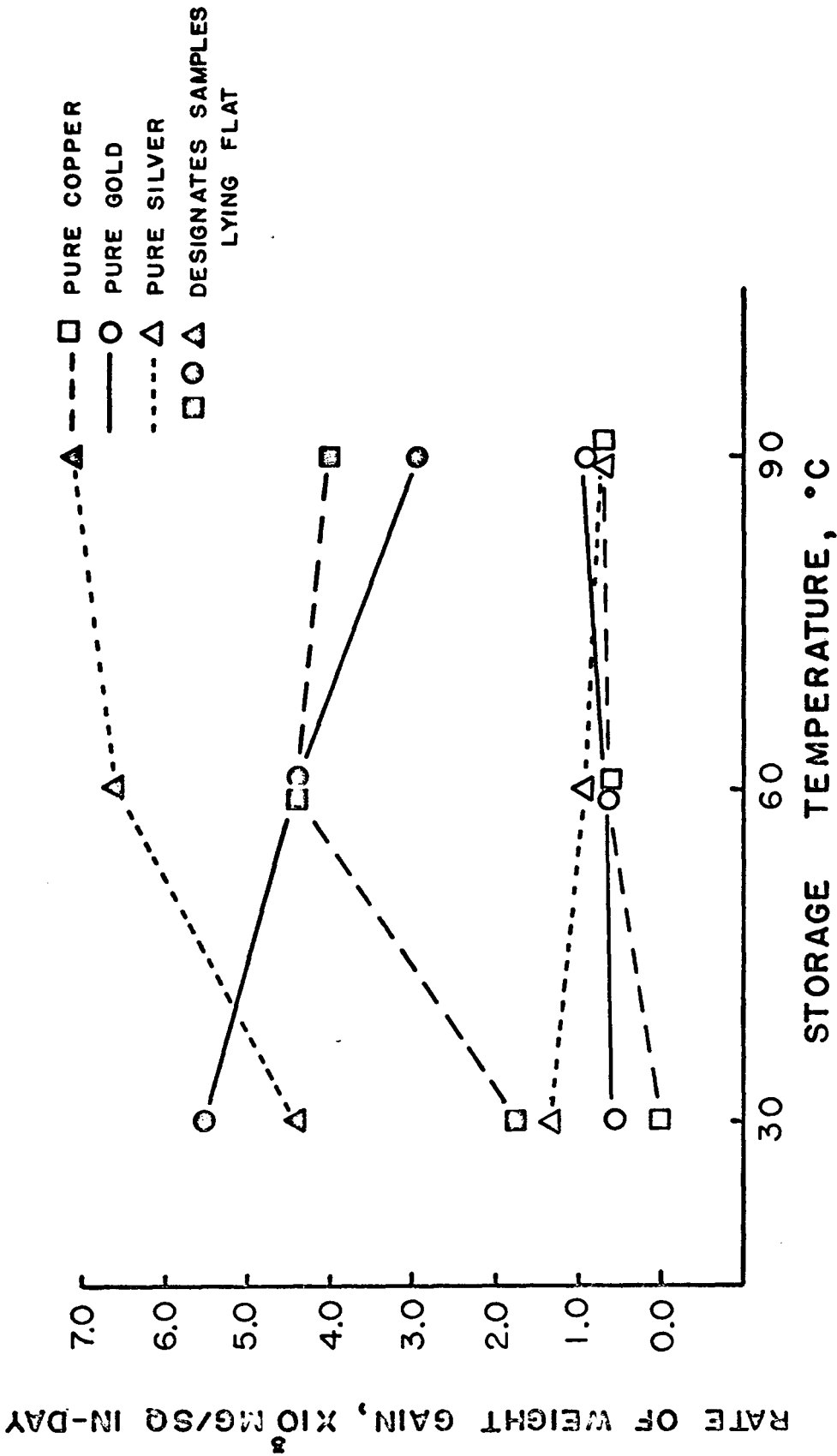


Figure 19. Effect of Temperature Upon Rate of Weight Gain for Pure Metal Samples Stored with Plastic Preparation "A"

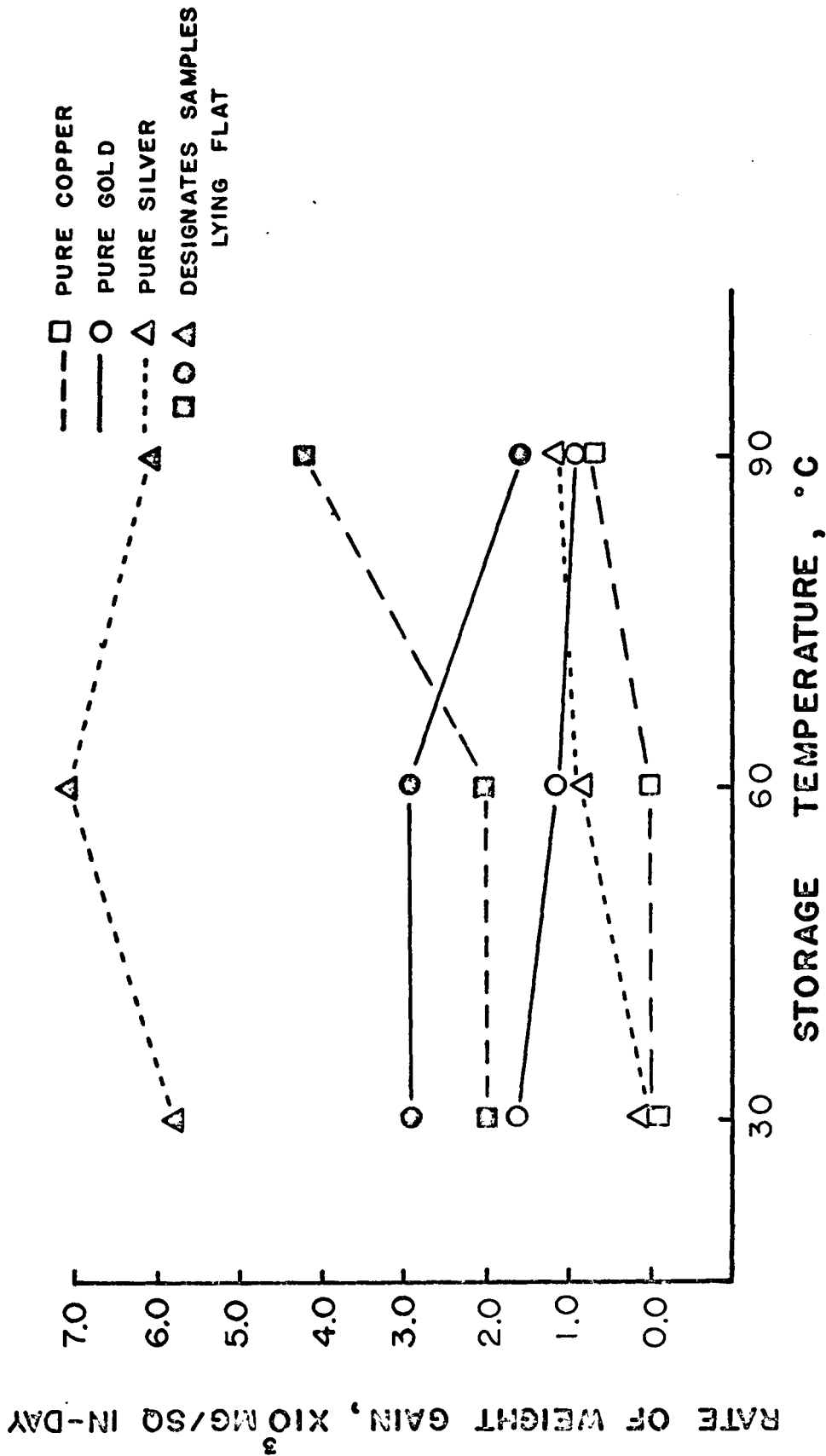


Figure 20. Effect of Temperature Upon Rate of Weight Gain for Pure Metal Samples Stored with Plastic Preparation "B"

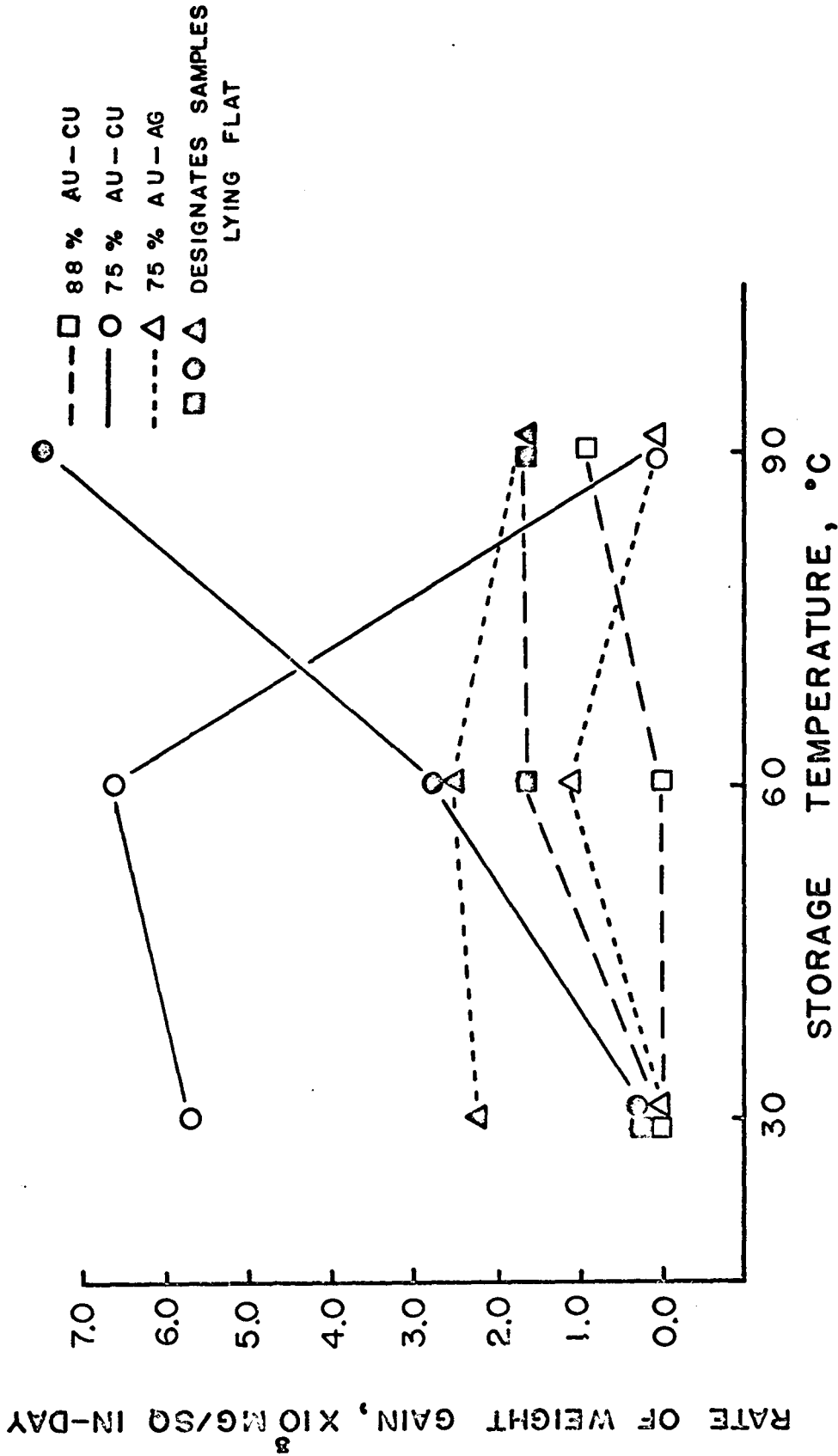


Figure 21. Effect of Temperature Upon Rate of Weight Gain for Gold Alloy Samples Stored with Plastic Preparation "A"

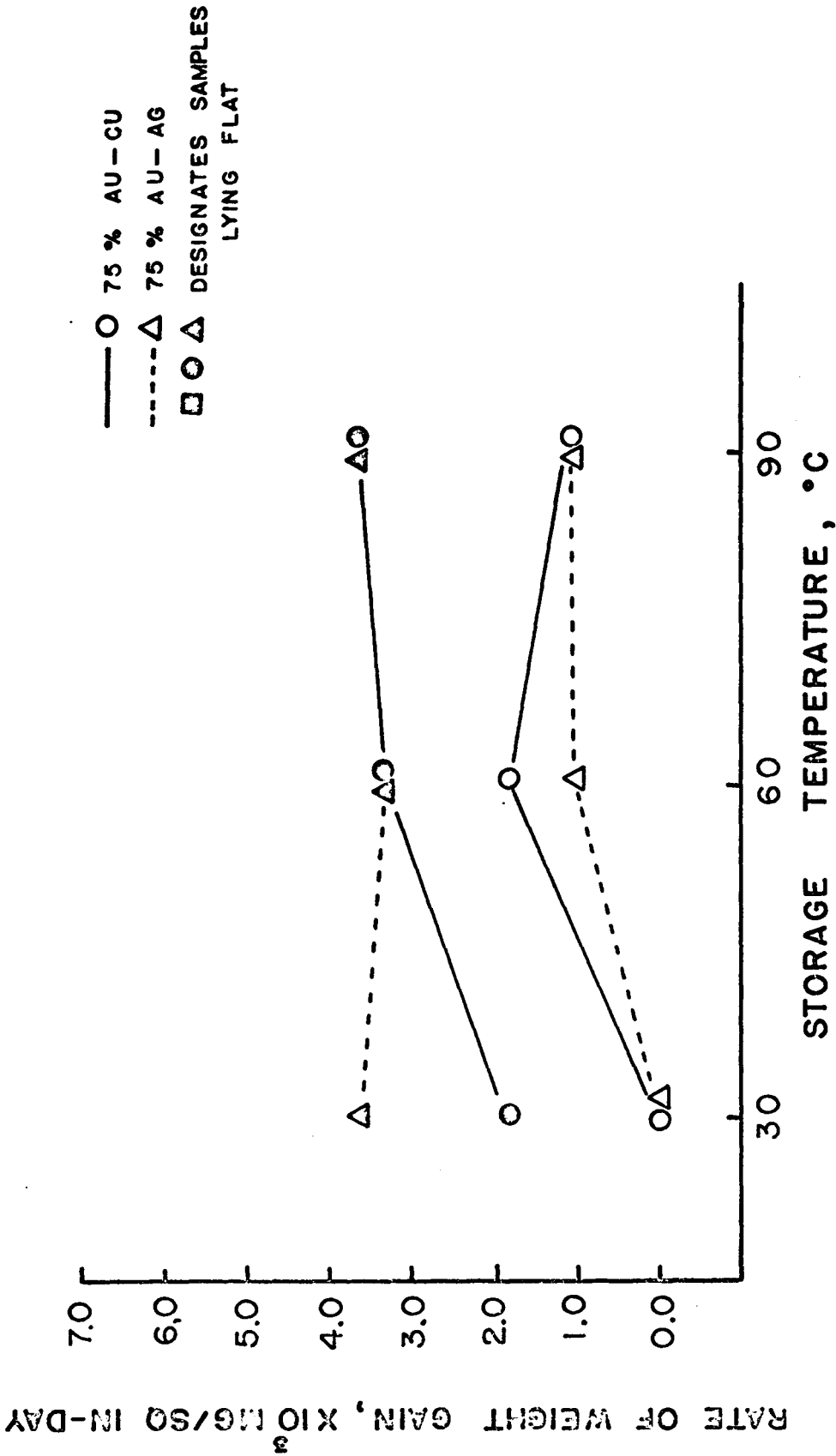


Figure 22. Effect of Temperature Upon Rate of Weight Gain for Gold Alloy Samples Stored with Plastic Preparation "B"

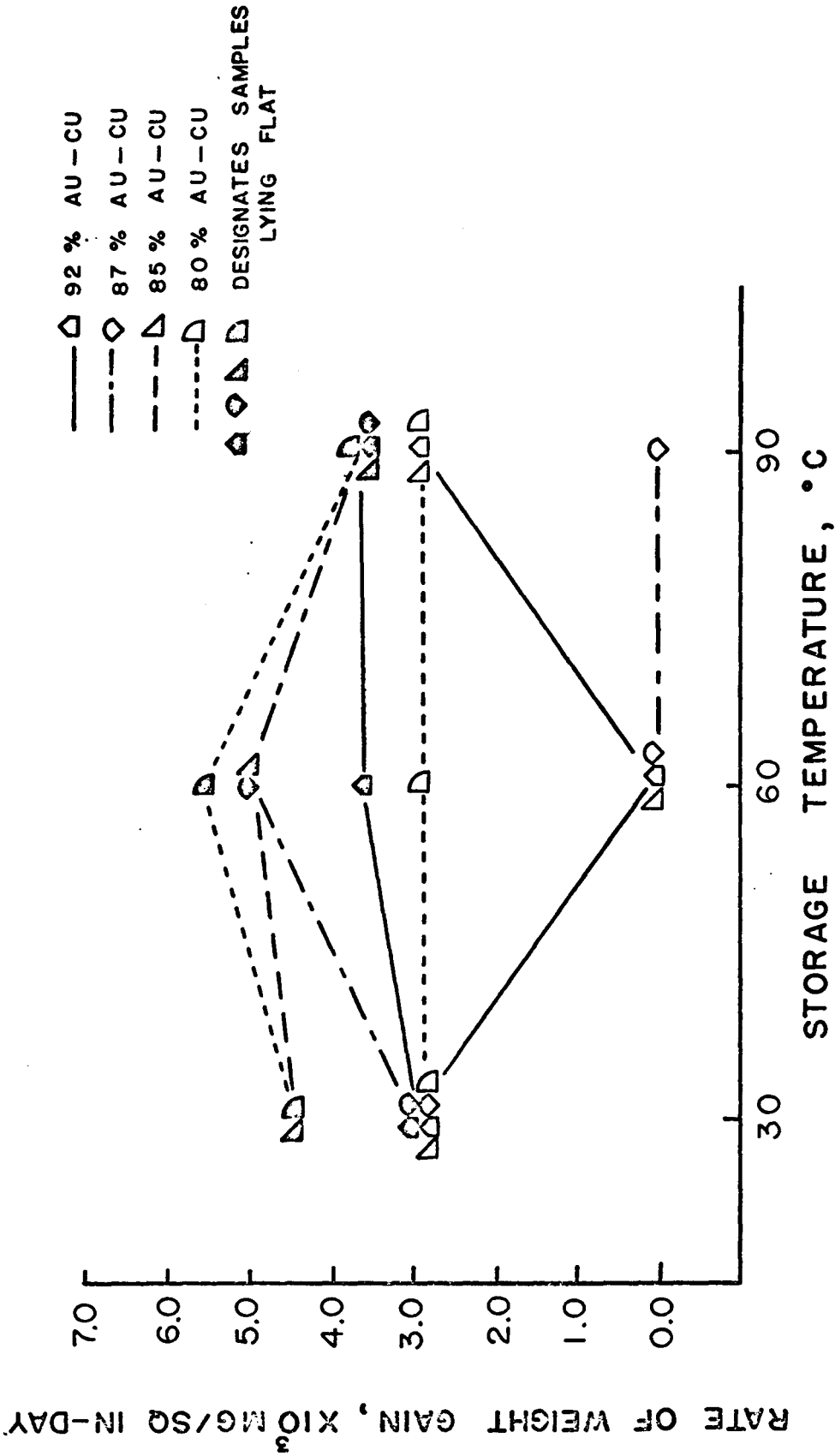


Figure 23. Effect of Temperature Upon Rate of Weight Gain for Electroplated Gold Alloy Samples Stored with Plastic Preparation "A"

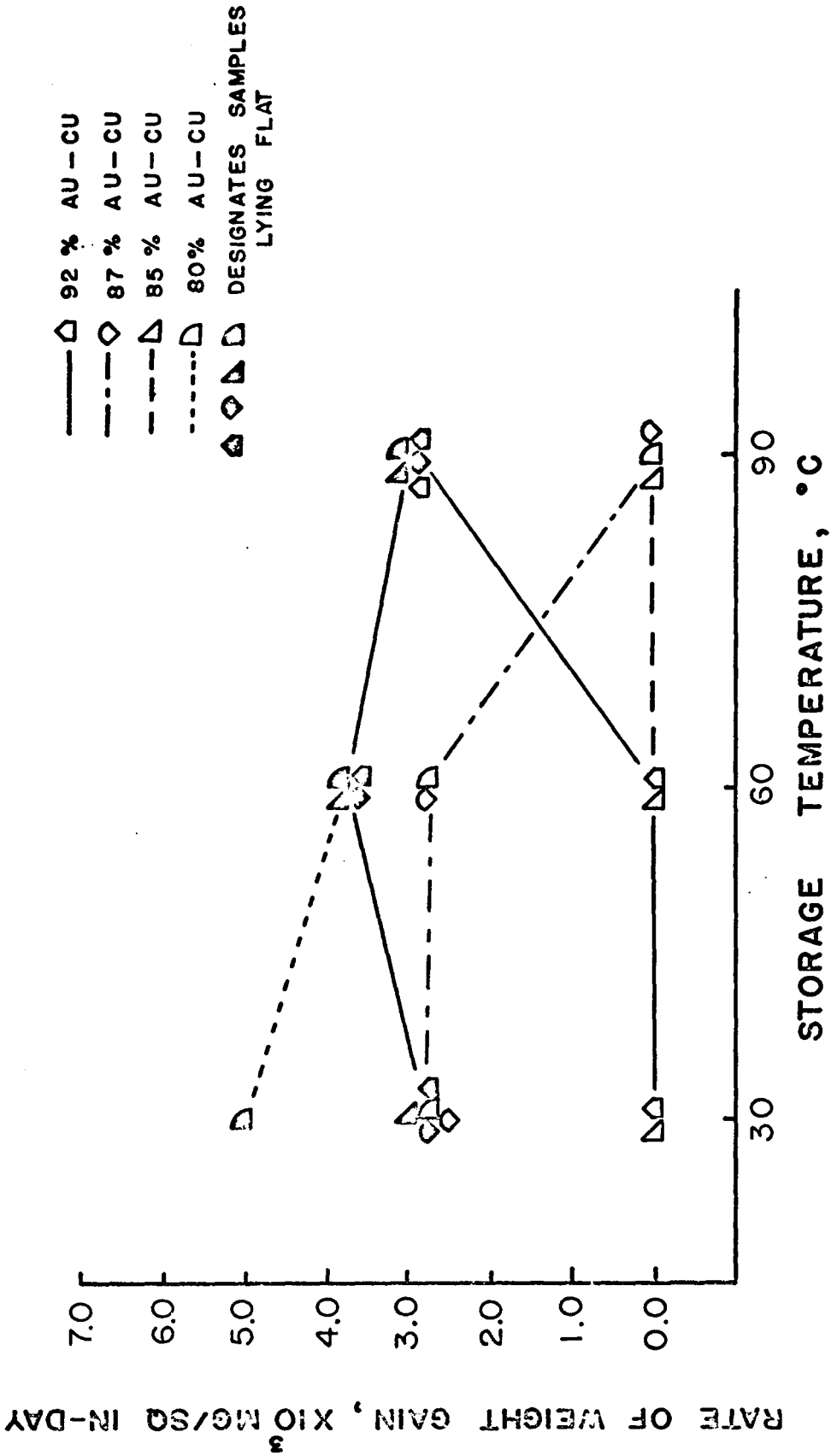


Figure 24. Effect of Temperature Upon Rate of Weight Gain for Electroplated Gold Alloy Samples Stored with Plastic Preparation "B"

IV. DISCUSSION

This section contains the discussion of procedure, discussion of results of the investigation, recommendations, and limitations of the investigation.

Discussion of Procedure

Experimental Precision. The one factor which contributed the most to the experimental inaccuracy of this investigation was the use of an analytical balance for measuring weight differences of one-tenth of a milligram. In measuring this small difference in weight, the effect of temperature and relative humidity may also become important. The total of the random error accounted for by the effects of temperature, relative humidity, and weighing error can be seen in Tables IV through XIII, pages 35 through 44. In these tables are listed the weight changes of the metal samples stored without epoxy. This accumulative effect represents a variability of 0.1 milligram in weighing and therefore any measurements differing by this amount are not significantly different and no conclusions can be drawn concerning film formation.

Sensitivity of Testing. The method by which film formation was measured in this investigation was very insensitive. This fact is demonstrated by the lag time between the first visual observation of film and the first measurable weight differences. After 15 days exposure of the metal samples to the epoxy, an obvious hazing and filming was observed on many of the samples. The first measurable weight difference, however, was not obtained for most of the samples until after 60 days exposure. This difference illustrates the need for an improved detection technique. Chaikin^(10,12) showed that he was successfully able to measure film formation after only three days exposure by the use of an electrical resistance probe and was able to visually observe the film after the same length of time by the use of an electron microscope. White⁽³⁸⁾ was able to determine surface contamination by surface wettability after only two hours exposure.

Discussion of Results of the Investigation

Formation of Haze. Haze was first observed to form on pure silver and pure copper at 60 and 90 °C after 15 days exposure. This was a visual observation. Haze, at 30 °C and on the different gold alloy samples, was

observed after 35 days exposure, again by visual observations. The film formation in all cases seemed to travel up the edges and front of the samples that were propped up on pins. The samples lying flat on the surface of the petri dishes seemed to form a film evenly over the whole surface.

Mechanism of Film Formation. The film formation on the metal samples propped up on pins seemed to travel up the edges and front of the samples. Because of the very slow progress of film formation on the samples in this position, some of the samples were taken off the pins and laid flat on the bottom of the petri dishes. As can be seen in Figures 1 through 18, pages 45 through 62, the samples lying flat then gained weight considerably faster. These facts have demonstrated that the probable mechanism of film formation consists of a heavy, stagnant, low-lying, vapor-phase transport from the epoxy, with the vapors adsorbed or reacted on the surface of the metal samples.

Frequency of Sample Observations. The necessity for opening the petri dishes each time the samples were weighed was thought to contribute to the slowness of film formation on the samples. If the film is formed from organic materials which are in the proximity of the metal samples, then high organic vapor concentrations at long

exposure times should cause an increased amount of film formation. Therefore, the opening of the petri dishes would allow the escape of the outgassed organic vapors from the epoxy that might have accumulated. To speed the development of film formation, the petri dishes should be opened a minimum number of times.

Since organic vapors were lost through leakage and periodic opening of dishes, the purpose of this investigation was to show that film formation did form at a measurable rate and not to measure the rate of film formation.

Mass Spectrometer Results. The analysis of the outgassed vapors from the two epoxy mixtures, epoxy "A" and epoxy "B", seemed amazingly alike. The major components of the vapors were toluene, propylene, carbon monoxide, water, acrolein, acetaldehyde, and trace amounts of other organic compounds which could not be identified. These analyses were very similar to the analysis obtained by Chaikin⁽¹⁰⁾.

For equal epoxy sample sizes and equal mass spectrometer sample sizes, the outgasses from the epoxy "A" showed larger peaks and several additional peaks which could not be identified. These results were in agreement with those obtained by Soldatos⁽³⁶⁾, who, by using more

than the stoichiometric amounts of hardener and higher curing temperatures improved the outgassing characteristics of his epoxy system.

Effect of Curing Conditions and Epoxy Compositions.

The epoxy samples used in this investigation were of two compositions, epoxy "A" and epoxy "B". The compositions and curing procedures for these epoxies are given in Table III, page 31. The major differences in these epoxies are that the epoxy "A" system used a stoichiometric amount of hardener and low curing temperatures, and the epoxy "B" system used 115 per cent of the stoichiometric amount of hardener and higher curing temperatures.

The basis for comparing the film forming characteristics of these systems was the rate of weight gain per unit area per day for each metal sample and exposure temperature.

By comparing Figures 19, 21, and 23, pages 65, 67, and 69, for the samples exposed to the epoxy "A", with Figures 20, 22, and 24, pages 66, 68, and 70, for the samples exposed to the epoxy "B", it becomes apparent from the results obtained that no definite conclusion on film formation can be drawn from comparison of epoxy "A" with epoxy "B". The metal samples exposed to epoxy "B"

were expected to gain less weight than those samples exposed to epoxy "A", since the terminal groups of the epoxy "B" would have been more completely tied up by the use of excess hardener, thus reducing the amount of thermal degradation as described by Neiman^(33,34). This was the result that was obtained by Soldatos⁽³⁶⁾, who, by using a stoichiometric excess of hardener (115 per cent) and relatively high curing (80 to 110 °C) and post curing (160 to 200 °C) temperatures, obtained epoxies which degraded slower and outgassed at a lower rate.

Effect of Exposure Temperature. The effect of exposure temperature upon the rate of film formation is shown in Figures 19 through 24, pages 65 through 70. The effect of elevated temperatures (60 and 90 °C) on the rate of film formation was inconclusive. It could be presumed that elevated temperatures would cause more outgassing and would increase the rate of vapor diffusion from the plastic, thereby furnishing more raw materials for polymer generation. Several explanations were presented by Chaikin⁽¹⁰⁾ to describe the inverse temperature effect which he observed. They were: (1) low molecular weight polymer or degradation products revolatilize; and (2) the polymer-producing reactions are not favored by elevated temperatures. The fact that the rate of film

formation was different for the different metal samples at different temperatures, indicates that the adsorption phenomenon is an important part of the mechanism of film formation.

Effect of Metal Composition. The basis for experimental conclusion on the effect of metal composition on film formation was the maximum weight increase per sample at each exposure temperature. The maximum weight increase is recorded in Table XVI, based on individual samples. This table points out that over an extended period of time, the effect of the metal composition on the final amount of film which is formed is small. The metal composition does make a difference in the rate of formation of film. As shown in Tables XIV and XV, pages 63 and 64, the alloy samples appear to have the higher rates with the rate increasing with decreasing gold composition.

The adsorption phenomena mechanism also explains the fact that different surfaces become contaminated at different rates ^(16,38) with Chaikin ⁽¹⁰⁾ showing that gold and silver are metals less susceptible to film formation when compared with gold alloys.

Prevention of Film Formation. It has previously been thought ^(2,24) that by the use of pure metals such

TABLE XVI

Maximum Weight Increase of Metal Samples Stored with Epoxy Samples

Metal Sample	Epoxy "A"			Epoxy "B"		
	Oven Temperature, °C			Oven Temperature, °C		
	30	60	90	30	60	90
Pure gold	0.3	0.2	0.1	0.2	0.2	0.1
Pure silver	0.3	0.3	0.3	0.2	0.3	0.4
Pure copper	0.1	0.2	0.2	0.1	0.1	0.2
88% Gold-copper alloy	0.0	0.2	0.4			
75% Gold-copper alloy	0.2	0.2	0.1	0.1	0.2	0.2
75% Gold-silver alloy	0.1	0.2	0.1	0.2	0.1	0.2
92% Gold-copper electroplated	0.2	0.2	0.2	0.2	0.2	0.2
87% Gold-copper electroplated	0.2	0.2	0.2	0.2	0.2	0.3
85% Gold-copper electroplated	0.3	0.2	0.2	0.2	0.2	0.2
80% Gold-copper electroplated	0.3	0.3	0.3	0.3	0.3	0.2

as pure gold, pure silver, and pure copper, film formation could be prevented. The results of this investigation point out that this is not true. These results are in agreement with those obtained by Chaikin⁽¹⁰⁾. White⁽³⁸⁾ and Chaikin⁽¹⁰⁾ have both shown that film formation can be minimized in some cases by the use of organic getters and reaction catalysis poisons contained in the system.

Recommendations

The recommendations resulting from this investigation which may be of value in future studies on organic film formation on precious metals are listed below.

Measuring Technique. The gravimetric method of measuring film formation is very insensitive and lends itself to the possibility of large error. The possible use of electron microscope observations, contact angle measurements, and contact resistance probes should be investigated for their potential as measuring techniques.

Preventive Means. Methods such as the use of organic adsorbants (activated carbon and activated alumina) and contamination-reaction poisons should be investigated for their potential as means of preventing film formation.

Mechanism. It is recommended that further studies be made to determine the true effect of metal sample configuration on film formation. The effect of height above the surface of the petri dish and the distance between contact surface and epoxy sample should be investigated.

Sample Size. It is recommended that the samples used in further investigations be of a uniform size with a frontal surface area of not less than one square inch. By having larger surface areas, the error in weighing would be minimized. Also, by having a uniform sample size, a true comparison can be made between samples without worrying about the possible distortion of effects.

Sealed Containers. The petri dishes used in this investigation were adequate with the measuring technique used, but sealed containers, such as ground glass equipment, should be used with a more sensitive film detection device. By using better sealing dishes and a more accurate measuring technique, actual rates of film formation on different metals could be determined. Also, the time needed to measure film formation would be decreased.

Limitations

The limitations imposed upon this investigation are listed in this section.

Epoxy. The only epoxy used in this investigation was epoxy novolac, D.E.N. 438, manufactured by Dow Chemical Company.

Hardener. The only hardener used for curing the epoxy novolac resin was 4-4' methylenedianiline (MDA).

Epoxy Composition. Composition of the hardener (MDA) in the epoxy resin was either 27 weight parts per 100 parts epoxy (epoxy "A") or 31.5 weight parts per 100 parts epoxy (epoxy "B").

Curing of Resin. The resin was cured with two standard procedures consisting of: for epoxy "A", curing in an oven for four hours at 65 °C, post curing for four hours at 125 °C; for epoxy "B", curing in an oven for two hours at 125 °C, post curing for four hours at 185 °C.

Curing Pressure. In all cases, the samples were cured at atmospheric pressure.

Metal Sample Compositions. The samples were thin foil pieces between one to four mills thick of pure gold, pure silver, and pure copper; 88 per cent gold-copper alloy rings; 75 per cent gold-copper and gold-silver

alloys; and electroplated samples of gold-copper alloy compositions ranging from 80 to 92 per cent gold.

Sample Size. All metal samples were approximately 1/2 inch by 1 inch in size except for the 88 per cent gold-copper alloy rings which were in the shape of washers with inside and outside diameters of 1/8 inch and 1/4 inch, respectively. The epoxy samples were all approximately 1-1/4 inch long rods, 3/8 inch in diameter.

Exposure Temperature. The samples were exposed to epoxy at 30, 60, and 90 °C.

Exposure Pressure. The samples were exposed at atmospheric pressure only.

Exposure Time. All samples were exposed from either 105 to 150 days.

Haze Detection Technique. A gravimetric technique was used with the aid of an analytical balance of ± 0.0001 gram sensitivity to observe changes in weight of the metal samples.

Sample Configuration. Metal samples, all bent down the center except for pure copper, were propped up on pins, bent such that they would support the metal samples. During the course of the investigation many of the samples were taken off the pins, straightened, and laid flat on

the bottom of the petri dishes. In all cases the metal samples were placed $1/4$ to $1/2$ inch away from the epoxy.

V. CONCLUSIONS

The following section contains the conclusions reached from the results of this investigation on film formation when the metal samples (pure gold, pure silver, pure copper, and gold alloys with copper and with silver) were exposed to epoxy novolac resins cured with 4-4' methylenedianiline.

The investigation led to the following conclusions:

1. The film forms from a heavy, stagnant, low-lying, vapor-phase from the epoxy, with the vapors adsorbed or reacted on the surface of the metal samples.
2. The contaminating materials are low molecular weight organic compounds consisting of unreacted monomer and degradation products.
3. Film formation is not affected to any appreciable extent by the combined effect of increased curing temperatures and increased hardener content.
4. The effect of increasing the temperature from 30 °C to 60 or 90 °C, on the rate of film formation was inconclusive.
5. Epoxy film formation was observed on all metal samples tested, pure gold, copper, and silver; gold-copper and gold-silver alloys.
6. The metal composition affects the rate of film formation with the rate increasing with decreased gold composition for both copper and silver alloys.

VI. SUMMARY

The purpose of this study was to determine the effect of exposure conditions, resin composition, and resin treatment on film formation on metal surfaces exposed to epoxy resin.

Epoxy rods were prepared from novolac hardener by 4-4' methylenedianiline (MDA). The curing and post curing temperatures were 60, 125 °C and 125, 160 °C. The composition of the epoxies used were 27.0 and 31.5 parts (MDA) per 100 parts epoxy.

The metals investigated were pure gold, silver, and copper; gold-copper alloys; gold-silver alloys; and electroformed gold-copper alloys. The alloys ranged in composition from 75 to 92 per cent gold. These samples were cleaned, weighed, placed in individual, covered, glass containers with the epoxy rods, and then were exposed at 30, 60, and 90 °C.

The change in weight of the metal samples was determined at intervals of about 30 days for five months. Weight increases of 0.1 to 0.4 milligram were observed for the samples exposed to the epoxy rods, and were negligible for samples stored without epoxy rods.

The contaminating materials, apparently, are organic compounds consisting of unreacted monomer and degradation products. The film forms from a heavy, stagnant, low-lying, vapor-phase from the epoxy, with the vapors adsorbed or reacted on the surface of the metal samples. Film formation is not affected to any appreciable extent by the combined effect of increased curing temperatures and increased hardener content. The effect of increasing the temperature from 30 °C to 60 or 90 °C, on the rate of film formation was inconclusive. Epoxy film formation was observed on all metal samples tested, pure gold, copper, and silver; gold-copper and gold-silver alloys. The metal composition affects the rate of film formation with the rate increasing with decreased gold composition for both copper and silver alloys.

VII. BIBLIOGRAPHY

1. American Petroleum Institute Research Project 44: "Mass Spectral Data," Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1961.
2. Angus, H. C.: Surface Films on Precious Metal Contacts, Brit. J. Appl. Phys., 13, 58-63 (1962).
3. Antler, M., L. V. Auletta, and J. Conley: An Automated Contact Resistance Probe, Rev. Sci. Inst., 34, 1317-22 (1963).
4. Arkhavor, V. I.: Main Stages of the Mechanism of the Interaction Between Metals and Gases, "Surface Interactions Between Metals and Gases" (V. I. Arkhavor and K. M. Gorgunova, Editors), Translated from Akademiia Nauk SSSR. Institut Fizicheskoi Khimii, Consultants Bureau, N. Y., 21-9 (1966).
5. Arslambekov, V. A.: Precise Gravimetric Method of Investigating the Kinetics and the Mechanism of Interaction Between Gases and Metals, "Surface Interactions Between Metals and Gases" (V. I. Arkhavor and K. M. Gorgunova, Editors), Translated from Akademiia Nauk SSSR. Institut Fizicheskoi Khimii, Consultants Bureau, N. Y., 149-58 (1966).
6. Bassin, J. D.: A Review of Plastics Hardeners, Soc. Plast. Engrs. J., 14, 36-8 (1958).
7. Biondi, F. J.: Cleaning Electron Device Parts, Bell Lab. Rec., 36, 288-93 (1958).
8. Brummer, S. B.: Structure and Composition of Organic Adsorption Layers on Pt Electrodes--Relation to Reaction Kinetics, Electrochemical Society, 113, Oct., 1041-4 (1966).

9. Chaikin, S. W., C. W. McClelland, J. Janney, and S. Landsman: Contamination and Electrical Leakage in Printed Wiring, Ind. Eng. Chem., 51, 305-308 (1959).
10. _____: Study of Effects and Control of Surface Contaminants on Electrical Materials, Stanford Research Institute, Menlo Park, Calif., SRI Project No. SU-2381 (1960).
11. _____, J. R. Anderson, and G. J. Santos: Electrical Probe Apparatus for Detection of Surface Films, Rev. Sci. Inst., 32, 1294-6 (1961).
12. _____: Mechanics of Electrical Contact Failure Caused by Surface Contamination, Electro Technology, 68, Aug., 70-6 (1961).
13. Christy, R. W.: Formation of Thin Polymer Films by Electron Bombardment, J. Appl. Phys., 31, 1680-3 (1960).
14. Churchill, D. and L. S. Bartell: Polarimetric Determination of Adsorption Spectra of Thin Films on Metal, J. Phys. Chem., 67, 2518-9 (1963).
15. Damaskin, B. B.: Rules of Adsorption of Organic Compounds on Electrode Surface, Russian Chemical Review, 34(10), 752-9 (1965).
16. DiMarzio, E. A. and Frank L. McCrackin: One-Dimensional Model of Polymer Adsorption, J. Chem. Phys., 43, 539-47 (1965).
17. Dow Chemical Company: D.E.N. Epoxy Novolac Resins, Dow Coating Sales, The Dow Chemical Company, Midland, Michigan, Form No. 170-143B (1967).
18. Forsyth, T. H.: A Study of Factors Affecting Film Formation on Gold Surfaces in the Presence of Epoxy Resins. Unpublished M. Sc. Thesis, Library, Va. Poly. Inst., Blacksburg, Va. (1966).

19. Foulke, D. G.: Chemical Analysis of Plating Solutions, "Electroplaters' Process Control Handbook," (D. G. Foulke and F. E. Crane, Jr., Editors). Reinhold Publishing Co., New York, N. Y., 185-7, 1963.
20. Frumkin, A. N.: Influence of Adsorption of Neutral Molecules and Organic Cations on the Kinetics of Electrode Processes, *Electrochimica Acta*, 9, 465-76 (1964).
21. _____: Dependence of the Adsorption of Organic Substances on the Potential of Metals, Translated from *Doklady Akademii Nauk SSSR*, 154, 1432-3 (1964).
22. Gilchrist, R.: New Procedure for the Analysis of Dental Gold Alloys, "Journal of Research of the National Bureau of Standards," 20, 745-53, 1938.
23. Grassi, N.: Chemistry of the Destruction Processes of Polymers, Translated from *Doklady Akademii Nauk SSSR*, 132, 1142-7 (1959).
24. Hermance, H. W. and T. F. Egan: Organic Deposits on Precious Metal Contacts, *Bell Sys. Tech. J.*, 37, 739-76 (1958).
25. Hirsch, E. E.: Image Formation by Electron Bombardment of Metal Targets, *Brit. J. Appl. Phys.*, 11, 547-50 (1960).
26. Kavtaradze, N. N.: Adsorption of Hydrogen, Carbon Monoxide, Ethylene, and Nitrogen on Transition Metals and the Nature of the Adsorption Complexes Formed, *J. Res. Inst. Catalysis*, 13, 196-208 (1965).
27. _____: Mechanism of the Chemical Adsorption of Gases on Metals, "Surface Interactions Between Metals and Gases" (V. I. Arkhavor and K. M. Gorgunova, Editors), Translated from *Akademiia Nauk SSSR. Institut Fizicheskoi Khimii, Consultants Bureau*, N. Y., 30-9 (1966).

28. Keefer, H. J. and R. H. Gumley: Relay Contact Behavior Under Non-Eroding Circuit Conditions, Bell Sys. Tech. J., 37, 777-814 (1958).
29. Ken-Ichi Tanaka and Kenzi Tamaru: A General Rule in Chemisorption of Gases on Metals, J. of Catalysis, 2, 366-70 (1963).
30. Krasil'shchikov, A. I., L. G. Antonova, and I. P. Ivanovskii: Adsorption, Ionization and Catalytic Activation of Gases on Metals, Translated from Kinetika i Kataliz, 1, 212-20, (1960).
31. Lieng-Huang Lee: Mechanisms of Thermal Degradation of Phenolic Condensation Polymers. Thermal Stability and Degradation Schemes of Epoxy Resins, Proc. Battelle Symposium Thermal Stability of Polymers, Columbus, Ohio (1963).
32. Miller, J. R. and J. E. Berger: A Comparative Study of Adsorption by Ellipsometric Radio-tracer Methods, J. Phys. Chem., 70, 3070-5 (1966).
33. Neiman, M. B., B. M. Kovarskaya, L. I. Golubenkova, and M. S. Akutin: The Thermal Degradation of Some Epoxy Resins, J. Polymer Sci., 56, 383-9 (1962).
34. _____: The Mechanism of the Thermal Destruction of Cured Epoxide Resins, Translated from Doklady Akademii Nauk SSSR, 135, 1147-9 (1960).
35. Skeist, I.: "Epoxy Resins." Reinhold Publishing Company, New York, N. Y., 1958.
36. Soldatos, A. C., A. S. Burhans, and L. F. Cole: Novel Cycloaliphatic High Performance Epoxy Resins, 23rd Annual Technical Conference, The Soc. Plastic Ind., Inc. (1963).
37. Sweeney, G. A.: "Modern Plastics Encyclopedia," 43, 165-70. Plastics Catalogue Corp., Bristol, Conn., 1966.

38. White, M. L.: "The Detection and Control of Organic Contaminants on Surfaces," Presented at Symposium on Clean Surfaces, will be published by Marcel Dekker, Incorporated (1968).

VIII. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to _____, Acting Head of the Chemical Engineering Department, Virginia Polytechnic Institute, who was always ready with timely suggestions, helpful advice, and thoughtful counsel, without which this investigation could not have been completed.

Thanks are extended to the Poly-Scientific Corporation for supplying the epoxy resin and the Tennessee Eastman Company whose fellowship made this research possible.

Finally, the author wishes to express his sincere appreciation to his wife, _____, for her encouragement and patience.

**The two page vita has been
removed from the scanned
document. Page 1 of 2**

**The two page vita has been
removed from the scanned
document. Page 2 of 2**

FILM FORMATION ON PRECIOUS METAL SURFACES
IN THE PRESENCE OF EPOXY RESINS

by

Lawrence J. Kyle

ABSTRACT

The purpose of this study was to determine the effect of exposure conditions, resin composition, and resin treatment on film formation on metal surfaces exposed to epoxy resin.

Epoxy rods were prepared from novolac hardened by 4-4' methylenedianiline (MDA). The curing and post curing temperatures were 60, 125 °C and 125, 160 °C. The composition of the epoxies used were 27.0 and 31.5 parts (MDA) per 100 parts epoxy.

The metals investigated were pure gold, silver, and copper; gold-copper alloys; gold-silver alloys; and electroformed gold-copper alloys. The alloys ranged in composition from 75 to 92 per cent gold. These samples were cleaned, weighed, placed in individual, covered, glass containers with the epoxy rods, and then were exposed at 30, 60, and 90 °C.

The change in weight of the metal samples was determined at intervals of about 30 days for five months. Weight

increases of 0.1 to 0.4 milligram were observed for the samples exposed to the epoxy rods, and were negligible for samples stored without epoxy rods.

The contaminating materials, apparently, are organic compounds consisting of unreacted monomer and degradation products. The film forms from a heavy, stagnant, low-lying, vapor-phase from the epoxy, with the vapors adsorbed or reacted on the surface of the metal samples. Film formation is not affected to any appreciable extent by the combined effect of increased curing temperatures and increased hardener content. The effect of increasing the temperature from 30 °C to 60 or 90 °C, on the rate of film formation was inconclusive. Epoxy film formation was observed on all metal samples tested, pure gold, copper, and silver; gold-copper and gold-silver alloys. The metal composition affects the rate of film formation with the rate increasing with decreased gold composition for both copper and silver alloys.