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BILGE INHIBITORS

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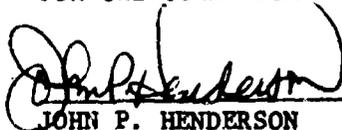
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20. Abstract continued

Several formulations have been developed which inhibit the corrosion of the most aggressive medium (urine) encountered in the bilge and related areas of aircraft. The results of corrosion-fatigue and crack-growth studies on aluminum alloys and high-strength steels confirm a reduction of nearly one-half an order of magnitude in the crack-growth rates in the presence of one of these formulations.

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PREFACE

This report was prepared by Dr. M. Khobaib with the assistance of Mrs. Laura Quackenbush. Work was performed under Contract F33615-78-C-5193 by the Research Applications Division of Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH, 45440. The contract was administered under the direction of the Air Force Wright Aeronautical Laboratories, Materials Laboratory (AFWAL/MLLN), Wright-Patterson Air Force Base, OH, with Dr. C. T. Lynch acting as the Government Project Monitor.

Studies were conducted during the period 1 August 1978 through 1 June 1981 jointly at the Systems Research Laboratories, Inc., Corrosion Facility and at the Materials Laboratory.

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## SECTION I INTRODUCTION

Corrosion costs the United States billions of dollars each year. The annual maintenance cost for military aircraft alone is several billion dollars. Some of the frequent maintenance or repair hot spots in an aircraft where corrosion causes a serious problem are the galley, bilge, and urinal areas. Severe corrosion of structural members (i.e., floors, sinks, frames, etc.) occurs below the urinal and, as a result, extensive repairs are necessitated. The use of some type of inhibitor to reduce the corrosion in these areas was formally discussed at the Corrosion Managers Conference<sup>1</sup> held in October of 1975. After successful completion of the Corrosion Inhibitor Program which resulted in the development of a nontoxic, multi-functional, and biodegradable corrosion inhibitor<sup>2</sup> to be used at the Air Force Rinse Facility at MacDill Air Force Base in Tampa, Florida, the Air Force Materials Laboratory made the decision to sponsor a research program for the development of a nontoxic inhibitor for use in urinal and related areas of aircraft.

The borax-nitrite-base inhibitor which was developed for incorporation into the Air Force Rinse Facility has provided excellent corrosion protection for aluminum, copper, and high-strength steels in normal as well as the chloride-contaminated water of the Air Force Rinse Facility. However, this combination was not found to be effective for the aggressive media found in the urinal areas of aircraft.

The present study was concerned with the development of a nontoxic corrosion inhibitor which would be effective against corrosion attack of the most aggressive medium (found in urinal areas) on ferrous and non-ferrous metals and alloys. Simulated urine consisting of more than twenty ingredients has been synthesized in the laboratory. Based upon extensive prior experience with borax-nitrite inhibitor formulations, corrosion tests were conducted on numerous formulations consisting of nontoxic water-soluble inorganic compounds such as borax, nitrite, phosphate, and silicate. Numerous other combinations such as molybdate-nitrite, borate-

benzoate, benzoate-piperazine, gluconate-nitrite, and succinate-nitrite were also studied. Several commercial inhibitors were screened for their effect upon electrochemical behavior, general corrosion, galvanic corrosion, and crevice corrosion. In general, this screening was conducted by means of electrochemical potentiostatic polarization techniques. As a result of screening and further research, the borax-nitrite inhibitor in the rinse formulation has been modified to prevent corrosive-attack on related aircraft structures by urine-contaminated solutions. Corrosion-fatigue and crack-growth studies on aluminum alloys and high-strength steel with the inhibited and uninhibited urine solutions have also been conducted. Introduction of the inhibitor reduces the crack growth in both aluminum alloys and high-strength steels. This inhibitor formulation is based upon nontoxic ingredients and provides excellent protection to the ferrous and nonferrous structures used in the galley, bilge, urinal, and related areas of aircraft.

## SECTION II

### TECHNICAL BACKGROUND

Corrosion costs have recently drawn national attention. A study conducted by NBS has indicated that corrosion is costing the United States approximately 70 billion dollars annually.<sup>3</sup> NBS estimated corrosion costs in USAF aircraft at base and depot levels to be 650 million to 1.3 billion dollars per year. Over the past few years, a considerable number of studies have been conducted within the U.S. Air Force regarding the total cost of corrosion prevention and control in aircraft. These studies unequivocally indicate that the total corrosion cost in terms of life-cycle management of aircraft and ground systems presents an intolerable burden to the Air Force in their attempts to maintain fleet effectiveness at a reasonable cost. The Air Staff has estimated total corrosion costs--including maintenance at the field level and replacement of corrosion-damaged parts--to be in excess of one billion dollars per year; these costs are increasing with the life of the aircraft. It has been established by the AFWAL Materials Laboratory and the Aeronautical Systems Division (ASD) that acquisition/maintenance costs currently are 30/70 on a life-cycle basis for an aircraft; these costs were 70/30 in the 1950's. This is treated in greater detail in a study conducted by Lynch and Moore.<sup>4</sup>

During the 1975 Biannual Workshop on Corrosion Prevention, sponsored jointly by the Air Force Materials Laboratory and the Air Force Office of Scientific Research, some of the results of the depot-level corrosion cost study conducted by the Air Force Logistics Command (AFLC) were presented<sup>5</sup> (data given in Table I). According to these estimates, corrosion costs reach as high as 40% of the total depot-level maintenance cost for the B-52-(G). This estimate includes only the corrosion-damaged spots which are clearly identifiable by maintenance crews. Other damage and failures known to be caused by corrosion are not reported as such under current maintenance practices.

Table I

<u>System</u>	DEPOT CORROSION REPAIR			
	<u>Program Depot Maintenance Manhours</u>	<u>Corrosion Manhours</u>	<u>Percentage</u>	<u>Annual Corrosion Cost</u>
B-52G(50)	22,358	9,100	40%	\$9,100,000
F-106(71)	3,932	807	21%	1,145,940
F-4E(135)	3,757	678	18%	1,830,600
C-141(90)	10,302	2,980	29%	5,364,000

The Air Force problem is similar to that of the Navy for the same aircraft (e.g., the F-4), but a much greater sum of money is spent by the Air Force because of the preponderance of large aircraft (C-5, C-141, C-135, B-52, etc.); hence, the cost of corrosion repair such as rebuilding the bilge areas of cargo aircraft is much greater.

Areas on an aircraft requiring frequent maintenance or repair include the galley, bilge, and urinal areas. Severe corrosion of structural members (i.e., floors, sinks, frames, etc.) occurs below the urinal, which necessitates extensive repairs. Usually moisture (due to the leakage or spillage of water or corrosive fluids) migrates into the aircraft structure under the galley and urinal areas, causing corrosion of the seat and cargo tiedown tracks, floor-beam caps, and supporting structures. Table II gives AFLC cost data on repair for the C-141 bilge area for FY76. These areas cannot be inspected without removing heavy floor panels or external sinks. Although this problem and its causes have been recognized for years, the idea of incorporating an inhibitor in the bilge, urinal, and galley areas was not formally discussed until October of 1976 at the Corrosion Managers Conference. At this meeting it was brought out that the Royal Air Force had already implemented such a plan. The frequent corrosion maintenance required on these areas necessitates the adoption of some corrosion-prevention practice. Such practices have already been applied by different organizations (other than the USAF) but are far from being perfected. The Royal Air Force has already implemented a plan to combat corrosion in these areas. The Boeing Materials Technology Laboratories have developed a water-displacing compound (Boeshield T-9) which is now being used in their commercial 747 jets; the results, according to Boeing are encouraging, but the effective life of the inhibitor is known to be only several months. At various meetings, other water-displacement compounds (namely, LPS1, LPS3, WD-40, etc.) have been discussed as possible inhibitors.

Research is currently being sponsored by the USAF on the development of a protective coating system for the C-5A bilge area<sup>6</sup> under a PRAM project



by the Lockheed Georgia Company. The results of the research are not yet available. Recently, AFLC studied the effect of corrosion-preventive compounds such as MIL-C-16173, Grade 4, in combating corrosion in the forward bilges of the C5-A aircraft.<sup>7</sup> The Naval Air Development Center has developed water-displacing and rust-inhibitor compounds--AML Guard and AML Chroma. These compounds have been tested under various conditions, and their effectiveness is presently being tested under additional conditions.<sup>8</sup> Although no data on these compounds are available in the literature as yet, they appear to have potential as inhibitors. Further research and development efforts are required in this area. The question of toxicity, in general, has not received much attention in the past, but now all of these compounds must be reconsidered from the point of view of toxicity.

Chromates and chromate-based inhibitors are widely used, and their effectiveness has long been recognized; however, their performance is poor in the presence of chloride ions.<sup>9</sup> Certain investigators claim that the commercially available water-displacement compounds, e.g., LPS, Boeshield T-9, AML Guard, and AML Chrome, act as effective inhibitors under certain conditions. Each of these water-displacement compounds has certain advantages, but all are known to have a short effective life. At the same time, their performance under the extreme conditions of the bilge environment is not yet known. Currently, a borax-nitrite-base inhibitor is being used at the Air Force Rinse Facility at MacDill AFB, Florida. Preliminary results are encouraging. This inhibitor<sup>2</sup> is a blend of different anodic and cathodic inhibitors and is very effective for both ferrous and non-ferrous alloys used in aircraft. The multi-functional inhibitor (being a combination of anodic and cathodic inhibitors) affects the rates of both anodic and cathodic corrosion reactions.<sup>10</sup> More importantly this inhibitor has been found to be very effective in retarding the crack-growth rate in aqueous environments.<sup>2</sup> The results are extremely significant, clearly demonstrating that general corrosion and galvanic corrosion as well as the environmental enhancement of crack-growth rates can be minimized or eliminated through the use of a suitable inhibitor.

The successful completion of the Corrosion Inhibitor Program<sup>2</sup> provided the basis for the initiation of a follow-on project called Bilge Inhibitors. The prime objective of this program was to evaluate existing inhibitors and develop new nontoxic ones for bilge and related areas which would meet federal and state environmental-protection requirements. The most aggressive medium in the urinal and related areas of aircraft appears to be urine. The lack of information on the corrosive attack of urine on metals was surprising. Since urine is ~ 1% NaCl, the initial step in the screening process was to analyze the performance of inhibitors which are generally used for preventing saline corrosion. The development work was based upon the results of a previous effort<sup>2</sup> to develop nontoxic, multifunctional water-soluble corrosion inhibitors for use in the Air Force Rinse Facility for fighter aircraft at MacDill Air Force Base, Florida. Several hundred inhibitor compounds and formulations have been studied with regard to their effect upon electrochemical behavior (general corrosion and crevice corrosion) and corrosion fatigue. As a result, a new formulation has been developed, which in laboratory tests has proven its effectiveness for use in the lower bay and galley areas of aircraft. This mixture contains no chromate, is biodegradable, and offers important advantages over chromate-based combinations.

### SECTION III EXPERIMENTAL INVESTIGATIONS

#### PROGRAM OVERVIEW

The first and foremost task was to establish the medium which exerts the maximum corrosive influence upon the urinal, bilge, and related areas of aircraft. The conclusion reached was that urine and urine leakage cause maximum corrosion damage. A major effort was put forth to develop a soluble (in bilge solution), nontoxic inhibitor to prevent corrosive attack in the above-mentioned areas.

The research was divided into five phases. In Phase I of the program, a literature survey was conducted to provide information necessary for formulating a synthetic urine solution. Simultaneously, a list of suitable candidates for inhibitor combinations was prepared. The main variables considered in the selection of inhibitors are given in Table III. The various types of inhibitors considered can be found in Table IV.

Over two hundred candidate formulations were investigated. Several commercial inhibitors were also screened, and the list of these inhibitors can be found in Table V. One of the foremost considerations in the development process was toxicity. Special attention was paid to the fact that the resulting formulations must be compatible with Environmental Protection Agency (EPA) standards and state laws governing ground-water and sewage-disposal discharge. Concurrently with the main effort of Phase I, specimens were fabricated for immersion testing and stress-corrosion and corrosion-fatigue tests to be conducted in Phases II-IV.

Phases II and III consisted of electrochemical characterization of the candidate inhibitor formulations. Anodic-, cathodic-, and linear-polarization tests were used for screening the selected formulations. Immersion tests were also conducted, followed by visual observation, to determine inhibitor effectiveness. In a few cases weight-loss measurements were carried out.

**TABLE III**  
**INHIBITOR CONSIDERATIONS**

**A. GENERAL CONSIDERATIONS**

1. Multifunctional  
Cathodic  
Anodic  
Chloride Absorbers  
Buffers
2. Solubility Range
3. Influence on Hydrogen Entry Rates
4. Toxicity
5. Cost

**B. COMPOUNDS**

1. Cathodic: Polyphosphate, Zinc, Silicate
2. Anodic: Orthophosphate, Chromate, Ferrocyanide, Nitrite
3. Combinations: Polyphosphate-Chromate  
Polyphosphate-Ferrocyanide  
Borax-Nitrite  
Benzoate-Nitrite  
Silicate-Chromate
4. Film Formers: Emulsified or Soluble Oils  
Octadecylamine  
Long-Chain Amines  
Alcohols and Carboxylic Acids

**C. MAJOR CONSIDERATIONS**

1. Stress Corrosion and Corrosion Fatigue
2. Special Bilge Environments
3. Long-Term Effectiveness
4. Method of Application

TABLE IV  
TYPES OF INHIBITORS CONSIDERED

- (a) Water-displacement compounds
- (b) Oil-base inhibitors
- (c) Vapor-phase inhibitors
- (d) Time-release compounds
- (e) Encapsulated inhibitors
- (f) Controlled solubility types

TABLE V  
 COMMERCIALY AVAILABLE INHIBITORS

<u>Inhibitor</u>	<u>Manufacturer</u>
Nalco 39L	} Nalco
Nalco 41L	
Nalco 918	
Nalco 26W	
Dequest	Monsanto
Betz 545	Betz Lab
Calgosil	} Calgon
CS	
Virco Pet 30	} Mobil
Mobil 100	
WD 40	WD-40 Company
Boeshield	Oxy Metal
AML Guard	U.S. Navy
Rust Inhibitor X-500, X-400	U. S. Rust
Drewguard	Drew Chemical
LPS	LPS

In Phase IV, low-cycle corrosion-fatigue tests were conducted to determine the most promising inhibitor formulation selected from Phase III against the environmental enhancement of fatigue cracks.

The screening and development process was continued in Phase IV. The inhibitor formulations which showed promise were scrutinized more carefully in Phase V. The formulation was finalized and the blended inhibitor compacted into 0.5-oz. cakes for field application. The field-application tests have not been conducted as yet (due to the unavailability of specific aircraft for testing at one of the Air Force bases.)

#### PHASE I - DATA COLLECTION, MATERIAL ACQUISITION, AND PRELIMINARY ANALYSIS

##### Formulation of Synthetic Urine

A detailed literature survey was conducted to obtain information on possible chemical formulations which might be compatible with the present application. No literature relative to corrosion inhibition of metals in contact with urine was found.

Initially several biological firms were contacted regarding the availability of synthetic urine. Although these firms produce synthetic urine, the constituents are limited to those required for standard clinical tests. In addition, the cost was prohibitive for our purposes, the average cost being \$30 per 100 ml. An extensive effort was made to synthesize urine in our own laboratory. All possible constituents of urine were obtained through a search of the clinical chemistry and urology literature. Since the number of constituents is quite high, only those which were regarded as potentially aggressive were selected. The selected ingredients--the constituents of our synthetic urine--are given in Table VI. The pH is slightly acidic but can be easily adjusted using sodium hydroxide or sodium carbonate.

TABLE VI  
INGREDIENTS OF SYNTHETIC URINE  
(Wt in gm/liter)

urea	20.60
5-hydroxyindoleacetic acid	0.0045
uric acid	0.052
glucuronic acid	0.431
oxalic acid	0.031
citric acid	0.462
glycolic acid	0.042
creatine	0.0721
guanidinoacetic acid	0.027
formic acid	0.013
glucose	0.072
ammonium sulfate	4.00
potassium phosphate	0.175
potassium chloride	0.0100
potassium bromide	0.008
sodium chloride	10.00
p-cresol	0.087
creatinine	1.500
acetone	0.0001
hydroxyquinoline-2 carboxylic acid	0.0028
potassium sulfate	0.134

## Corrosion Behavior of Synthetic Urine

Potentiodynamic anodic- and cathodic-polarization tests on Al 7075-T6 in natural and synthetic urine have been conducted. The results are shown in Fig. 1. Immersion tests were also conducted under similar conditions (with natural and synthetic urine). The corrosion behavior was found to be comparable for the natural and synthetic urine.

## Selection of Potential Inhibitor Candidates

Major firms dealing with inhibitors were contacted, and commercially available inhibitor samples were collected along with detailed literature on toxicity, biodegradability, etc. The screening of the inhibitors from the generic types shown in Table III was a complex process with the toxicity consideration being given the highest priority. If an inhibitor species was obviously toxic based upon data in the literature,<sup>11</sup> it was eliminated from further consideration. Chromates, molybdates, and aniline adducts are some examples of inhibitors which were eliminated on these grounds. However, some restraint was exercised since almost all materials might conceivably be toxic under special circumstances. Specific guidelines on toxicity were not available; therefore, qualitative judgments were made in assessing relative toxicity.

## PHASE II - DETERMINATION OF EFFECTIVENESS OF INHIBITOR SYSTEMS

The determination of effectiveness of inhibitor systems was an involved process due to the large number of possible compatible inhibitors. Initially it was difficult to trace the source of a commercially available inhibitor. Even more difficult and time consuming was the screening process for the possible vast number of combinations obtainable through considerations listed in Table III.

The anodic-cathodic combination, in general, is capable of inhibiting either corrosion process which occurs locally on the structure. At the

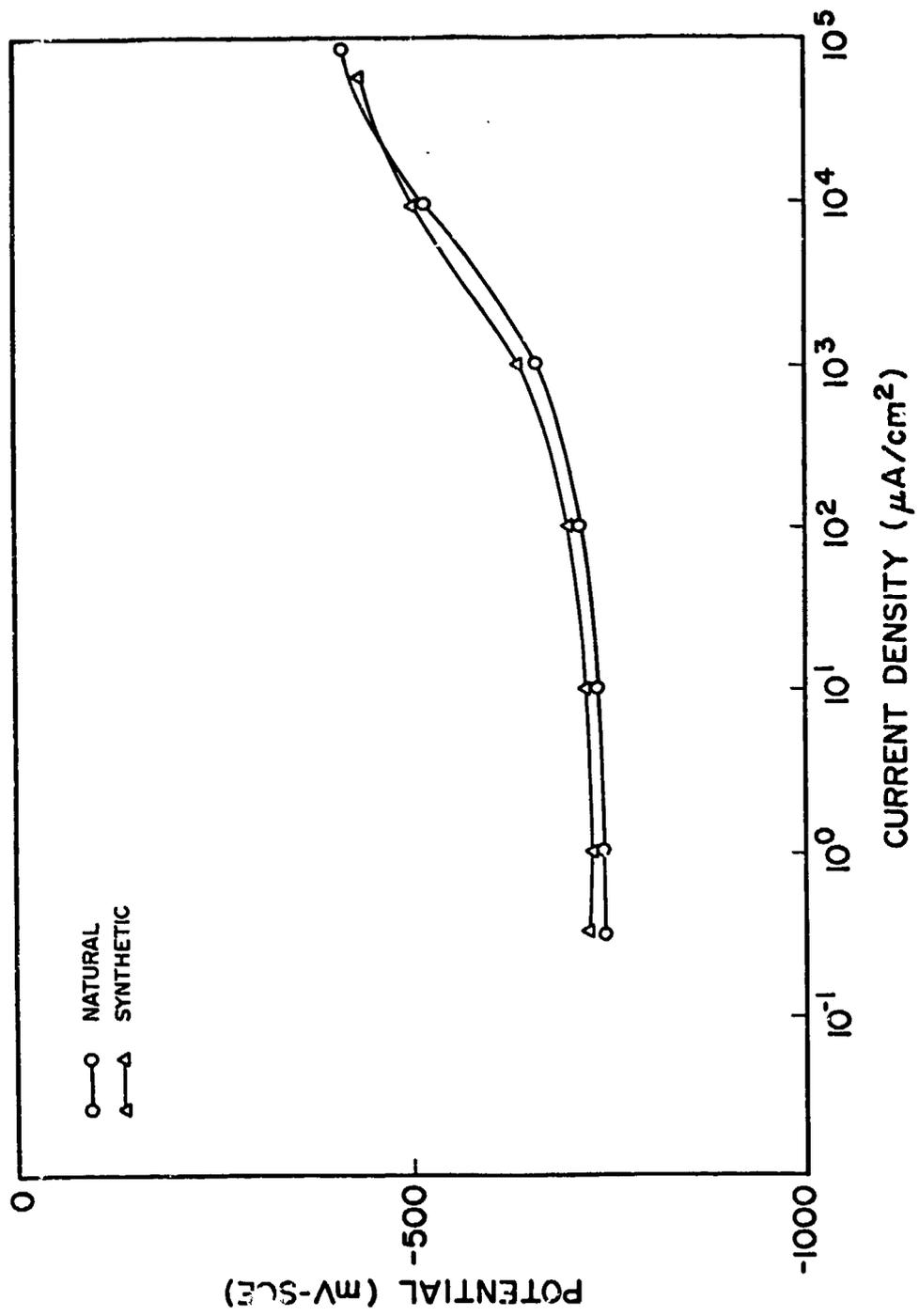


Figure 1. Polarization Curves of Al in Natural and Synthetic Urine.

same time, polarization is more effective with a mixture of anodic and cathodic than with either separately. The situation is quite complex because either inhibitor may vary in concentration from several parts per million up to a few percent; and, in general, a narrow band of composition exists within which the optimum can be obtained. In addition, the synergistic effect of several other ingredients such as the film former, chloride, absorber, and chelating agents was determined. These ingredients in various combinations constituted a massive number of formulations to be tested.

Based upon experience,<sup>2</sup> the first step toward the development of an effective inhibitor was the search for a combination anodic-cathodic inhibitor. Since the chloride concentration in the urine solution is nearly 1%, a chloride absorber along with a film former in some formulation was also included as a potential ingredient of prospective inhibitor formulations.

The first potential candidate to be screened was the rinse inhibitor.<sup>2</sup> Other borate-nitrite-base inhibitor candidates included many sets of formulations consisting of benzoate, gluconate, sarcosine, oleate, etc. Both polarization and immersion tests were conducted on a great number of these formulations.

#### Candidate Commercial Inhibitors

Several commercially available inhibitors recommended for use in saline water were chosen for screening. The immersion as well as the potentiodynamic anodic and cathodic tests were conducted with inhibitors obtained from Cortec, NalCo, Mobil, Dearborn, Betz Labs, U.S. Rust, etc. The immersion results are shown in Table VII, and the polarization curves are plotted in Figs. 2 and 3. Some of these inhibitors were used in low concentrations along with the borax-nitrite-base inhibitor. Results of the immersion tests for Al and Al, brass, and steel immersed together are shown in Tables VIII and IX.

TABLE VII

## IMMERSION TEST RESULTS ON COMMERCIAL INHIBITORS

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
1	Al 7075-T6	Cortec VCI 317; 3% by wt. in urine solution.	9.25	9.10	Two weeks One month Four months	Clean and shiny. Clean, oily patches developed on surface. Clean, oily patches developed on surface.	Good.
2	Al 7075-T6	Cortec VCI 317; 2% by wt. in urine solution.	8.75	8.60	Two weeks One month Two months	Clean and shiny. Clean and shiny. Clean and shiny.	Excellent.
3	Al 7075-T6 Brass Steel	Cortec VCI 317 (20:1) in synthetic urine.	8.6	8.45	Two weeks Three months Two weeks Three months Two weeks Three months	Clean and shiny. Clean and shiny. Clean and shiny. Clean. Dark, one pit. Dark, one large pit.	Fair.
4	Al 7075-T6	Cortec VCI 336; 2% by wt. in urine solution.			Two weeks One month Four months	Edges lightly corroded. Edges lightly corroded. Pits all over the edges and near the hole; surface still protected.	Needs improvement.
5	Al 7075-T6 Copper Steel	1% Dearborn 537 + NaOH to adjust pH in urine solution.	9.25	9.25	Two weeks Four weeks Two months Four weeks Two months Two weeks Two months	Clean and shiny. Clean and shiny. Clean, but some hard deposits. Attack near the hole. Dull patches all over. Attack near the hole. Fine pits.	Poor.

TABLE VII (Continued)

Spec. No.	Specimen	Electrolyte Mt Z	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
6	Al 7075-T6	4000 ppm Dregard 100+ M <sub>2</sub> H <sub>2</sub> to adjust pH in urine solution.	8.25	8.20	Two weeks	Clean.	Fair.
	Copper				Four weeks	Clean.	
					Five months	Edges lightly attacked. Pits on edges and surface.	
7	Al 7075-T6	0.25% Boeshield T-9 in synthetic urine.	5.65	5.60	Two weeks	Clean.	Poor.
	Brass				Four weeks	Clean.	
	Steel				Five months	Clean and good.	
					One month	Clean and shiny.	
					Six months	Badly corroded.	
8	Al 7075-T6	Specimens coated with X-P500, dried overnight, and then immersed in synthetic urine.			One month	Clean and shiny.	Pair.
	Brass				Four months	Clean and shiny.	
	Steel				One month	Clean	
					Four months	Clean	
					One month	Some fine pits.	
					Four months	Many pits.	
					Six months	Badly corroded.	

TABLE VII (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks			
			Initial	Final						
9	Al 7075-T6	Specimens coated with XP-400A, dried overnight and then immersed in synthetic urine.	-	-	One month	Dull.	Bad.			
	Brass				Three months	dull, pits on the edges.				
	Steel				One month	Clean.				
10	Al 7075-T6	Mobil 0.01% Virco Pet 30 in synthetic urine.	6.80	6.85	One month	Clean.				
					Copper	Three months		Lots of pits.		
					Steel	One month		Dark.		
									Three months	Lot of pits and fill-form type of corrosion.
									One week	Clean and shiny.
									One month	Large pits.
11	Al 7075-T6	AML Guard - one coat dried for 30 min the second coat dried for 10 min. in synthetic urine.	6.85		One week	Clean.	Bad.			
					Brass	One month		Pits all over.		
					Steel	One month		Clean.		
									One week	Clean, fine pits.
									Two weeks	Clean but patchy.
									Ten weeks	Large pits wherever the coating broke down, Clean but patchy.
					Two weeks	Large pits.				
					Two weeks	Clean but patchy.				
					Ten weeks	Clean but patchy. 60% area pitted.				

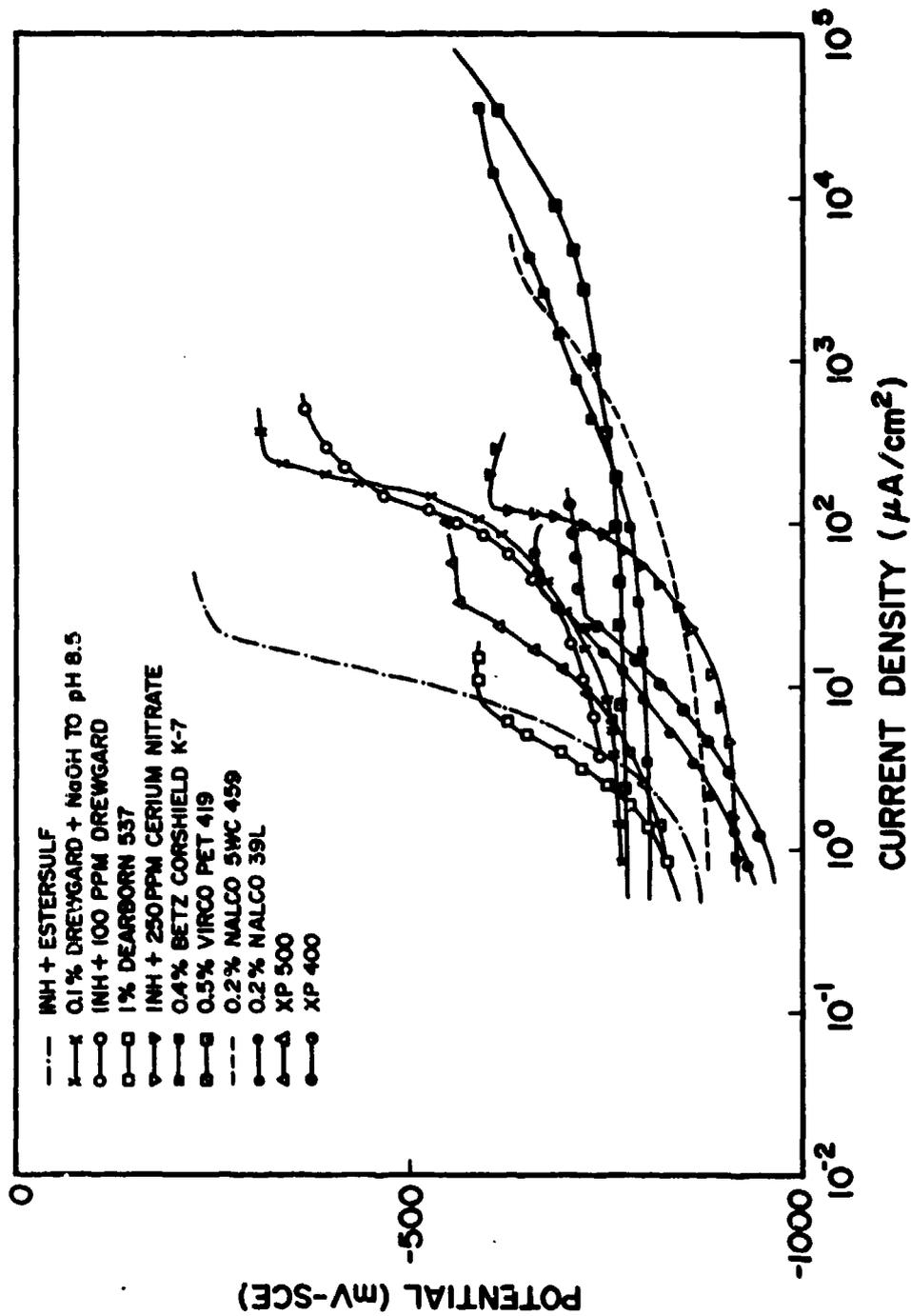


Figure 2. Polarization Curves of Al in Synthetic Urine with Several Commercial Inhibitors.

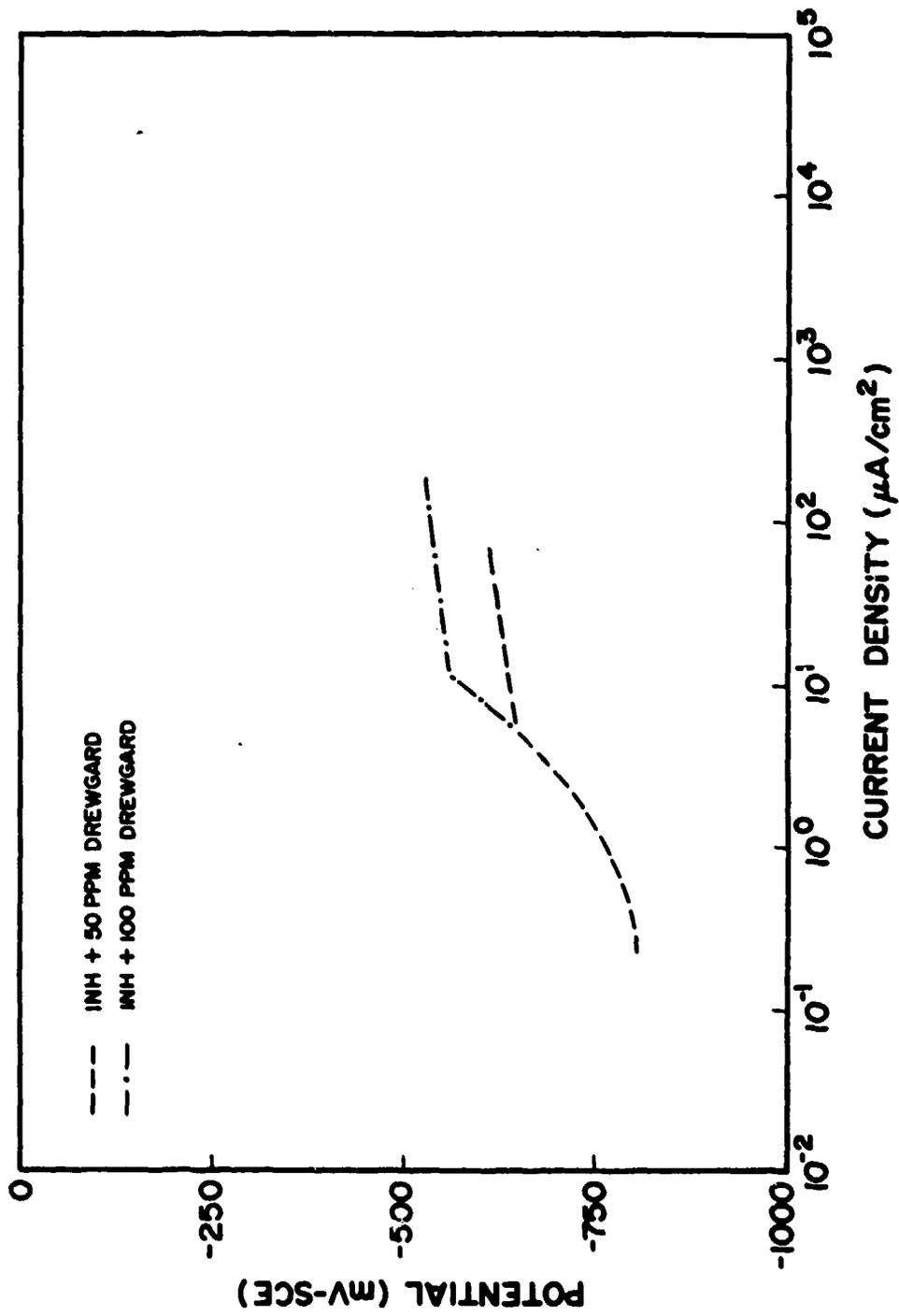


Figure 3. Polarization Behavior of Al in Synthetic Urine with DREWGARD.

TABLE VIII

## IMMERSION TEST RESULTS ON Al 7075-T6

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
1	Al 7075-T6	0.35 borate + 0.3 nitrate + 0.1 nitrite + 0.01 silicate + 10 ppm MBT + 50 ppm phosphate + NaOH to raise pH in urine solution.	8.90	8.80	1 week 3 weeks	Air bubbles at one edge, specimen clean. Specimen turned dark, no visible pit. Specimen taken out.	Needs better inhibition.
2	Al 7075-T6	0.35 borate + 0.3 nitrate + 0.1 nitrite + 0.01 silicate + 10 ppm MBT + 50 ppm phosphate + $\text{Na}_2\text{CO}_3$ to raise pH in urine solution.	9.0	8.95	1 week 3 weeks 2 months	Bubbles at one corner. Few pits and darkening of specimen. 90% area had streaks.	Bad.
3	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT in urine solution.	8.65	8.60	2 months 3 months	70% surface had streaks of corroded area; no pit. 70% surface had streaks of corroded area; no pit.	Needs better inhibition.
4	Al 7075-T6	0.35 borate + 0.3 nitrite + 0.3 nitrate + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT in urine solution.	8.65	8.54	2 months 4 months	Clean and shiny. Clean and shiny.	Good.
5	Al 7075-T6	0.35 borate + 0.30 molybdate + 0.20 nitrate + 0.10 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + NaOH to raise pH in urine solution.	8.90	8.85	1 month 2 months	One pit on one side. The other side had streaks of corroded area. One pit on one side. The other side had streaks of corroded area.	Bad.
6	Al 7075-T6	0.30 borate + 0.25 molybdate + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT in urine solution.	8.70	8.65	2 months 4 months	Clean and shiny. Clean and shiny.	Very good.
7	Al 7075-T6	0.20 borate + 0.2 nitrate + 0.2 nitrite + 250 ppm isopropylamine + 50 ppm phosphate + 10 ppm MBT in urine solution.	8.60	7.95	2 months 4 months 7 months	Clean and shiny. Clean and shiny. Clean and shiny.	Excellent.

TABLE VIII (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
8	Al 7075-T6	0.30 borate + 0.2 nitrate + 0.1 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + MeOH to raise pH in urine solution.	9.05	8.70	2 months	90-95% surface had deep streaks of corroded area.	Bad.
9	Al 7075-T6	0.3 borate + 0.2 nitrate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 25 ppm 100 oil in urine solution.	8.75	8.40	1 month 2 months	The surface lightly corroded. Surface lightly corroded.	Needs better inhibition.
10	Al 7075-T6	0.35 borate + 0.1 nitrite + 0.3 nitrate + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 25 ppm Triton K-114 in urine solution.	8.20	8.00	2 weeks 2 months 6 months	Clean and shiny. Clean and shiny. Clean and shiny.	Excellent.
11	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.1 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 100 ppm Cafac 15-710 in urine solution.	8.25	7.95	2 weeks 1 month	Clean and shiny. Clean and shiny.	V. Good.
12	Al 7075-T6	0.35 borate + 0.3 nitrate + 0.1 nitrite + 0.01 silicate + 50 ppm phosphate + 100 ppm 100 oil (pH raised with MeOH) in urine solution.	8.75	8.35	2 weeks 2 months 6 months	Clean and shiny. Clean, very light patch of oil film. Clean, very light patch of oil film.	Very good.
13	Al 7075-T6	0.35 molybdate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 100 ppm Triton K-114 in urine solution.	6.95	6.75	2 weeks 1 month	Clean and shiny. Clean and shiny.	Very good.

TABLE VIII (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
14	Al 7075-T6	0.35 borate + 0.1 nitrate + 0.5 nitrite + 0.01 silicate + 50 ppm phosphate + 20 ppm MBT + 100 ppm Cortec 317.	7.90	8.20	2 weeks 2 months	Clean and shiny. Clean and shiny.	Very good.
15	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.1 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 100 ppm tributylamine in urine solution.	8.25	8.20	2 weeks 1 month 2 months	Clean and shiny. Clean and shiny. Lightly corroded.	Good.
16	Al 7075-T6	0.22 borate + 0.12 nitrate + 0.5 benzoate in urine solution.	-	-	2 weeks 3 months	Clean and shiny. Clean and shiny but several large pits.	Bad.

TABLE IX

## TEST RESULTS ON ALUMINUM, COPPER, AND STEEL SPECIMENS IMMersed TOGETHER

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
1	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 100 ppm oil in urine solution.	7.90	7.90	2 weeks	Copper ions attacking Al.	Bad.
	Steel				2 weeks	Clean and shiny; few fine pits.	
	Copper				2 weeks	Dissolving in solution. (Taken Out).	
2	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 250 ppm isoptopylamine in urine solution.	8.45	8.30	2 weeks	50% area pitted.	Bad.
	Copper				2 weeks	Dissolving in solution.	
	Steel				2 weeks	Several pits.	
3	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.3 nitrate + 0.1 silicate + 100 ppm ZnSO <sub>4</sub> + 25 ppm Triton X-114 in urine solution.	8.60	8.40	2 weeks	Clean and shiny.	Good.
	Copper				3 months	Clean and shiny.	
	Steel				2 weeks	Clean.	
4	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.02 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm Triton X-114 + 100 ppm ZnSO <sub>4</sub> in urine solution.	8.75	8.60	2 weeks	Clean and shiny.	Fair.
	Copper				3 months	Clean and shiny.	
	Steel				2 weeks	Dull.	
5	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 25 ppm Triton X-114 + 20 ppm ZnSO <sub>4</sub> .	7.75	7.60	2 weeks	Clean and shiny.	Bad.
	Copper				4 weeks	Started pitting.	
	Steel				2 weeks	Clean but dull.	
6	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 10 ppm MBT + 25 ppm Triton X-114 + 20 ppm ZnSO <sub>4</sub> .	7.75	7.60	2 weeks	Dissolving into solution	Bad.
	Copper				4 weeks	Clean and shiny.	
	Steel				2 weeks	Dull. (Taken out).	



TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
10	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 50 ppm Richonate 1850 + 100 ppm ZnSO <sub>4</sub> + 50 ppm phosphate + 50 ppm MBT in synthetic urine.	7.65	7.70	1 month	Clean and shiny.	Very good.
	4 months				Clean and shiny.		
	8 months				Clean and shiny.		
11	Brass	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 60 ppm phosphate + 30 ppm MBT + 100 ppm Richonate 1850 + 100 ppm Dequest 2010 + 20 ppm ZnSO <sub>4</sub> in synthetic urine.	8.3	8.2	1 month	Clean and shiny.	Bad.
	8 months				Clean and shiny (pits on edges).		
	1 month				Clean and shiny (pits on edges).		
	One week				Clean, but corrosion streaks.		
	One week				Clean.		
12	Steel	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 200 ppm K-soup + 75 ppm Richonate 1850 in synthetic urine.	8.45	8.4	One week	Clean.	Excellent.
	Al 7075-T6				Two weeks	Clean and shiny.	
	Brass				Three months	Clean and shiny.	
	Steel				Two weeks	Clean and shiny.	
					Three months	Clean and shiny.	
					Two weeks	Clean.	
					Three months	Clean, but few pits at the edges.	
13	Al 7075-T6	0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 100 ppm MBT + 100 ppm BT + 350 ppm K-soup + 75 ppm Richonate 1850 + 100 ppm ZnSO <sub>4</sub> in synthetic urine.	6.7	6.7	Two weeks	Clean and shiny.	Excellent.
	Brass				Ten weeks	Clean and shiny.	
	Steel				Two weeks	Clean and shiny.	
					Ten weeks	Clean and shiny.	
					Ten weeks	Clean and shiny, one fine pit on one corner.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
14	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 100 ppm ZnSO <sub>4</sub> + 100 ppm MBT + 50 ppm phosphate + 75 ppm Richonate 1850 in synthetic urine.	9.35	9.25	Two weeks	Clean and shiny.	Excellent.
	Two months				Clean and shiny.		
	Two weeks				Clean and shiny.		
	Two months				Clean and shiny.		
15	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.1 nitrate + 0.01 silicate + 125 ppm phosphate + 65 ppm MBT + 75 ppm Richonate 1850 + 200 ppm sodium gluconate + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.20	8.10	Two weeks	Streaks and pits.	Bad.
	Four weeks				Streaks and pits.		
	Two weeks				Clean.		
	Two weeks				Clean.		
16	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm BT + 50 ppm MBT + 75 ppm Richonate 1850 + 500 ppm ZnSO <sub>4</sub> in synthetic urine.	8.30	8.35	Two weeks	Clean and shiny.	Excellent.
	Ten weeks				Clean and shiny.		
	Five months				Clean and shiny.		
	Two weeks				Clean and shiny.		
	Brass				Ten weeks	Clean, one small light patch.	Very good.
	Steel				Five months	Clean, small light patches.	
					Two weeks	Clean and shiny, few fine pits on edges.	
					Ten weeks	Clean and shiny, few fine pits on edges.	
					Five months	Clean and shiny, few pits on edges, no pits around hole.	Very good.

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
17	Al 7075-T6 Brass Steel	0.35 borate + 0.2 nitrate + 0.2 nitrate + 0.01 silicate + 0.01 phosphate + 0.01 MBT + 125 ppm Richonate 1850.	8.5	8.50	One month	Clean and shiny.	Excellent.
					One month	Clean and shiny.	
					One month	Clean and shiny, no pits.	
18	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 20 ppm MBT + 50 ppm Cerium nitrate in urine solution.	8.20	8.20	Two weeks	Dull, several pits.	Bad.
					Two weeks	Dull.	
					Two weeks	Fine pits on edges.	
19	Al 7075-T6 Copper Steel	0.22 borate + 0.24 nitrite + 1.0 benzoate in urine solution.	5.60	5.50	Two weeks	Clean but dull.	Bad.
					Four months	Very badly corroded.	
					Two weeks	Clean but dull.	
20	Al 7075-T6 Brass Steel	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 25 ppm MBT + 250 ppm Cortec 317 in synthetic urine.	8.05	8.00	Two weeks	Clean but dull.	Bad.
					Four months	Very badly corroded.	
					Two weeks	Clean but dull.	
21	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm potassium soap in urine solution.	8.30	8.25	Two months	Clean and shiny.	Excellent.
					Eight months	Dull, some very fine pits.	
					Eight months	Clean, some dull spots.	
20	Al 7075-T6 Brass Steel	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 25 ppm MBT + 250 ppm Cortec 317 in synthetic urine.	8.05	8.00	Two months	Clean, some dull spots.	Poor.
					Eight months	Clean, some dull spots.	
					Eight months	Edges full of pits.	
21	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm potassium soap in urine solution.	8.30	8.25	Two months	One large pit on surface also.	Poor.
					Four weeks	Clean and shiny.	
					Two months	Clean and shiny.	
21	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm potassium soap in urine solution.	8.30	8.25	Three months	Clean and shiny.	Excellent.
					Four weeks	Clean and shiny.	
					Two months	Clean and shiny.	
21	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm potassium soap in urine solution.	8.30	8.25	Two months	Clean and shiny.	Excellent.
					Three months	Clean and shiny.	
					Four weeks	Clean and shiny.	
21	Al 7075-T6 Copper Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm potassium soap in urine solution.	8.30	8.25	Two months	Clean and shiny.	Excellent.
					Three months	Clean and shiny.	
					Four weeks	Clean and shiny.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
22	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 500 ppm phosphate + 50 ppm MBT + 100 ppm oleate in synthetic urine.	8.45	8.42	One month	Clean and shiny.	Very good.
	Four months				Clean and shiny.		
	Eight months				Clean and shiny.		
	Brass				One month	Clean and shiny.	
	Steel				Eight months	Clean and shiny.	
					One month	One pit near the oleate otherwise clean.	
23	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 50 ppm BT + 200 ppm K-soap in synthetic urine.	8.90	8.90	Two weeks	Clean and shiny.	Excellent.
	Brass				Three months	Clean and shiny.	
	Steel				Two weeks	Clean and shiny.	
24	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 50 ppm BT + 200 ppm K-soap in synthetic urine.	8.95	8.85	Three months	Clean.	
	Brass				Two weeks	Fine pits around the hole, otherwise clean and shiny.	
	Steel				Three months	Clean and shiny.	
25	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 50 ppm BT + 200 ppm K-soap + 75 ppm Estersulf in synthetic urine.	8.45	8.50	Two weeks	Clean and shiny.	Excellent.
	Brass				Three months	Clean.	
	Steel				Two weeks	Clean and shiny.	
					Three months	Clean and shiny.	
					Two weeks	Clean and shiny.	
					Three months	Clean and shiny.	
					Two weeks	Clean and shiny.	
					Three months	Clean, one fine pit at one corner.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
26	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.2 ni- trate + 0.01 silicate + 50 ppm phos- phate + 100 ppm MBT + 100 ppm BT + 200 ppm K-soap + 100 ppm ZnSO <sub>4</sub> in synthetic urine.	8.30	8.25	Two weeks	Clean and shiny.	Excellent.
	Three months				Clean and shiny.		
	Two weeks				Clean and shiny.		
27	Al 7075-T6	0.2 nitrite + 0.2 nitrate + 0.01 sil- icate + 50 ppm phosphate + 50 ppm MBT + 50 ppm BT + 250 ppm K-soap in synthetic urine.	8.30	8.30	Two weeks	Clean and shiny.	Excellent.
	Three months				Clean and shiny.		
	Two weeks				Clean and shiny.		
28	Al 7075-T6	0.05 nitrite + 0.2 nitrate + 0.01 silicate + 125 ppm phosphate + 60 ppm MBT + 150 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> + 250 ppm K-soap + NaOH in synthetic urine.	8.50	8.55	Two weeks	Clean and shiny.	Excellent.
	Two months				Clean and shiny.		
	Two months				Clean and shiny.		
29	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 ni- trate + 0.01 silicate + 50 ppm phos- phate + 100 ppm MBT + 100 ppm BT + 200 ppm K-soap + 75 ppm Estersulf in synthetic urine.	8.55	8.55	Two weeks	Clean and shiny.	Excellent.
	Ten weeks				Clean and shiny.		
	Five months				Clean, not as shiny.		
	Brass				Two weeks	Clean and shiny.	
	Ten weeks				Clean and shiny.		
	Five months				Clean and shiny.		
	Steel				Two weeks	Clean.	Excellent.
	Ten weeks				Clean, edge touching the beaker wall has some pits.		
	Five months				Clean edge touching the beaker wall has some pits.		

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	PH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
30	Al 7075-T6	0.05 nitrate + 0.2 nitrate + 0.01 silicate + 125 ppm phosphate + 60 ppm MBT + 100 ppm Richonate 1850 + 150 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> 250 ppm K-soap + NaOH in synthetic urine.	9.10	9.15	Two weeks	Clean and shiny.	Excellent.
	Two months				Clean and shiny.		
	Four months				Clean, several surface pits.		
31	Brass	0.2 nitrite + 0.2 nitrate + 0.2 silicate + 100 ppm phosphate + 50 ppm MBT + 100 ppm oleate in synthetic urine.	8.65	8.70	Two weeks	Clean and shiny.	Excellent.
	Two months				Clean and shiny.		
	Four months				Clean and shiny.		
32	Steel	0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 100 ppm MBT + 100 ppm BT + 350 ppm K-soap in synthetic urine.	8.30	8.30	Two weeks	Clean and shiny.	Excellent.
	Three months				Clean and shiny.		
	Five months				Clean and shiny.		
33	Brass	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 125 ppm phosphate + 60 ppm MBT + 100 ppm Richonate 1850 + 210 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.15	8.20	Two weeks	Clean and shiny.	Excellent.
	Three months				Clean and shiny.		
	Five months				Clean and shiny, but pits around the hole.		

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
34	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 125 ppm phos- phate + 60 ppm MBT + 100 ppm RIchonate 1850 + 200 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.15	8.15	Two weeks	Clean and shiny.	Excellent.
	Three months				Clean and shiny.		
	Three months				Clean and shiny.		
35	Brass	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 125 ppm phos- phate + 60 ppm MBT + 100 ppm RIchonate 1850 + 200 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.50	8.40	Three months	Clean and shiny, but three fine pits around the hole.	Excellent.
	Steel				Clean and shiny.		
	Two weeks				Clean and shiny.		
36	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 ni- trate + 0.01 silicate + 125 ppm phos- phate + 60 ppm MBT + 100 ppm Kicho- nate 60-B + 150 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.80	8.75	Two weeks	Clean and shiny.	Excellent.
	Brass				Clean and shiny.		
	Steel				Clean and shiny.		
37	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 125 ppm phos- phate + 60 ppm MBT + 100 ppm RIchonate 1850 + 200 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	8.15	8.20	Two weeks	Clean and shiny.	Good.
	Brass				Dull, three large pits.		
	Steel				Clean and shiny.		

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Mt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
38	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.1 silicate + 125 ppm phosphate + 60 ppm MBT + 100 ppm Richonate 1850 + 150 ppm Dequest 2010 + 40 ppm ZnSO <sub>4</sub> in synthetic urine.	9.55	9.50	Two weeks	Clean and shiny.	Very good.
	Four months				Clean but dull.		
	Two weeks				Clean and shiny.		
Steel					Two months	Clean and shiny.	
					Four months	Clean.	
					Two weeks	Clean and shiny, fine pits around hole.	
39	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm Ester-sulf in synthetic urine.	8.20	8.15	Four months	Dark, fine pits, one large pit.	Good.
	One month				Clean and shiny.		
	Four months				Clean and shiny.		
40	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.1 nitrate + 0.01 silicate + 50 ppm MBT + 50 ppm phosphate + 50 ppm polyamate + 100 ppm Ester-sulf in synthetic urine.	8.80	8.70	One month	Clean, pits around hole	Fair.
	Four months				Clean, several pits around hole.		
	Two weeks				Clean.		
41	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 100 ppm phosphate + 50 ppm MBT + 50 ppm Triton X-114 + 50 ppm piperazine in synthetic urine.	8.65	8.65	Ten weeks	Clean, few corrosion streaks.	Very good.
	Two weeks				Clean.		
	Two weeks				Clean.		
Steel					Ten weeks	Clean, pits near the hole.	
					One month	Clean and shiny.	
					Six months	Clean and shiny.	
Steel					One month	Clean and shiny.	
					Six months	Clean, but pits around the hole.	
					Six months	Clean, but pits around the hole.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	PH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
42	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 100 ppm phosphate + 50 ppm MBT + 100 ppm oil + 50 ppm piperazine in synthetic urine.	8.35	8.30	One week	Clean and shiny.	Bad.
	Six weeks				Several large pits.		
	One week				Clean.		
43	Copper	0.35 borate + 0.1 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm oil + 25 ppm piperazine+NaOH in synthetic urine.	8.45	8.45	One week	Clean.	Very bad.
	One week				Fine pits.		
	One week				Several streaks of pits.		
44	Al 7075-T6	0.5% potassium soap + 100 ppm Riche-mate 1850 + NaOH in synthetic urine.	7.80	7.85	One month	Pitted all over.	Bad.
	Brass				Patchy.		
	Steel				Pits all over the edges.		
	Brass				Dull, one pit, otherwise no corrosion.		
	Steel				Dull, large pits.		
	Steel				Dull, no pit.		
45	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 0.05 Zn Gluconate in synthetic urine.	8.85	8.80	One month	Dark, no pit.	Good.
	Brass				Clean, but lightly darkened.		
	Steel				Very badly pitted.		
	Brass				Clean and shiny.		
	Steel				Few pits, but clean.		
	Steel				Few patches.		
46	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 75 ppm Riche-mate 1850 + 25 ppm Zn Gluconate in synthetic urine.	8.30	8.30	One month	Few patches, sign of corrosion.	Poor.
	Brass				Clean and shiny.		
	Steel				Clean and shiny.		
	Brass				Clean, but several fine pits.		
	Steel				Clean, but one big black patch.		
	Steel				Clean, no pit.		

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	PH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
47	Al 7075-T6	0.35 borate + 0.05 nitrite + 0.2 ni- phosphate + 0.01 silicate + 50 ppm phos- phate + 20 ppm MBT + 50 ppm wgard in urine solution.	8.25	8.20	Two weeks	Dull and clean.	Good.
	Copper				Two months	Dull and clean.	
	Steel				Four weeks	Clean.	
					Two weeks	Clean, but few patches.	
					Two months	Clean and shiny.	
					Two months	Fine pits on edges.	
49	Al 7075-T6	35 borate + 0.2 nitrite + 0.02 silil- icate + 100 ppm phosphate + 50 ppm MBT + 100 ppm Na-Sul BSB in synthetic urine.	8.00	8.05	One month	Clean and shiny.	Good.
	Brass				Six months	Clean.	
	Steel				One month	Clean and shiny.	
					Six months	Clean and shiny.	
					One month	Clean and shiny, but several small pits around the hole.	
					Six months	Clean and shiny, but several small pits around the hole.	
49	Al 7075-T6	0.05 Nitrite + 0.1 Nitrate + 0.01 silil- icate + 50 ppm MBT + 50 ppm phosphate + 50 ppm polyamate 922 + 100 ppm BSB + 100 ppm K-soap in synthetic urine.	8.30	8.30	Two weeks	Clean and shiny.	Poor.
	Steel				Ten weeks	Clean, lot of deposits on the surface.	
					Two weeks	Clean and shiny.	
					Ten weeks	Clean, lot of deposits on the surface.	
					Two weeks	Clean and shiny, corro- sion just starting near the hole.	
					Ten weeks	Pitted and dark.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
50	Al 7075-T6 Brass Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm MBT + 100 ppm BSN in synthetic urine.	8.20	8.15	One month	Clean and shiny.	Good.
					Four months	Clean and shiny.	
					One month	Clean and shiny.	
					Four months	Clean, few pits around hole.	
51	Al 7075-T6 Brass Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm Mobil's dimethyl methylphosphonate in synthetic urine.	8.2	8.25	Two weeks	Dull, patches of corrosion.	Bad.
					Two weeks	Clean.	
					Two weeks	Several pits.	
					Two weeks	Dull, patches of corrosion.	
52	Al 7075-T6 Brass Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm Mobil's dimethyl methylphosphonate in synthetic urine.	8.2	8.25	Two weeks	Dull, patches of corrosion.	Bad.
					Two weeks	Clean.	
					Two weeks	Several pits.	
					Two weeks	Dull, several pits.	
53	Al 7075-T6 Brass Steel	0.35 borate + 0.05 nitrite + 0.2 nitrate + 0.01 silicate + 50 ppm phosphate + 50 ppm Richonate 60-B + Richamide 6445 + NaOH in synthetic urine.	8.70	8.65	Two weeks	Clean.	Bad.
					Two weeks	One large pit near the hole.	
					Two weeks	Clean and shiny.	
					Two weeks	Clean and shiny.	
54	Al 7075-T6 Brass Steel	0.2 borate + 0.3 sodium molybdate + 0.2 nitrite + 0.01 silicate + 50 ppm phosphate + 100 ppm ZnSO <sub>4</sub> + 100 ppm benzotriazole + 50 ppm Triton X-114 in synthetic urine.	8.35	8.30	One month	Clean and shiny.	Very good.
					Four months	Clean and shiny.	
					Eight months	Clean and shiny.	
					One month	Clean and shiny.	
		Four months	Clean and shiny.				
		Eight months	Clean and shiny.				
		One month	Clean and shiny.				
		Four months	Clean and shiny.				
		Eight months	Clean, only one or two fine pits at edges.				

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
55	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 100 ppm phosphate + 50 ppm MBT + 50 ppm Triton X-114 + 50 ppm potassium soap in synthetic urine.	8.50	8.55	One week	Pale.	Bad.
	Two months				Pale and pitted.		
	One week				Dull.		
	Two months				Dull.		
56	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.02 silicate + 100 ppm phosphate + 50 ppm MBT + 100 ppm oil + 100 ppm potassium soap in synthetic urine.	8.45	8.45	One week	Fine pit.	Fair.
	Two months				One large pit also.		
	Two weeks				Clean and shiny.		
	Two months				Clean and shiny.		
57	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 100 ppm MBT + 50 ppm phosphate + 250 ppm Boeshield T-9 in synthetic urine.	8.15	8.15	Two weeks	Pale patches.	Excellent.
	Two months				Pale patches.		
	Two weeks				Clean.		
	Two months				Clean, pits on edges.		
58	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 nitrate + 0.01 silicate + 100 ppm MBT + 50 ppm phosphate + 100 ppm Boeshield in synthetic urine.	8.3	8.25	Two weeks	Clean and shiny.	Very Good.
	Two months				Clean and shiny.		
	Four months				Clean.		
	Two weeks				Clean.		
	Brass				Two months	Clean and shiny.	
	Steel				Two months	Clean and shiny.	
					Four months	Clean and shiny.	
					Two weeks	Clean and shiny.	
	Brass				Two months	Clean and shiny.	
	Steel				Four months	Clean and shiny.	
					Two weeks	Clean and shiny.	
					Two months	Dull, one pit near hole.	
					Four months	Light dark, one pit near hole.	

TABLE IX (Continued)

Spec. No.	Specimen	Electrolyte Wt %	pH		Time of Exposure	Surface Appearance Visual observation	Remarks
			Initial	Final			
59	Al 7075-T6	0.35 borate + 0.2 nitrate + 0.2 ni- trate + 0.01 silicate + 100 ppm MBT + 50 ppm phosphate + 250 ppm Boeshield T-9 in synthetic urine.	8.15		Two weeks	Clean and shiny.	Very good.
	Two months				Clean and shiny.		
	Three months				Clean, not as shiny.		
	Brass				Two weeks	Clean and shiny.	
	Steel				Two months	Clean and shiny.	
					Three months	Clean and shiny.	
60	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 50 ppm phos- phate + 50 ppm BT + 75 ppm Triton X-114 + 500 ppm ZnSO <sub>4</sub> in coffee.	8.30	3.20	Two weeks	Clean, one pit appearing	
	Brass				Two months	Clean, one pit.	
	Steel				Three months	Clean, pits around hole.	
61	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 50 ppm phos- phate + 50 ppm MBT + 75 ppm Triton X-114 + 500 ppm ZnSO <sub>4</sub> in 50% coffee + 50% synthetic urine.	8.15	8.00	1 month	Clean and shiny.	Excellent.
	Brass				8 months	Clean and shiny.	
	Steel				1 month	Clean, light patches.	
62	Al 7075-T6	0.35 borate + 0.2 nitrite + 0.2 ni- trate + 0.01 silicate + 50 ppm phos- phate + 50 ppm MBT + 75 ppm Triton X-114 + 500 ppm ZnSO <sub>4</sub> in 10% coffee + 90% synthetic urine.	8.25	8.25	1 month	Clean and shiny.	Very Good.
	Brass				8 months	Clean.	
	Steel				1 month	Clean, but dull.	
					1 month	Clean.	Clean, edges lightly corroded.
					8 months	Clean, edges lightly corroded.	

### Water-Displacement Compounds as Candidate Materials

Boeshield T-9 is being used as a corrosion inhibitor for corrosion hot spots by Boeing Company for their commercial aircraft. Water-displacement compounds AML Guard and AML Chrome have been developed by the Naval Air Development Center (NADC) for similar corrosion inhibition. Samples of these compounds were obtained from Oxy Metals and NADC, and immersion tests as well as electrochemical tests were conducted with synthetic urine on Al 7075-T6. The results are given in Table IX, and the polarization curves are shown in Figs. 4 and 5. More familiar water-displacement compounds--namely, LPS1, LPS3, WD-40, and UM--were also tested for their effectiveness as inhibitors for the bilge areas of aircraft. The results of immersion tests are shown in Table IX, and the polarization curves are shown in Figs. 6-8.

#### Immersion Tests

Immersion tests with more than 200 different mixtures (potential inhibitors) were conducted. Selected results and inhibitor-performance data are shown in Table IX. Several of these mixtures are commercially available inhibitors used for corrosion protection of ferrous and nonferrous metals, while others were formulated from the information in the literature<sup>12-13</sup> and experience gained during the testing.

Very systematic immersion tests were carried out on high-strength aluminum alloys (2024-T3 and 7075-T6), high-strength 4340 steel, copper, cast iron, and brass. Standard 60 x 30 x 3.125 mm (4 x 2 x 1/8 in.) test coupons were used for the immersion tests on aluminum alloys. Smaller coupons measuring 50 x 25 x 3.125 mm (3 x 1 x 1/8 in.) were used for high-strength steel, copper, cast iron, and brass. The specimen surface and pH of the electrolyte were checked periodically. After an immersion period of 1000 hr, the specimens were removed from the solution. In some cases, specimens were exposed over a six-month period. Each specimen was inspected very carefully for discoloration, roughening, general corrosion, corrosion

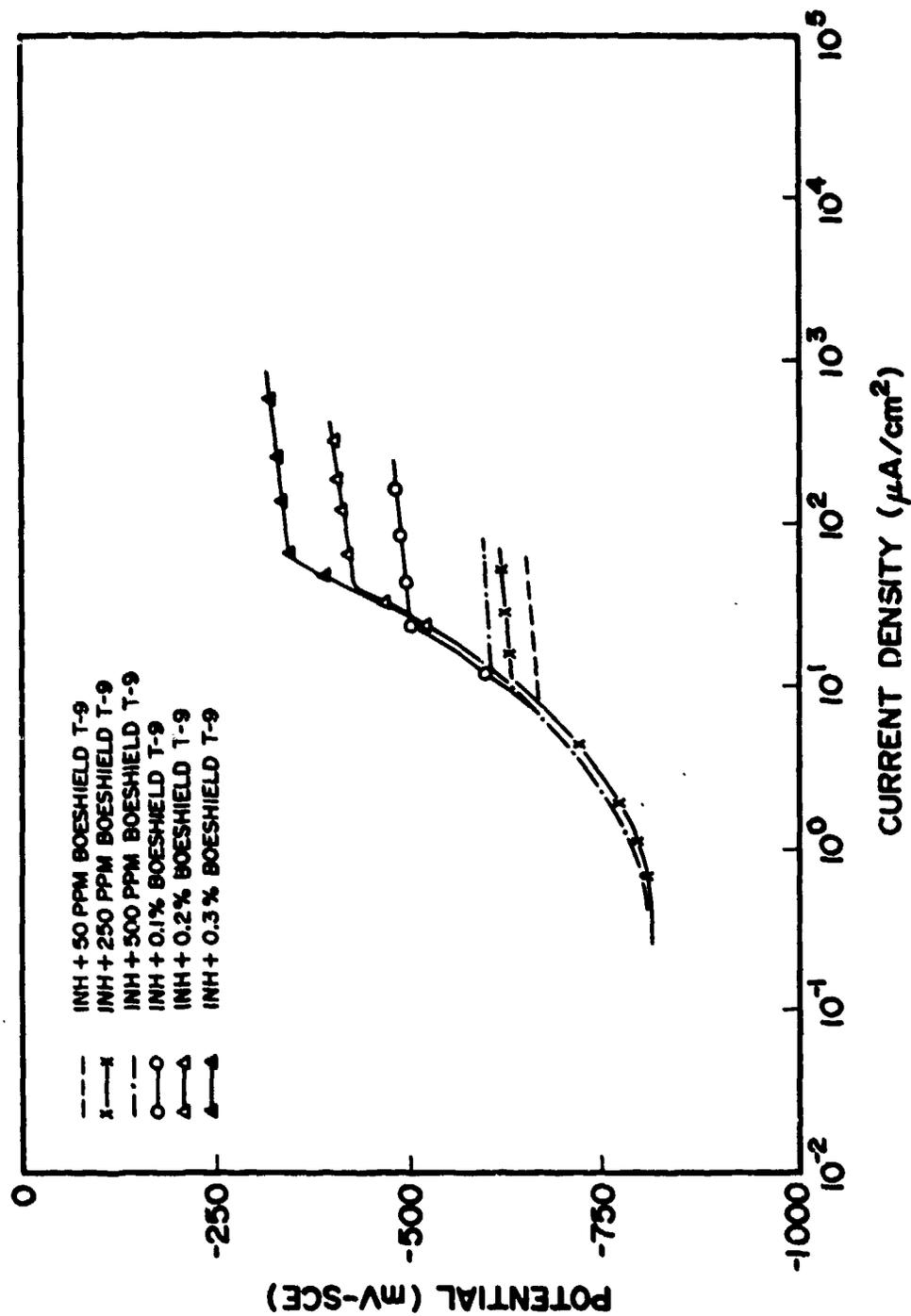


Figure 4. Polarization Behavior of Al in Synthetic Urine Inhibited with Boeshield T-9.

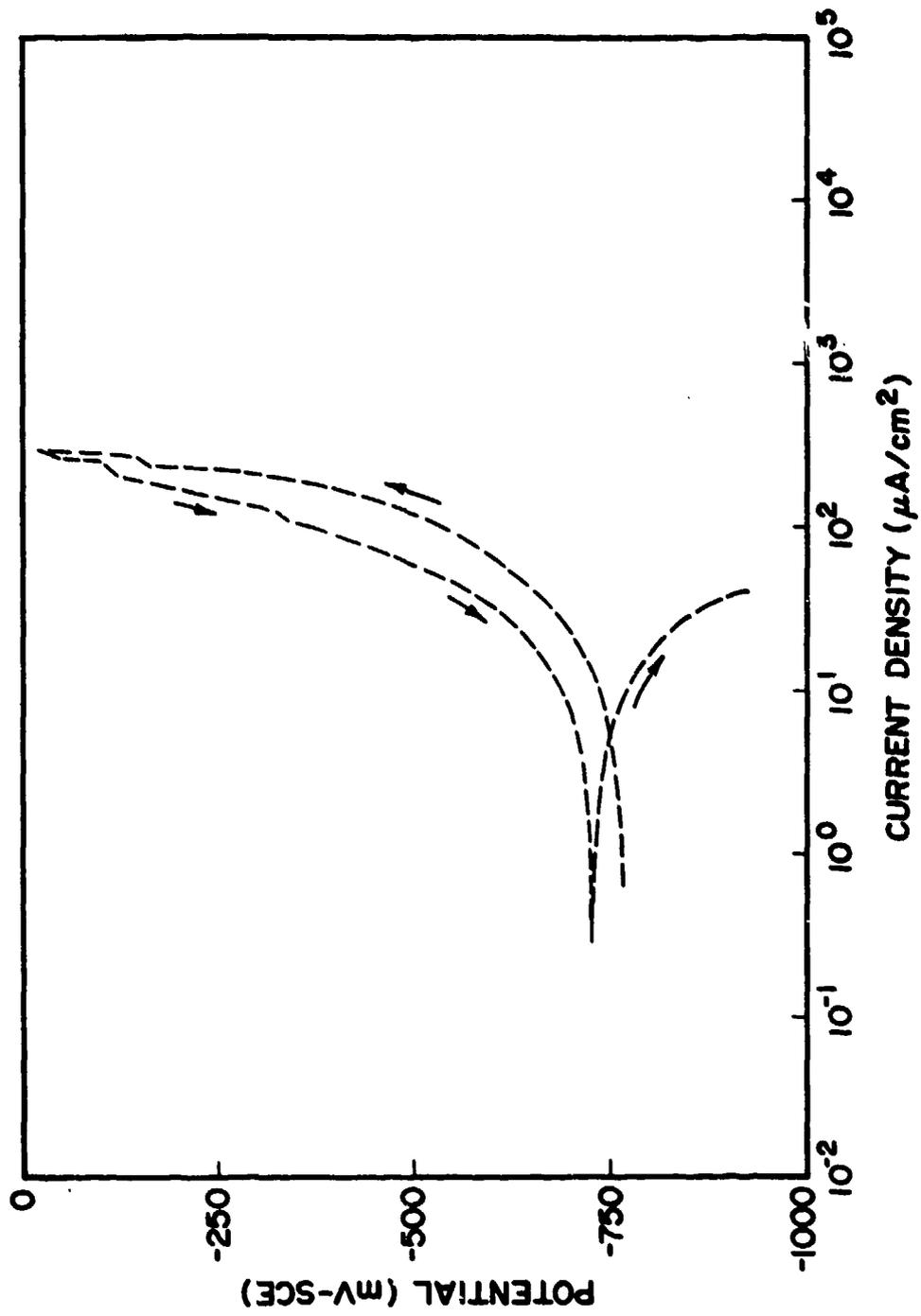


Figure 5. Polarization Behavior of Al in Synthetic Urine Inhibited with AML Guard.

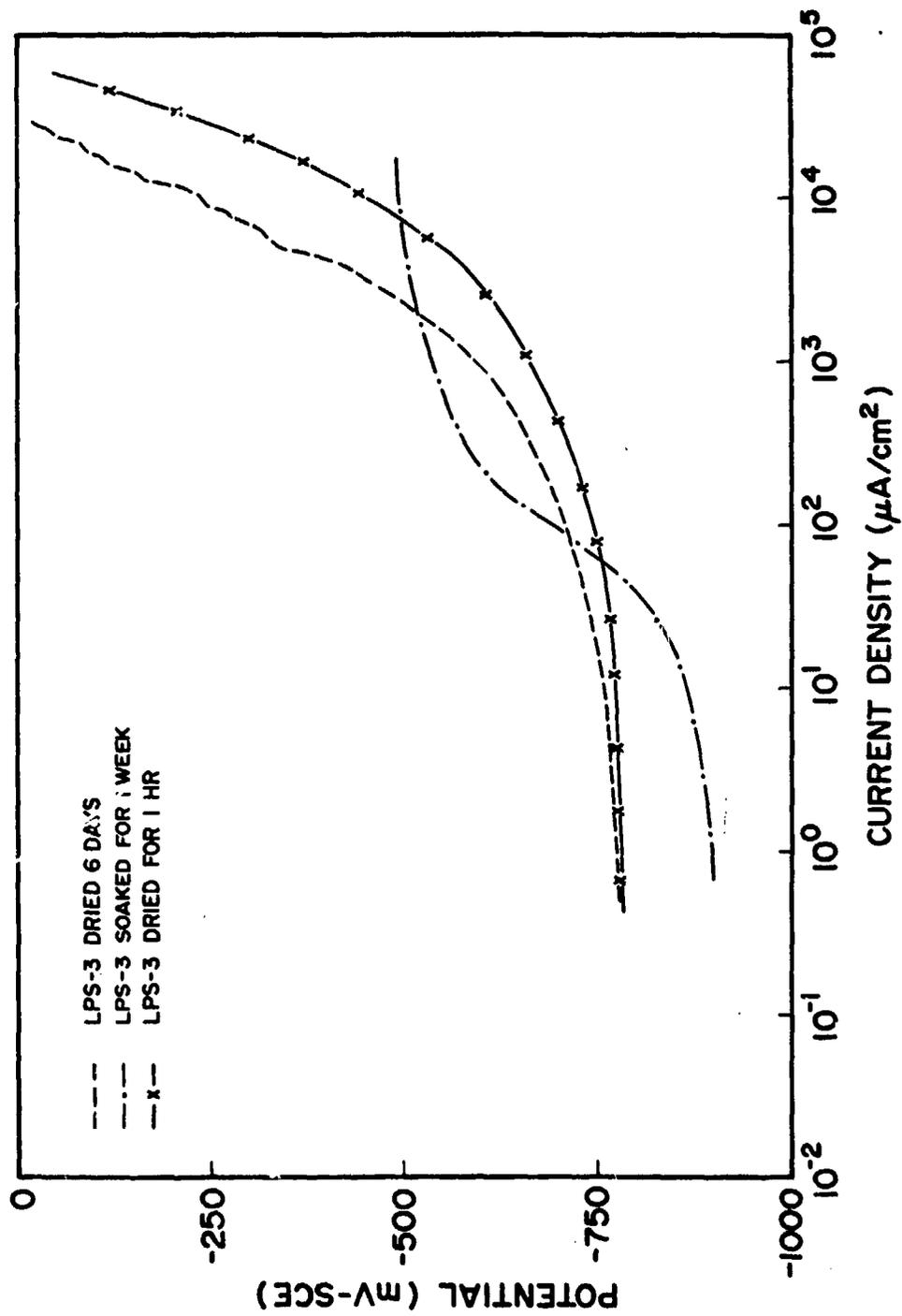


Figure 6. Polarization Behavior of Al in Synthetic Urine Inhibited with LPS 3.

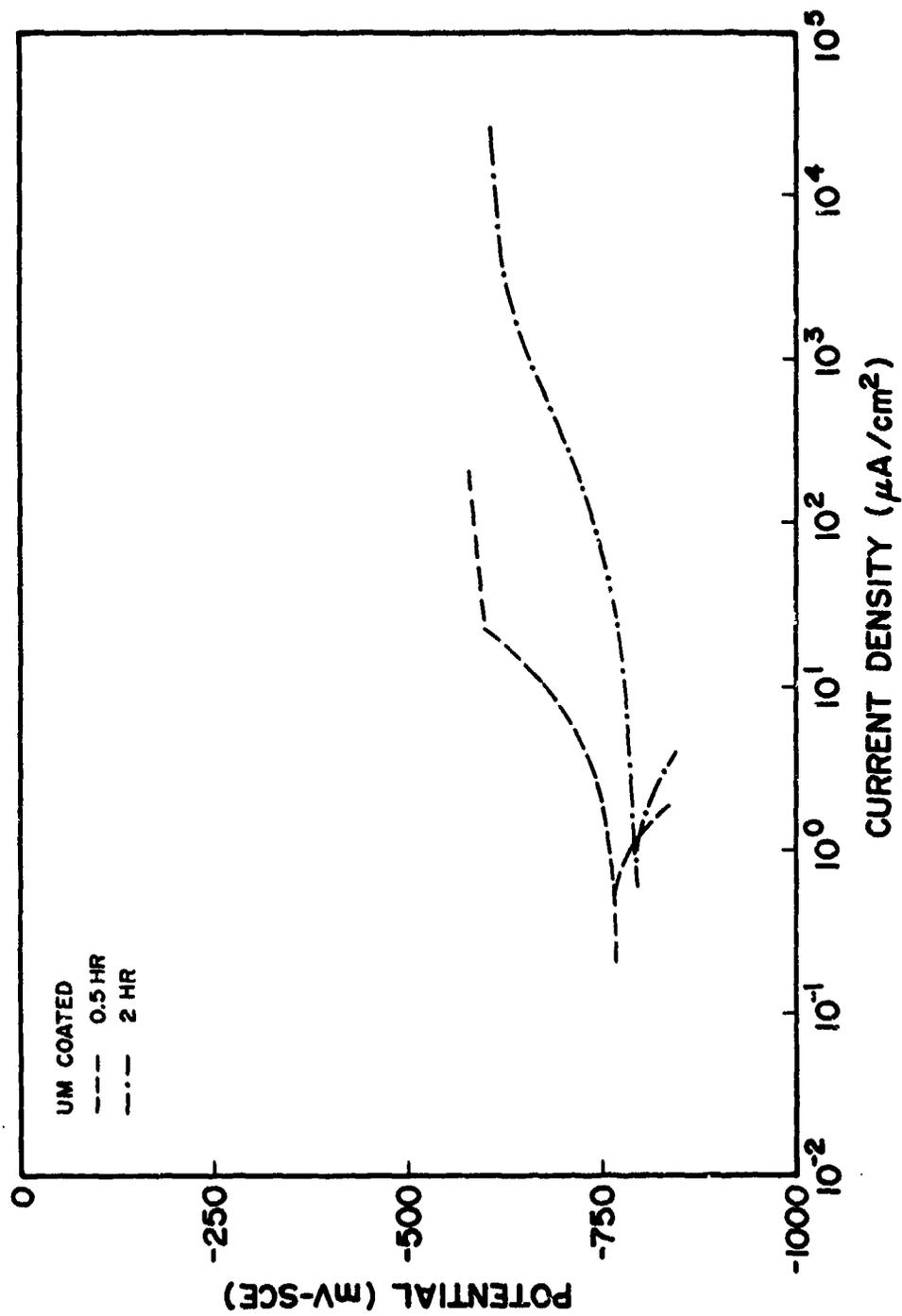


Figure 7. Polarization Behavior of Al in Synthetic Urine Inhibited with UM.

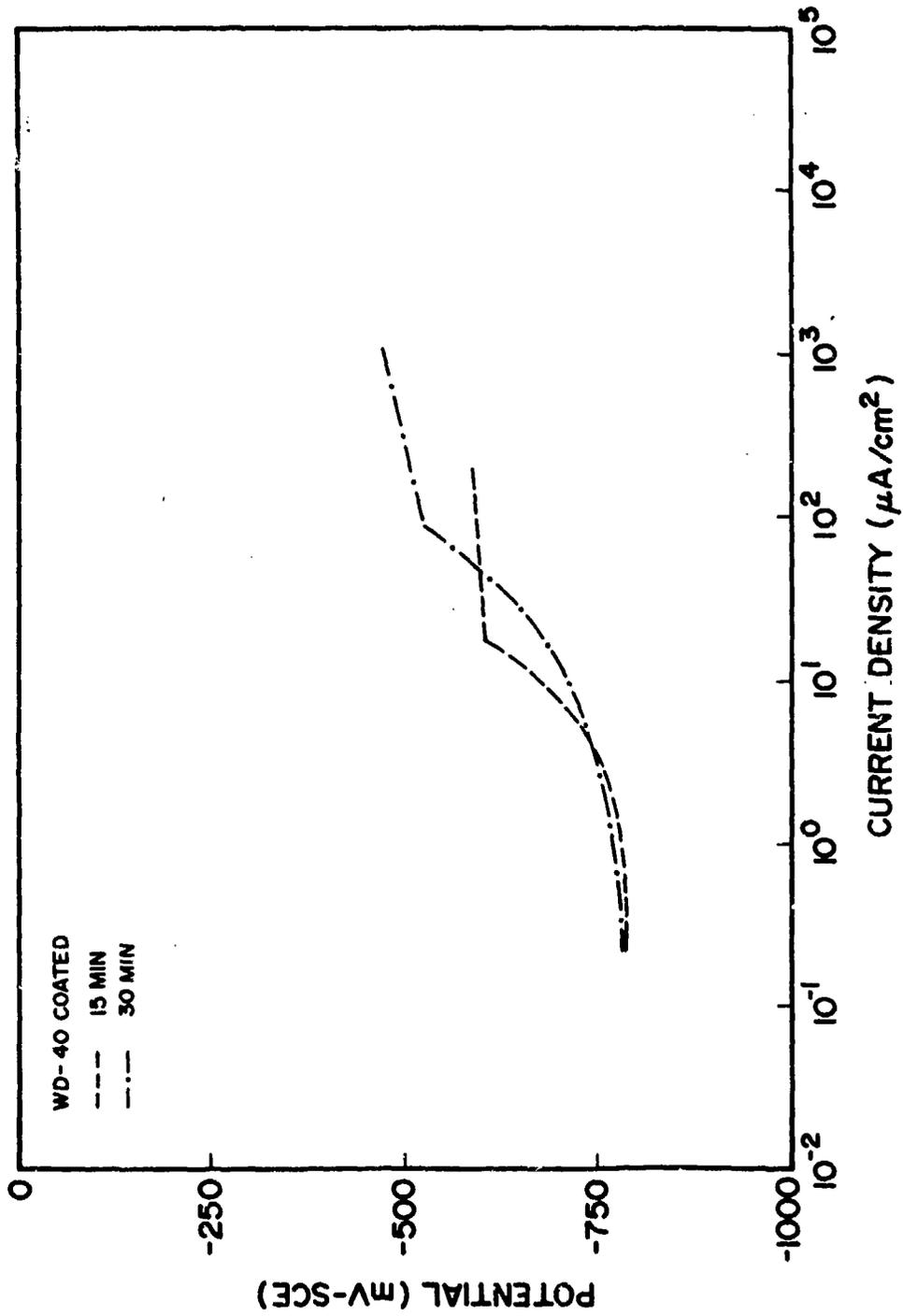


Figure 8. Polarization Behavior of Al in Synthetic Urine Inhibited with WD-40.

products, and size and location of pits. Then the specimens were cleaned in a solution of 2% chromic acid + 5% phosphoric acid at 80°C (175°F) for a period of 5-25 min., depending upon the thickness of the corrosion products. The weight loss measured for some specimens was converted to mils per year (mpy) according to

$$\text{mpy} = \frac{534W}{DAT}$$

where W = weight loss (mg)

D = density of specimen (gm/cm<sup>3</sup>)

A = area of specimen (sq. in.)

T = exposure time (hr).

#### Polarization Measurements

Since immersion tests are time consuming and it was almost impossible to carry out such tests on a massive number of possible formulations in the limited time frame, screening of the inhibitors was assisted by fast and more refined techniques such as anodic, cathodic, and linear polarization. All tests were carried out in accordance with ASTM Standard G5-72, "Standard Recommended Practice for Standard Reference Method For Making Potentiostatic and Potentiodynamic Polarization Measurements." The measurements were conducted by means of an automated PAR unit consisting of a corrosion cell, potentiostat/galvanostat, log converter, programmer, and X-Y recorder. The experimental arrangement is shown in Fig. 9.

#### PHASE III - OPTIMIZATION OF INHIBITOR FORMULATION

Generally, inhibitor performance was tested by immersing one metallic sample in a single inhibitor formulation. In some cases pieces of aluminum, high-strength steels, copper, brass, and cast iron were suspended together in one electrolyte to check the effectiveness of the inhibitor for metallic parts prone to galvanically coupled conditions. A galvanic couple was prepared as shown in Fig. 10. Pieces of aluminum, copper, brass, and steel sheet

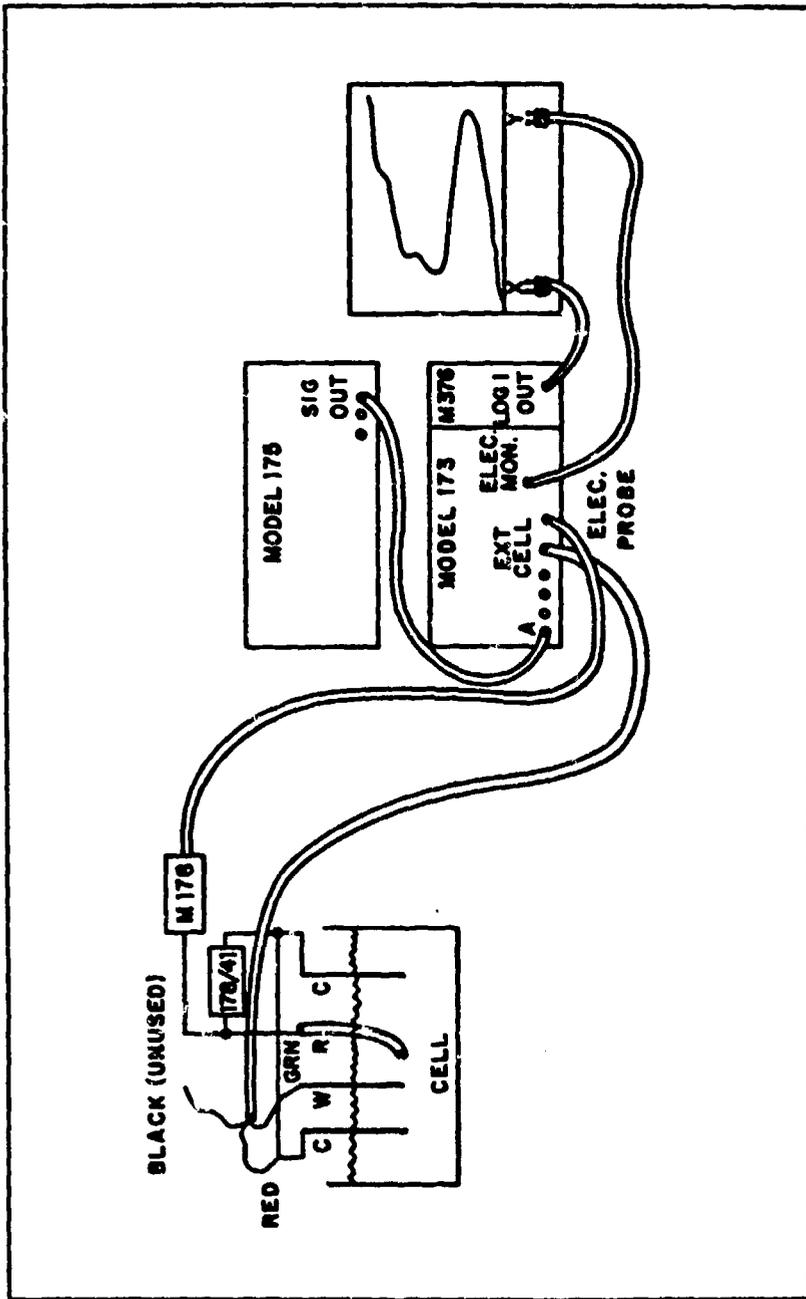


Figure 9. Test Setup for Corrosion Measurements.

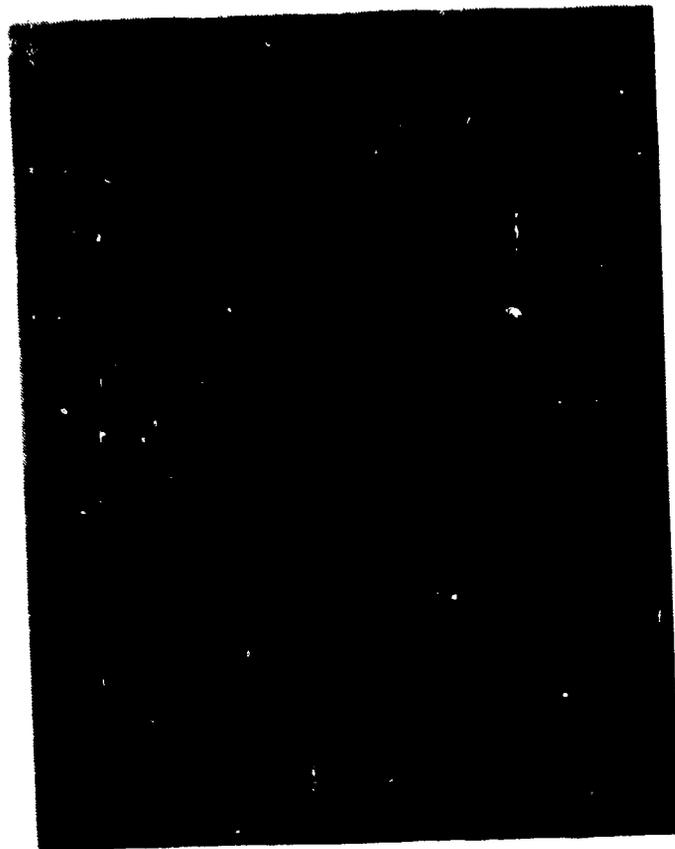


Figure 10. Galvanic Couple.

were connected through a stainless-steel rod and individually bolted with stainless-steel nuts. The results of these tests are also included in Table IX.

The performance of the inhibitor was tested on hulk fasteners also. A hulk fastener was mounted on a 1-in.-thick Al 7075-T6 plate and immersed in inhibited water for a period of six months. Figure 11(a) shows the surface appearance of a hulk fastener/Al 7075-T6 plate assembly along with the bolt and nut which were immersed independently. The surface showed no sign of corrosion. Figures 11 (b) and (c) are magnified views of the assembly after a six-month exposure. The assembly was then cut open to examine for crevice corrosion at the interface of the aluminum plate and the bolt and nut. This assembly is shown in Figs. 12 (a) and 12 (b). There was no sign of corrosion on either the bolt or the nut and aluminum/plate interface.

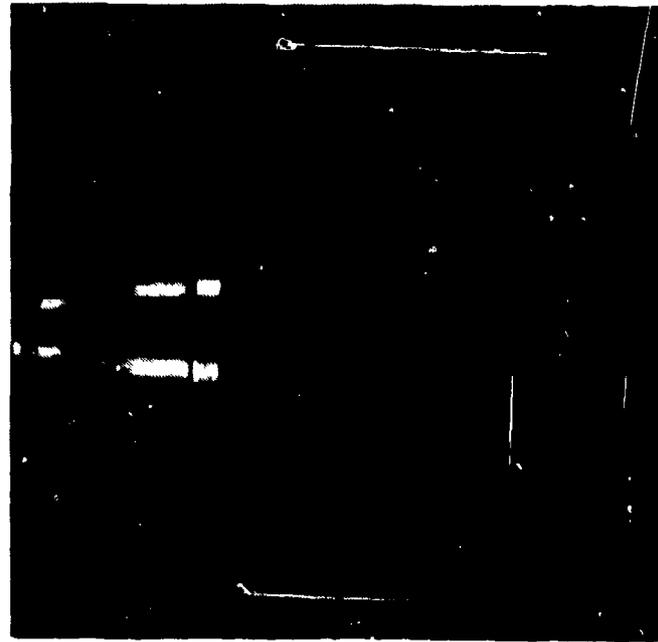
#### Polarization Behavior of Diluted (in Terms of Sodium Chloride) Synthetic Urine

After several polarization and immersion tests had been conducted with the synthetic-urine solution on the aluminum specimens, the high concentration of sodium chloride found in the urine solution was suspected to be the most aggressive species. Diluted synthetic-urine solutions containing varying concentrations (from 0% to 1%) of sodium chloride were prepared. Anodic-polarization and immersion tests with inhibited and uninhibited solutions were conducted to determine the effectiveness of the rinse inhibitor. The results are shown in Figs. 13 and 14.

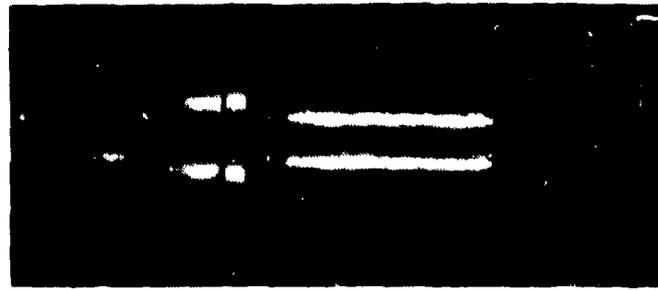
The effect of coffee spills, etc. was studied by preparing mixtures of coffee and synthetic urine in several combinations and in different concentrations. The immersion results are included in Table IX.



(a)



(b)



(c)

Figure 11. (a) Surface Appearance of Hulk Fastener/Al Plate Assembly; (b) Magnified View of Fastener/Plate Assembly; and (c) Magnified View of Hulk Fastener.



(a)



(b)

Figure 12. (a) Inside View of Hulk Fastener After Cutting Apart; (b) View of Interface of Plate and Fastener.

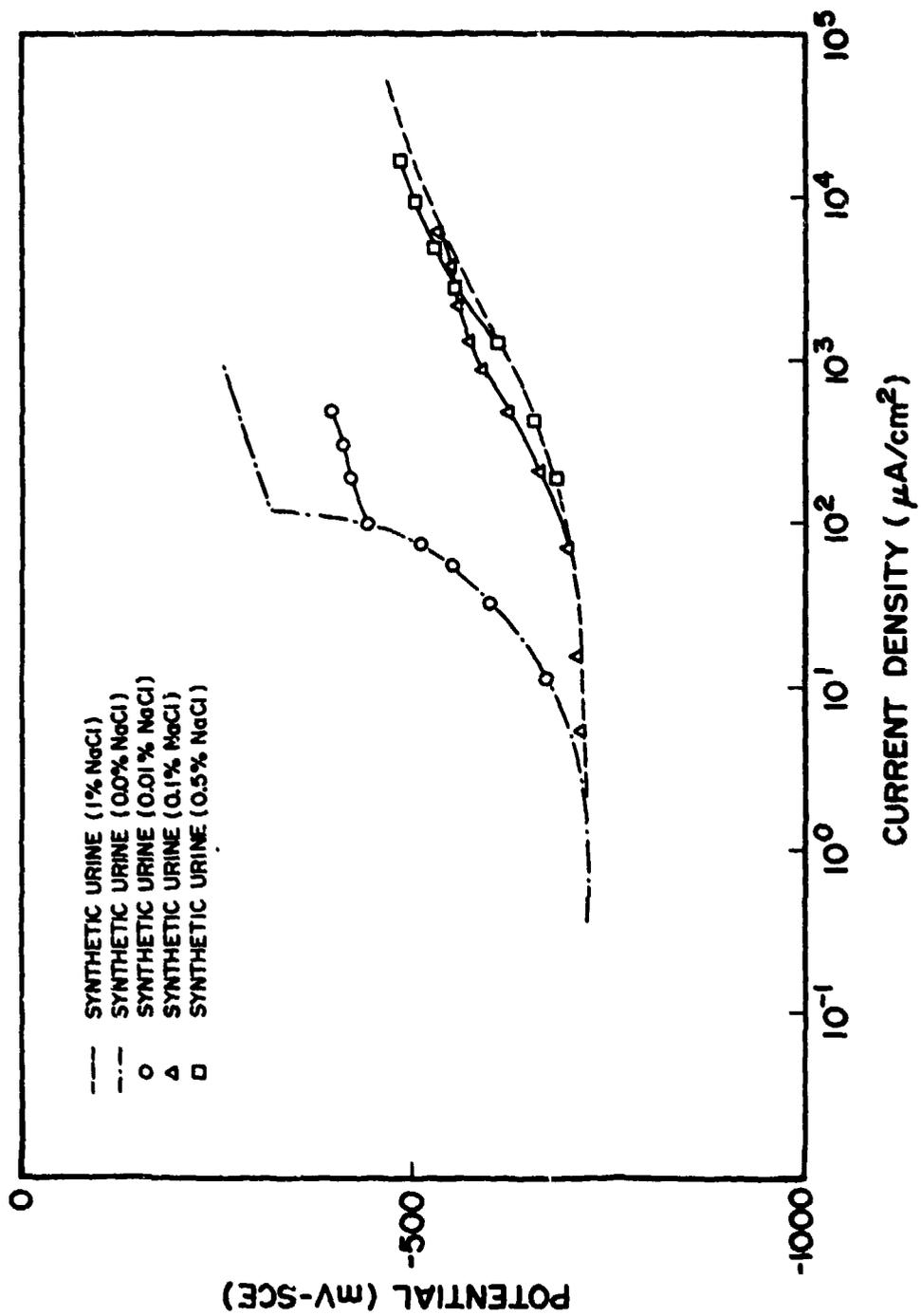


Figure 13. Polarization Behavior of Al in Diluted Synthetic Urine.

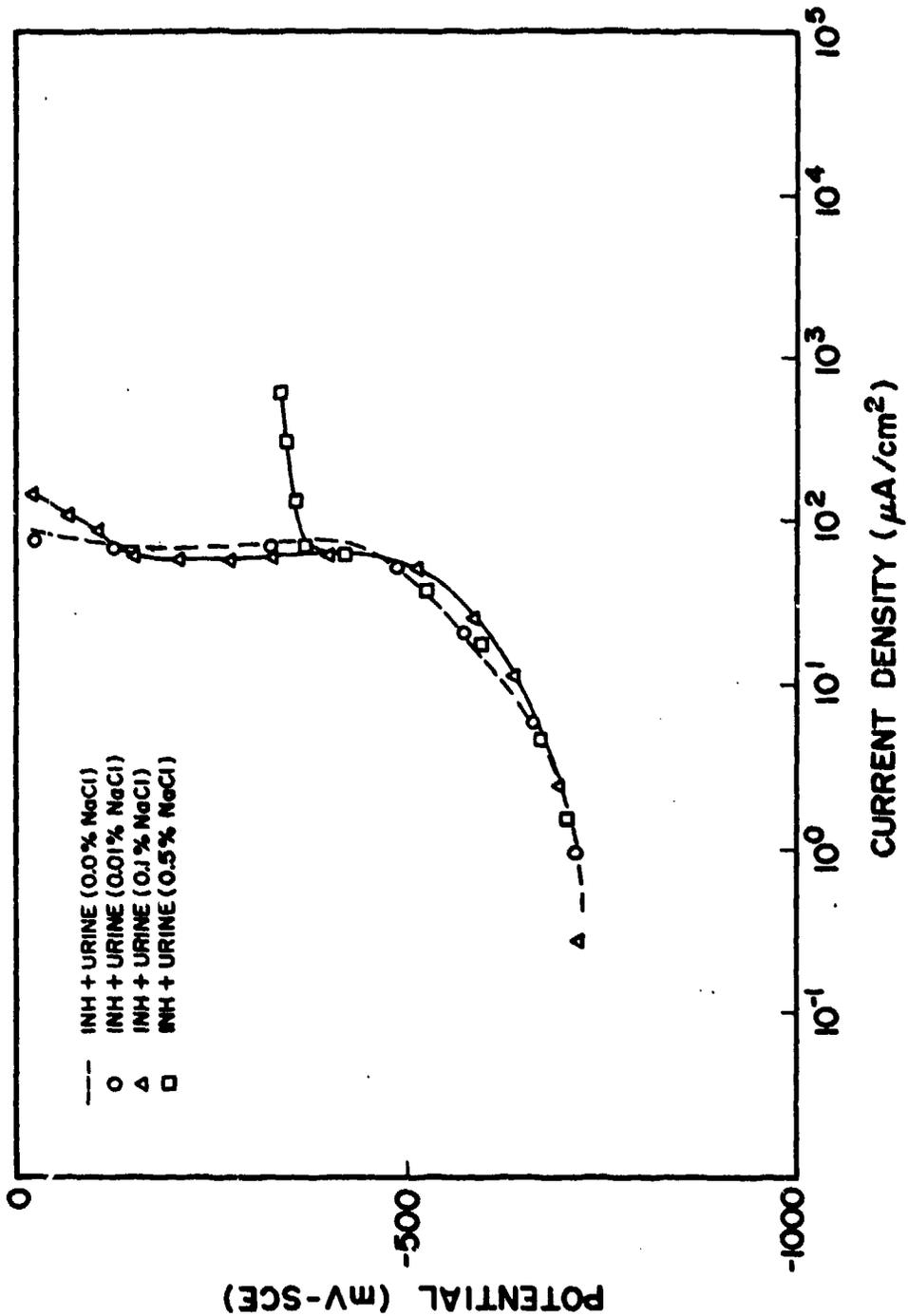


Figure 14. Polarization Behavior of Al in Inhibited Diluted Synthetic Urine.

### Effects of the Addition of Film Formers, Chloride Absorbers, and Chelating Agents

An extensive R&D effort was carried out to modify the rinse inhibitor by adding ingredients such as film formers, chloride absorbers, and several chelating agents. The effect of the addition of low concentrations of isopropylamine is shown in Table VIII and Fig. 15. This also includes the effect of the addition of piperazine to the rinse inhibitor. The effects of the additions of small amounts of cupferon and ammonium cerium nitrate are also shown in Table IX and in Figs. 16 and 17. Some of the sulfonates such as 100 oil (a calcium sulfone) and other sulfonates of sodium also were found to have some beneficial effect. The polarization results are shown in Fig. 18 and the immersion results in Table IX. Some other surfactants claimed to have very good wetting properties were also used. Samples were obtained from several commercial suppliers such as DuPont, Richardson, Stauffer, and Emery. The effects of their addition to the rinse inhibitor upon the polarization behavior are shown in Figs. 19-21 and Table IX. The results with Richonate obtained from Richardson and Triton X-114 from Rohm and Hass were promising, as shown by Figs. 22 and 23 and Tables VIII AND IX. Variation of the composition of nitrate and pH adjustment to the rinse inhibitor, along with either Triton X-114 or Richonate 1850, had a beneficial effect. One of the best results to date has been obtained through the addition of another surfactant--Estersulf-- to the rinse inhibitor. Polarization plots obtained with Al 7075-T6, steel, copper, and brass are shown in Fig. 24.

During the course of this continuing investigation, it was discovered that several formulations (such as rinse inhibitor + isopropylamine, and rinse inhibitor + 100 oil) are quite effective in inhibiting urine corrosion of aluminum. Unfortunately, the presence of copper or iron ions in the electrolyte has a very damaging effect. When pieces of Al 7075-T6, steel, and copper were immersion tested in the same electrolyte, the interfering ions of Al, Fe, and Cu reduced the efficiency of the inhibitors and, in some

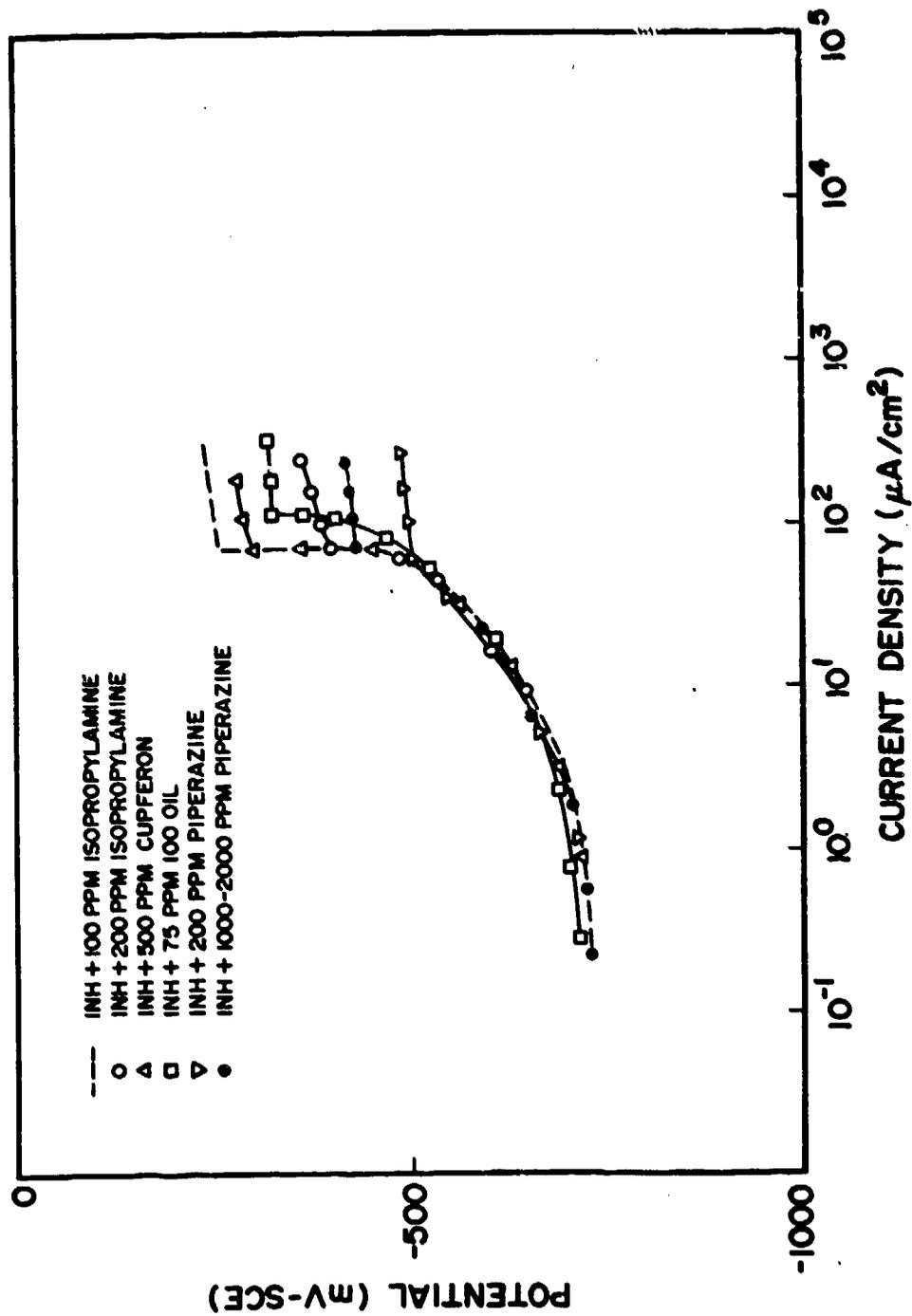


Figure 15. Effect of Isopropylamine Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

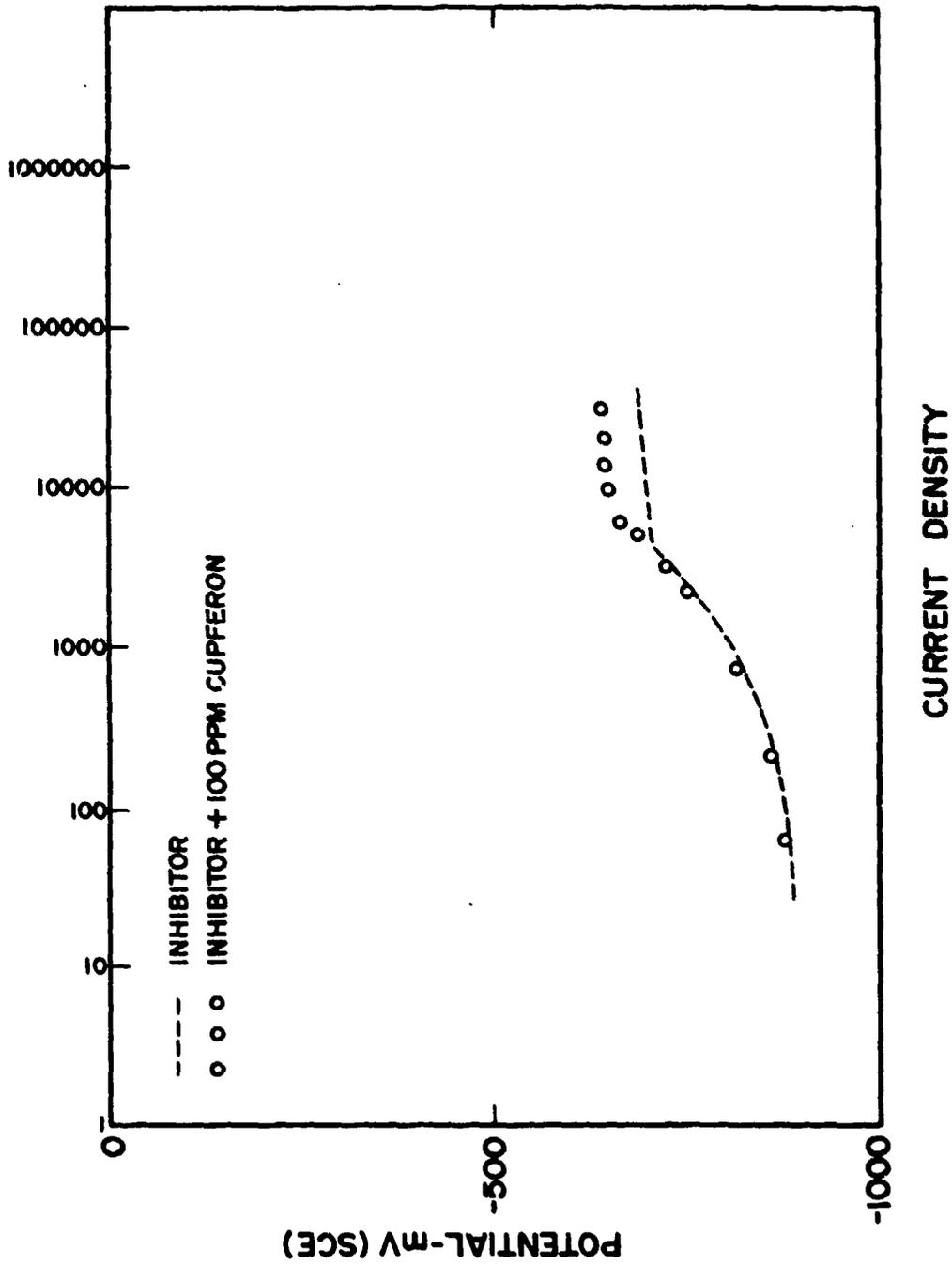


Figure 16. Effect of Cupferon Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

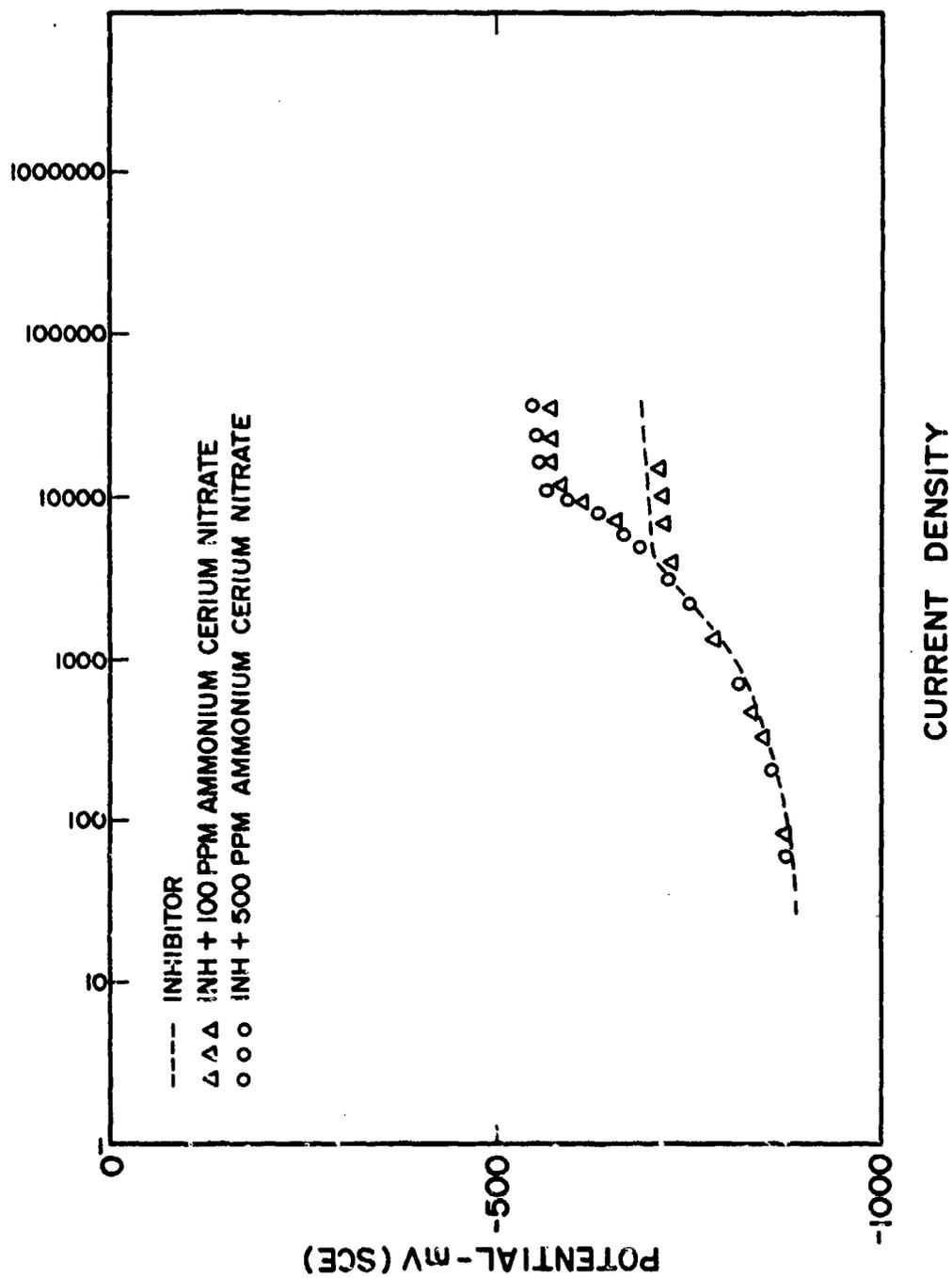


Figure 17. Effect of Ammonium Cerium Nitrate Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

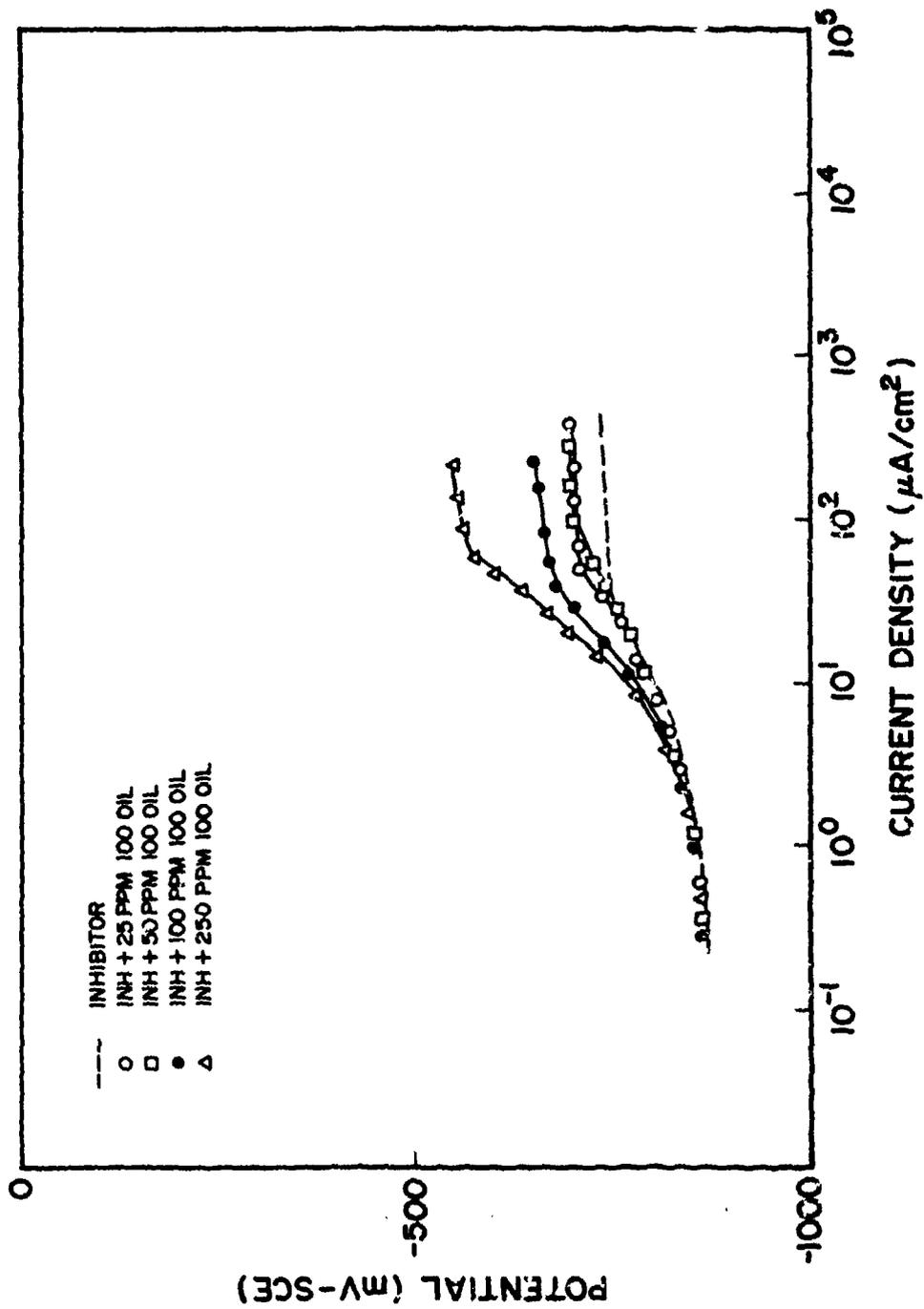


Figure 18. Effect of 100 Oil Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

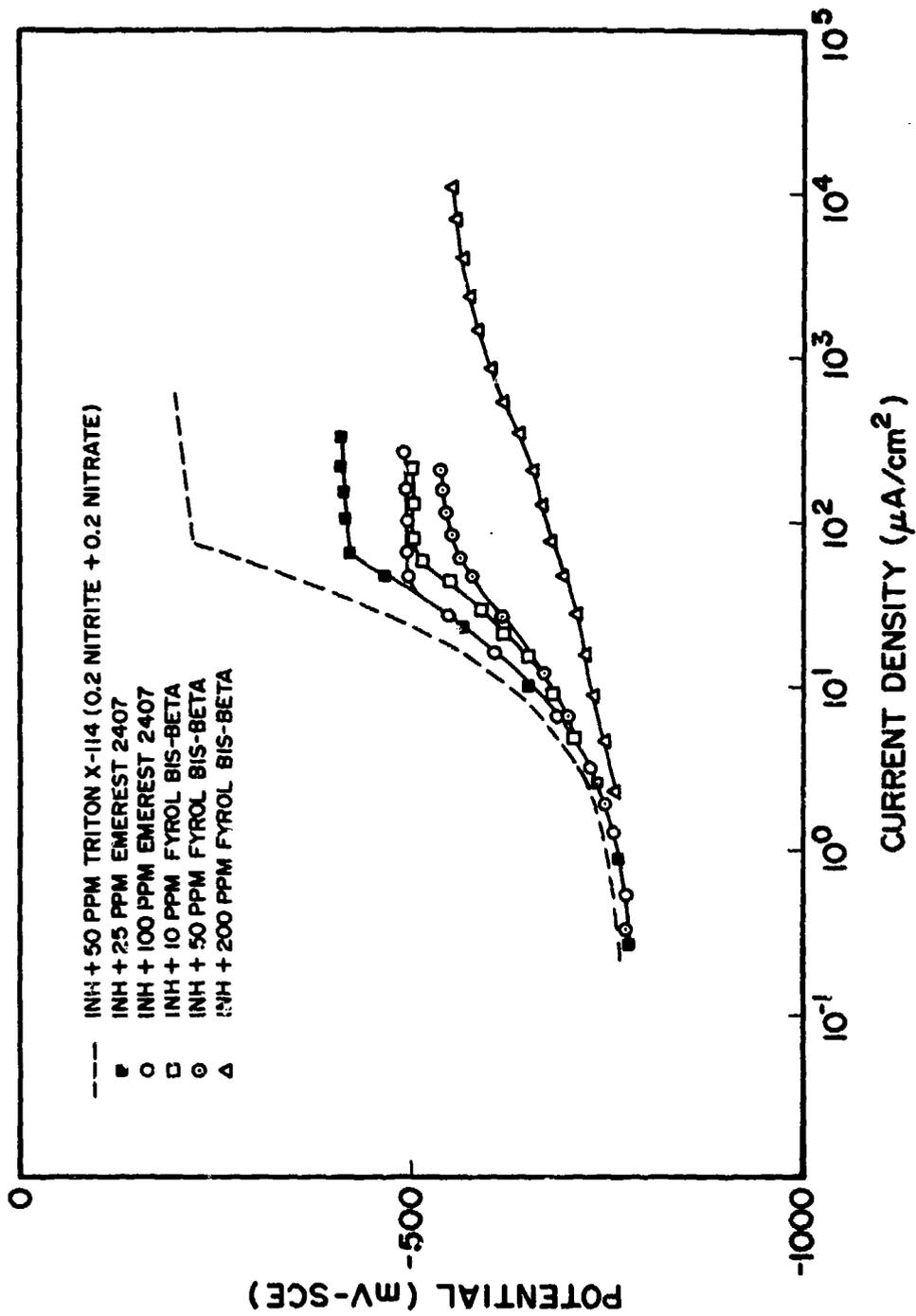


Figure 19. Effect of Zonyl Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

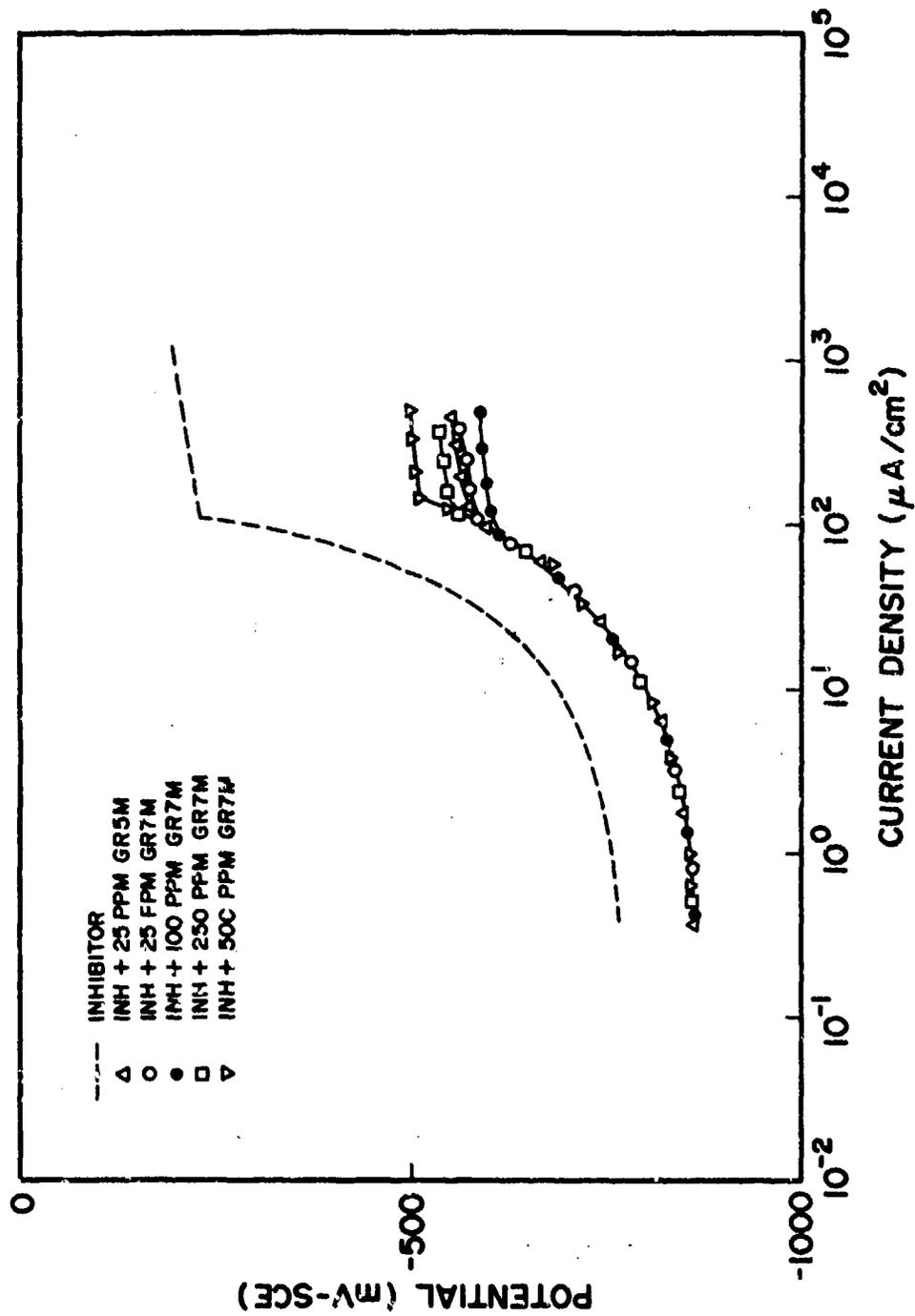


Figure 20. Effect of GRM Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

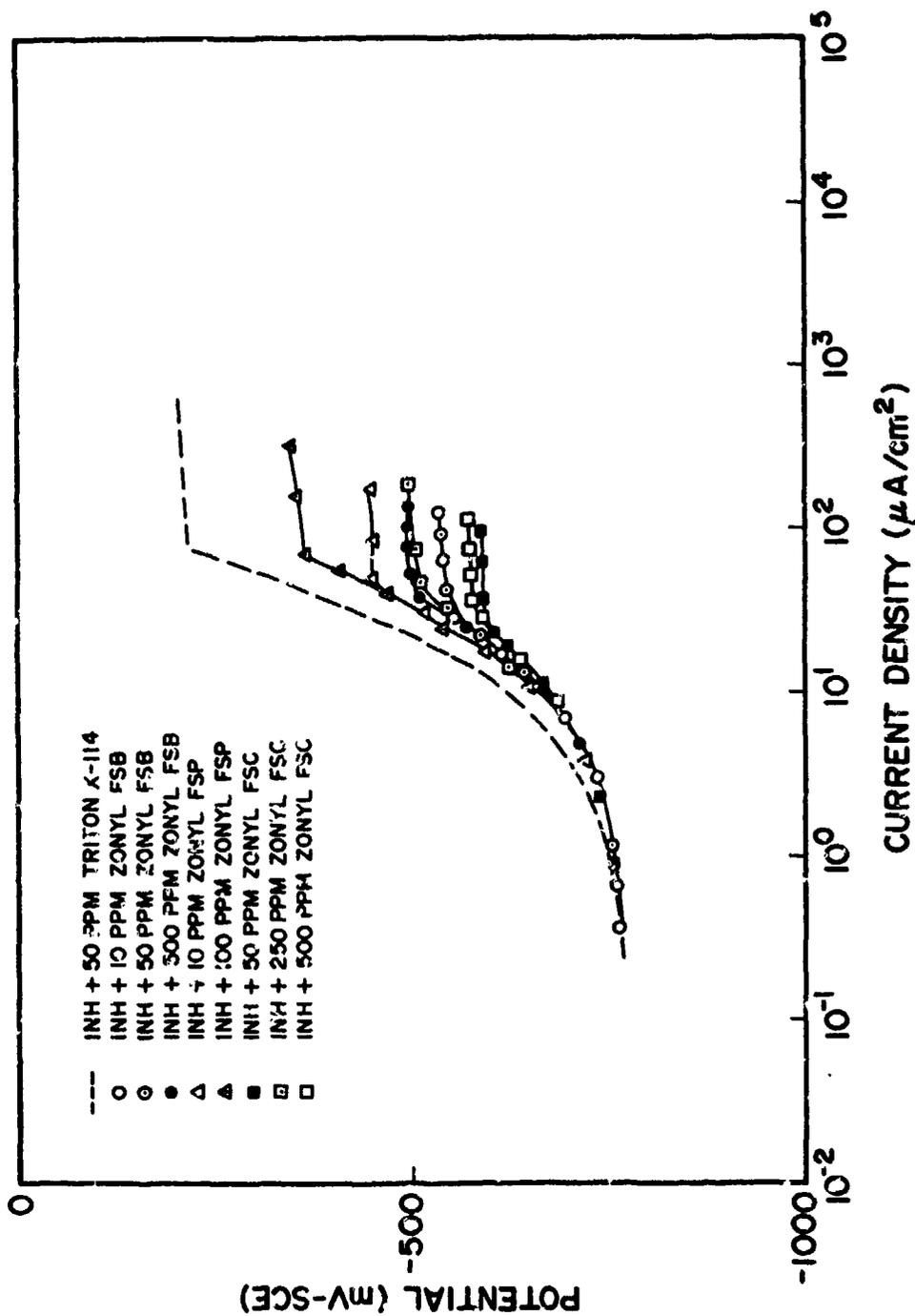


Figure 21. Effect of Fyrol-Bis-Beta and Emmerest Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

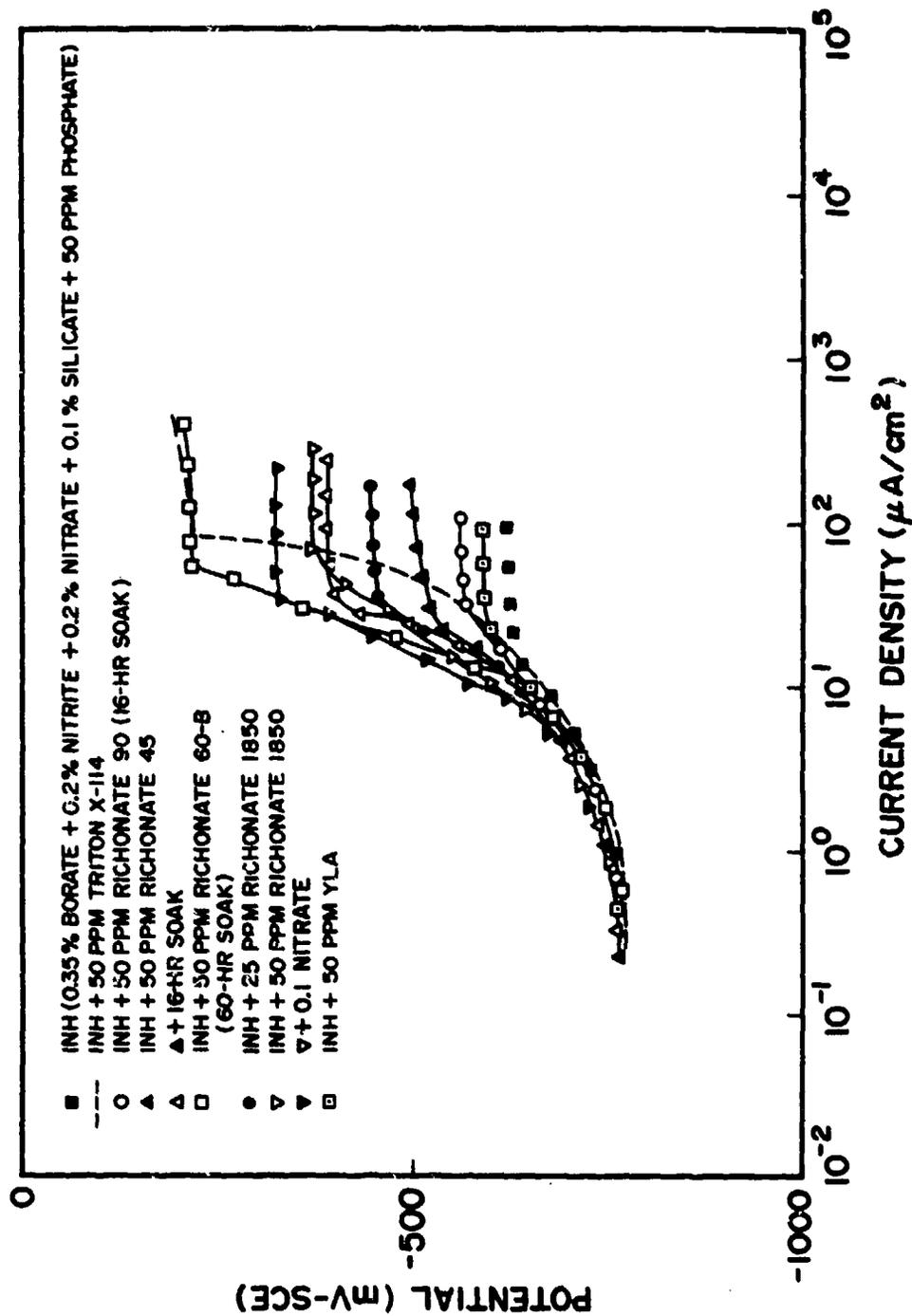


Figure 22. Effect of Richonate Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

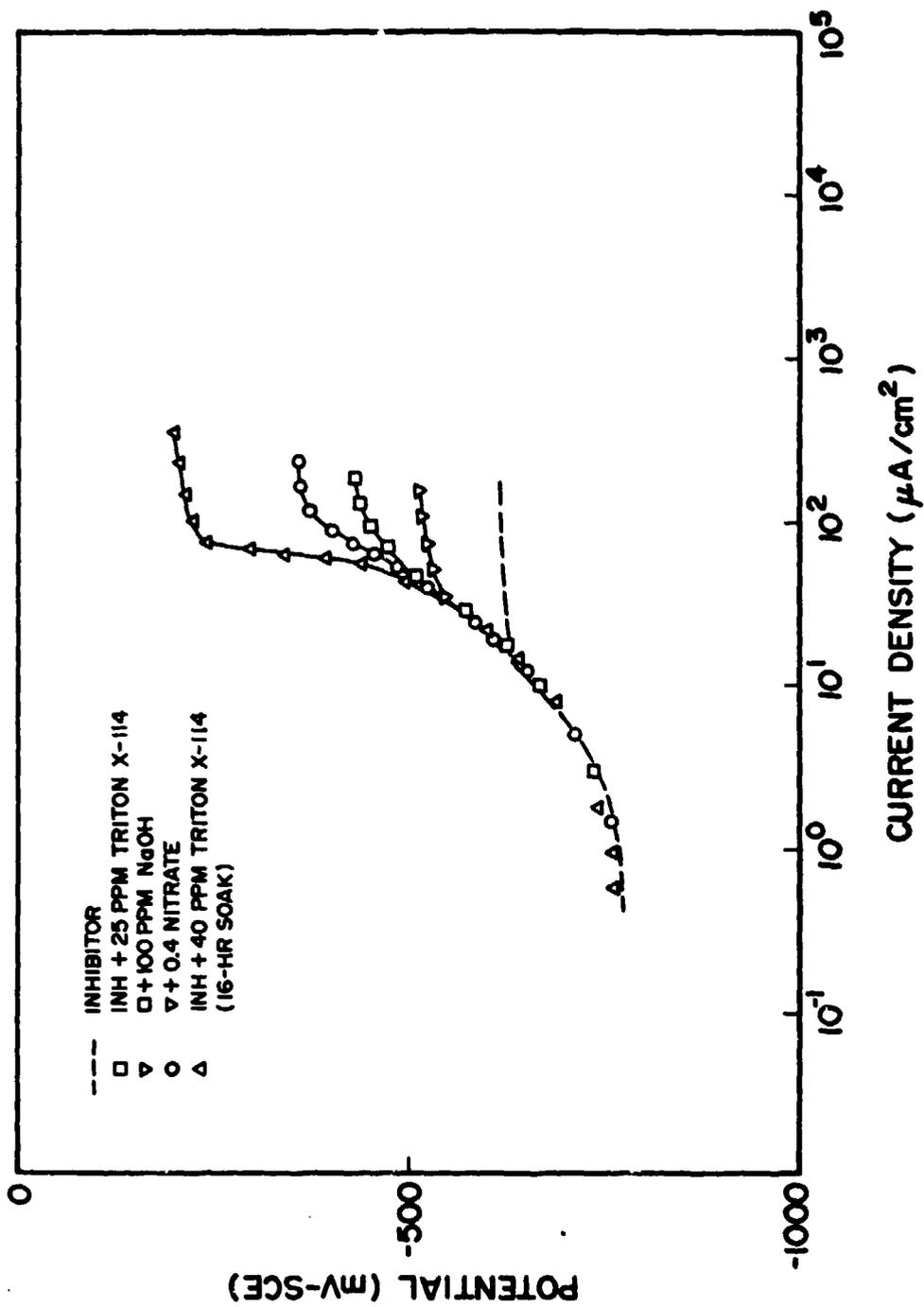


Figure 23. Effect of Triton X-114 Addition on the Polarization Behavior of Al in Inhibited Synthetic Urine.

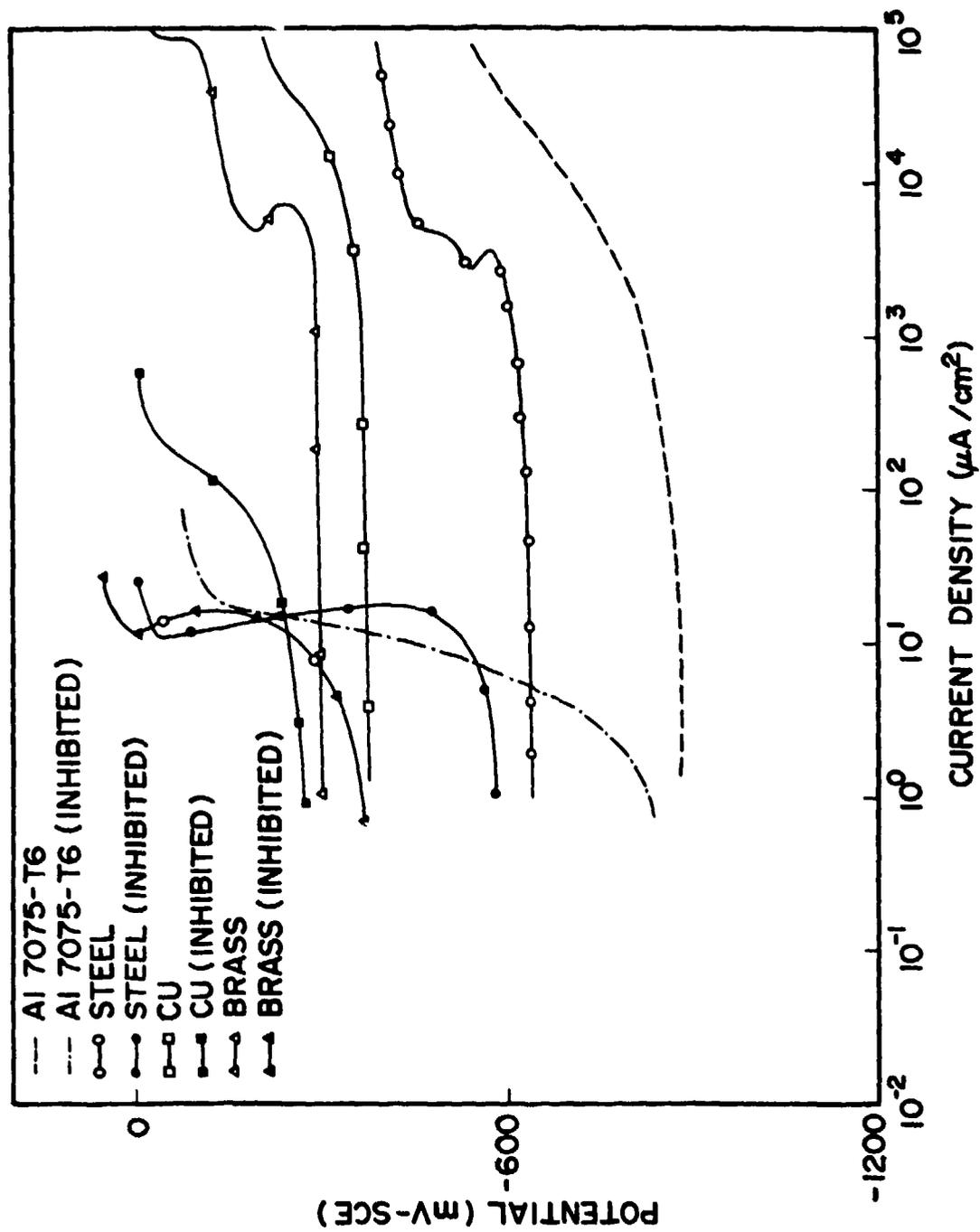


Figure 24. Polarization Behavior of Al, Cu, Brass, and Steel in Inhibited Synthetic Urine.

cases, severe pitting of aluminum occurred. The rinse inhibitor was further modified in an attempt to minimize pitting. Addition of  $ZnSO_4$  improved the efficiency; the results are shown in Table IX.

Some effort has been put forth to replace the borate in the rinse inhibitor with small concentrations of potassium soap. Other compounds such as zinc gluconate and sodium sarcosine were also investigated. The results are shown in Figs. 25-31 and in Tables VIII and IX.

#### PHASE IV - STRESS-CORROSION AND CORROSION-FATIGUE TESTS

Low-cycle corrosion-fatigue tests were conducted to determine the effectiveness of the inhibitor formulations in these dynamic situations. Compact-tension plane-strain fracture-toughness specimens (high-strength steels such as 4340 and aluminum alloys of series 7000 in T6 in the ST orientation), as shown in Fig. 32, were used to determine the effect of inhibitor additions upon the crack-growth rates in synthetic as well as natural urine. A detailed description of the corrosion-fatigue tests is included in Ref. 16.

Sinusoidal tension-tension cycling was used at a frequency of 0.1 Hz. Most tests with Al 7075-T6 were performed at a maximum load of 1200 lb, while the 4340 steels were loaded up to 2,500 lb and a stress ratio,  $R(\sigma_{\min}/\sigma_{\max})$ , of 0.1. The specimens were initially precracked to a fatigue-crack length of - 2.54 mm (0.10 in.). The crack length was monitored using a double-cantilever-beam gauge and an amplifier-recorder system. The crack-opening displacement (COD) was recorded as a function of fatigue cycles.

In order to determine the crack lengths from COD data, compliance measurements were carried out for all aluminum alloys. Tests were conducted in air, and crack lengths were determined using optical and COD measurements simultaneously on the MTS machine.

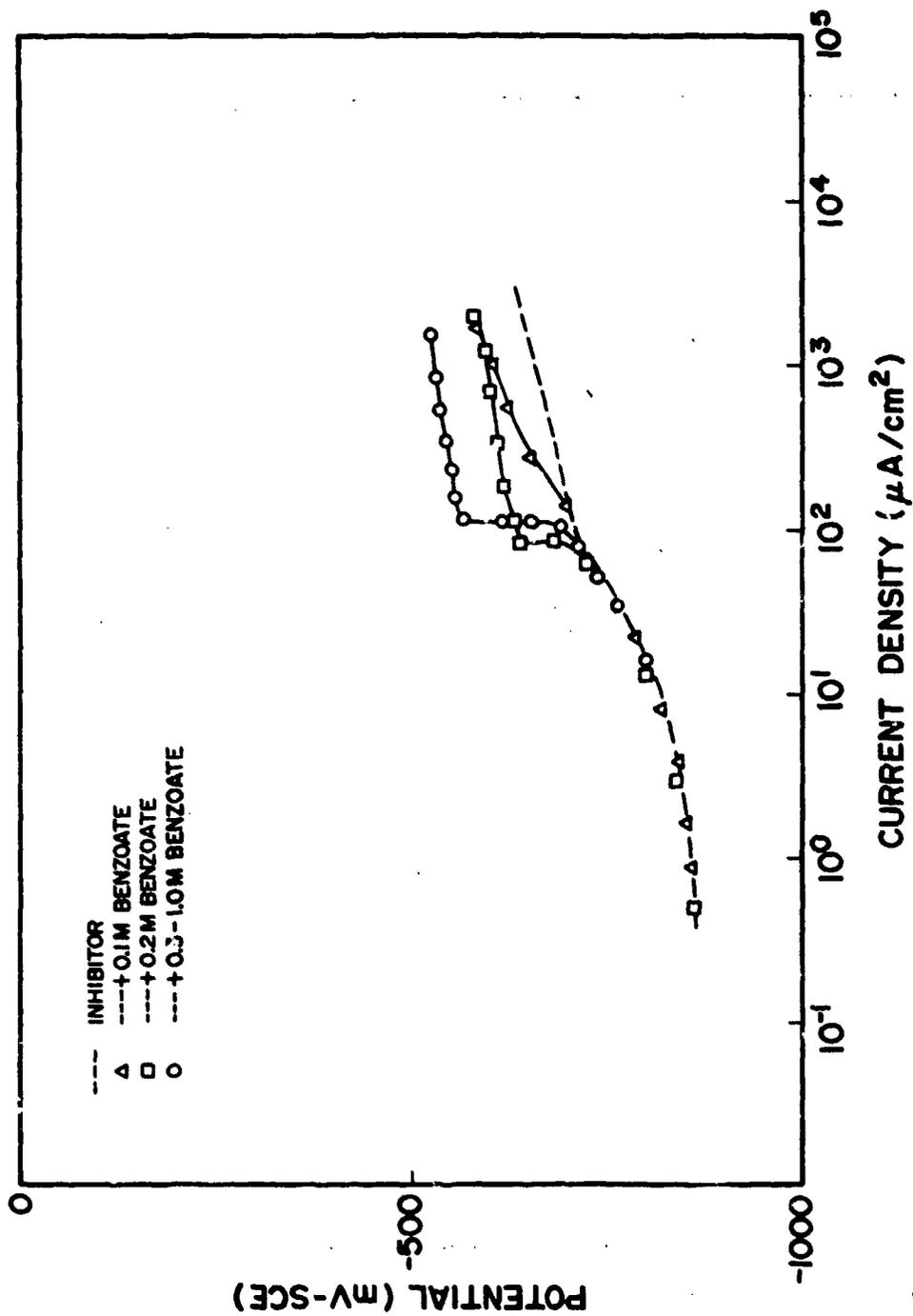


Figure 25. Effect of Benzoate Addition upon the Polarization Behavior of Al in Synthetic Urine.

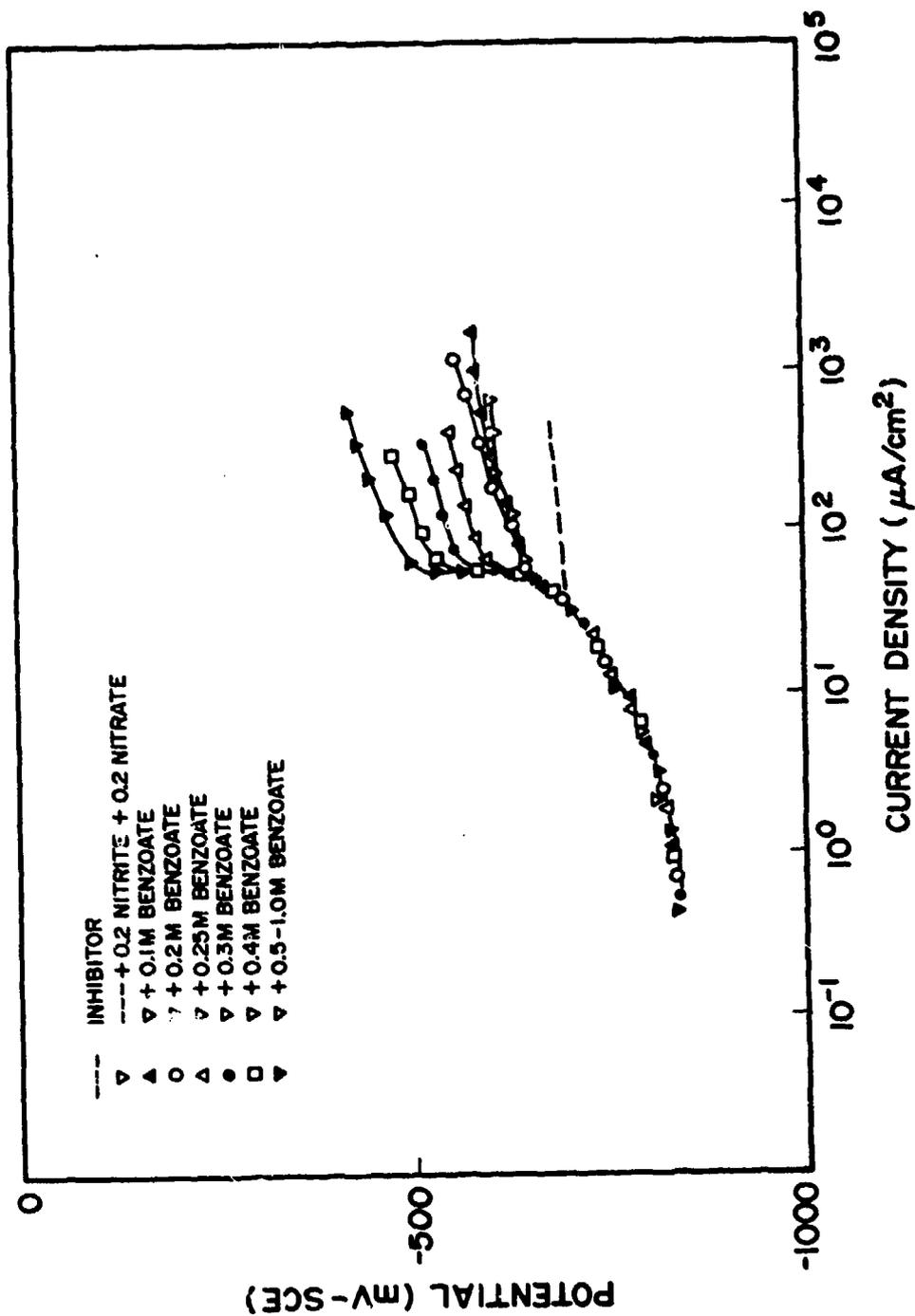


Figure 26. Effect of Benzoate and Nitrate Addition upon the Polarization Behavior of Al in Synthetic Brine.

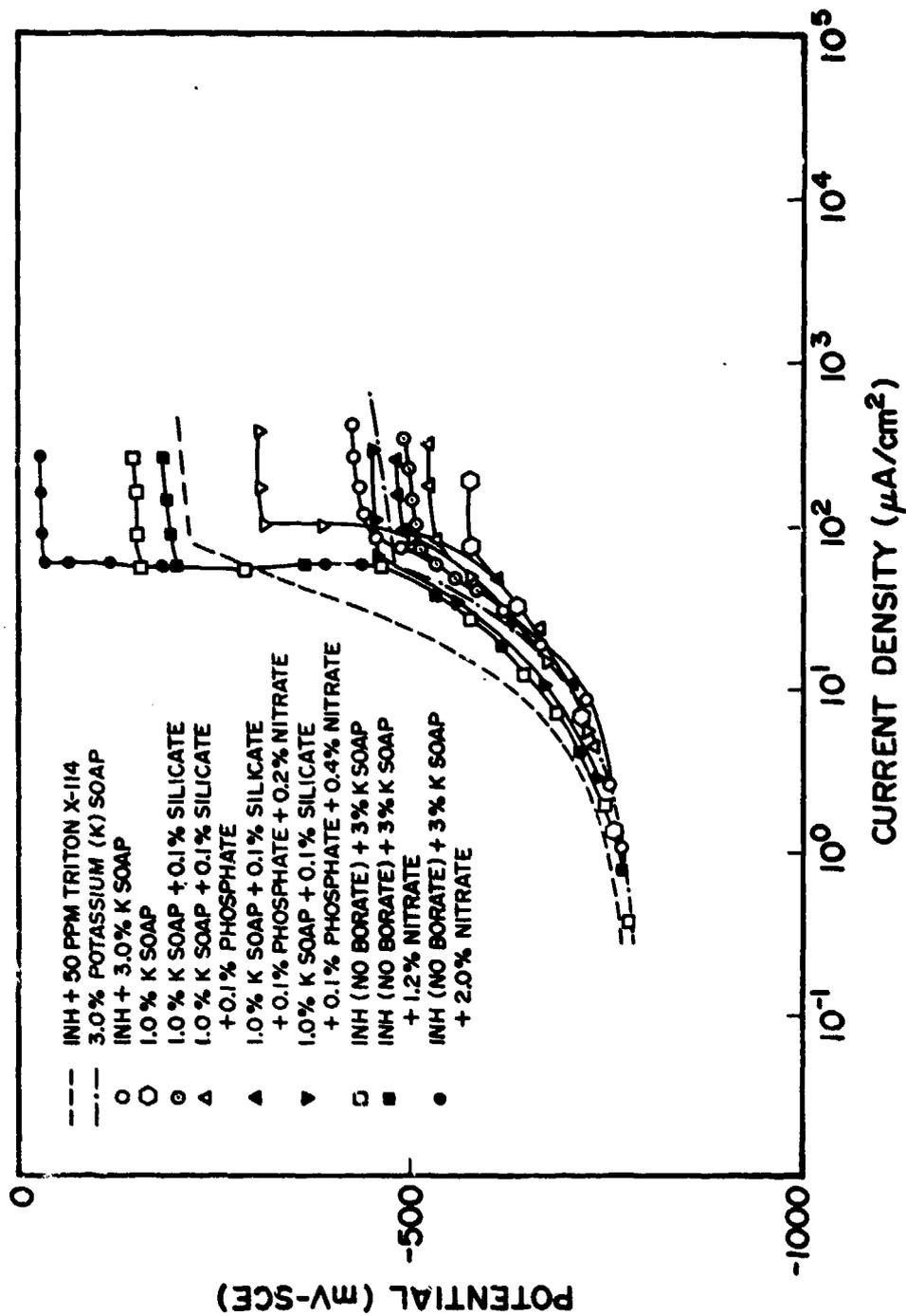


Figure 27. Effect of Potassium-Soap Addition upon the Polarization Behavior of Al in Synthetic Urine.

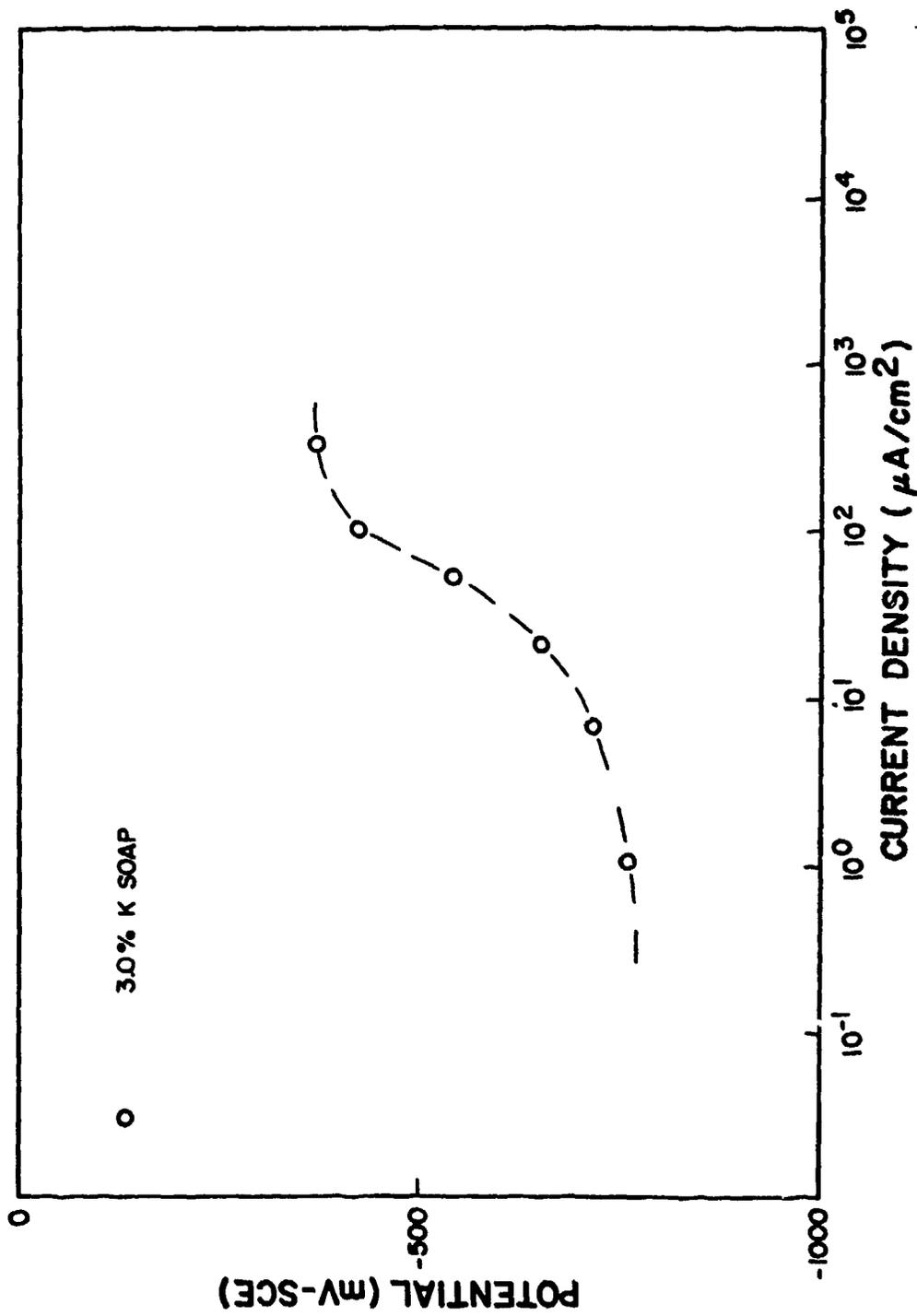


Figure 28. Effect of Potassium-Sosp Addition upon the Polarization Behavior of Al in Synthetic Urine.

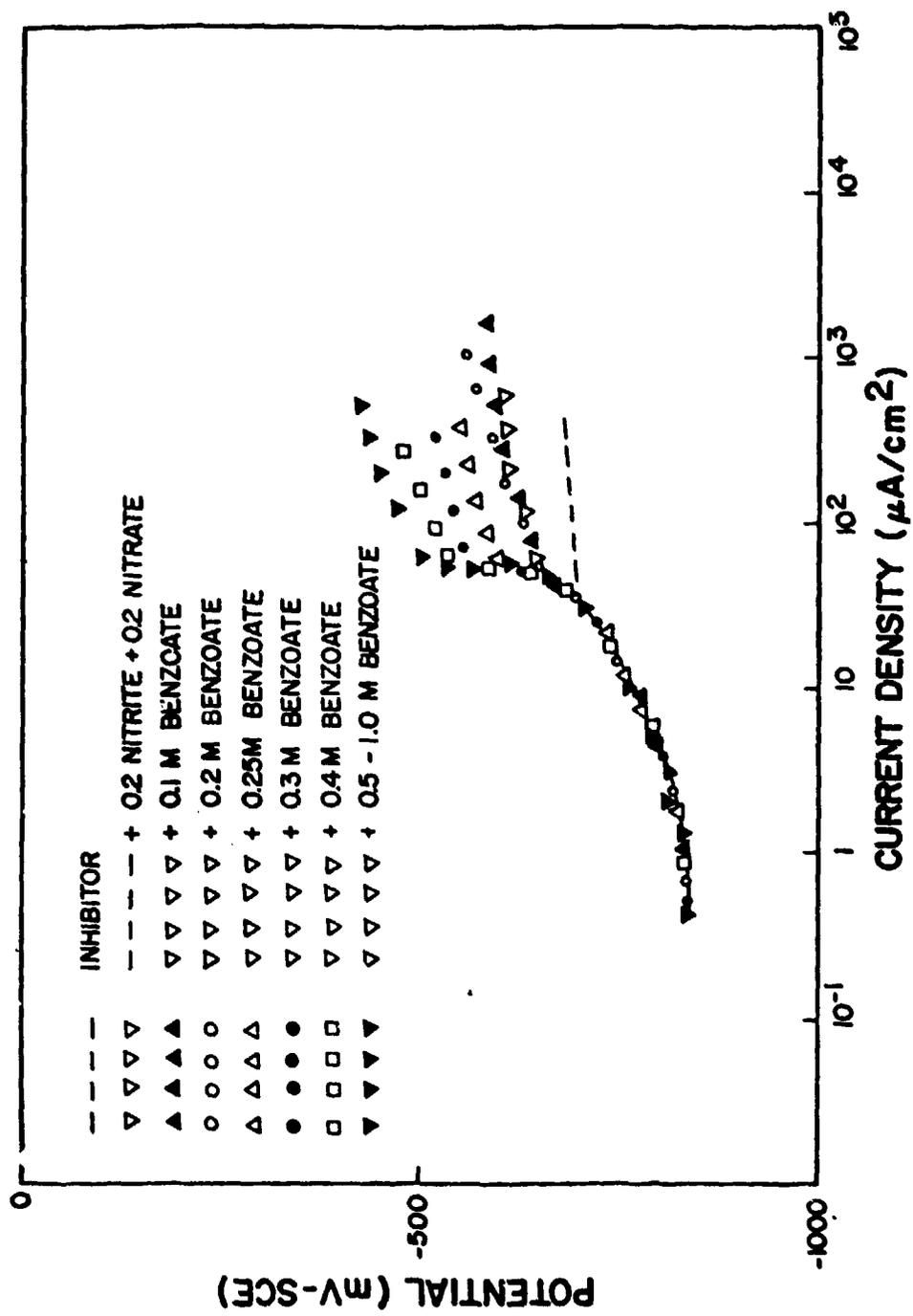


Figure 29. Effect of Benzoate Addition upon the Polarization Behavior of Al in Synthetic Urine.

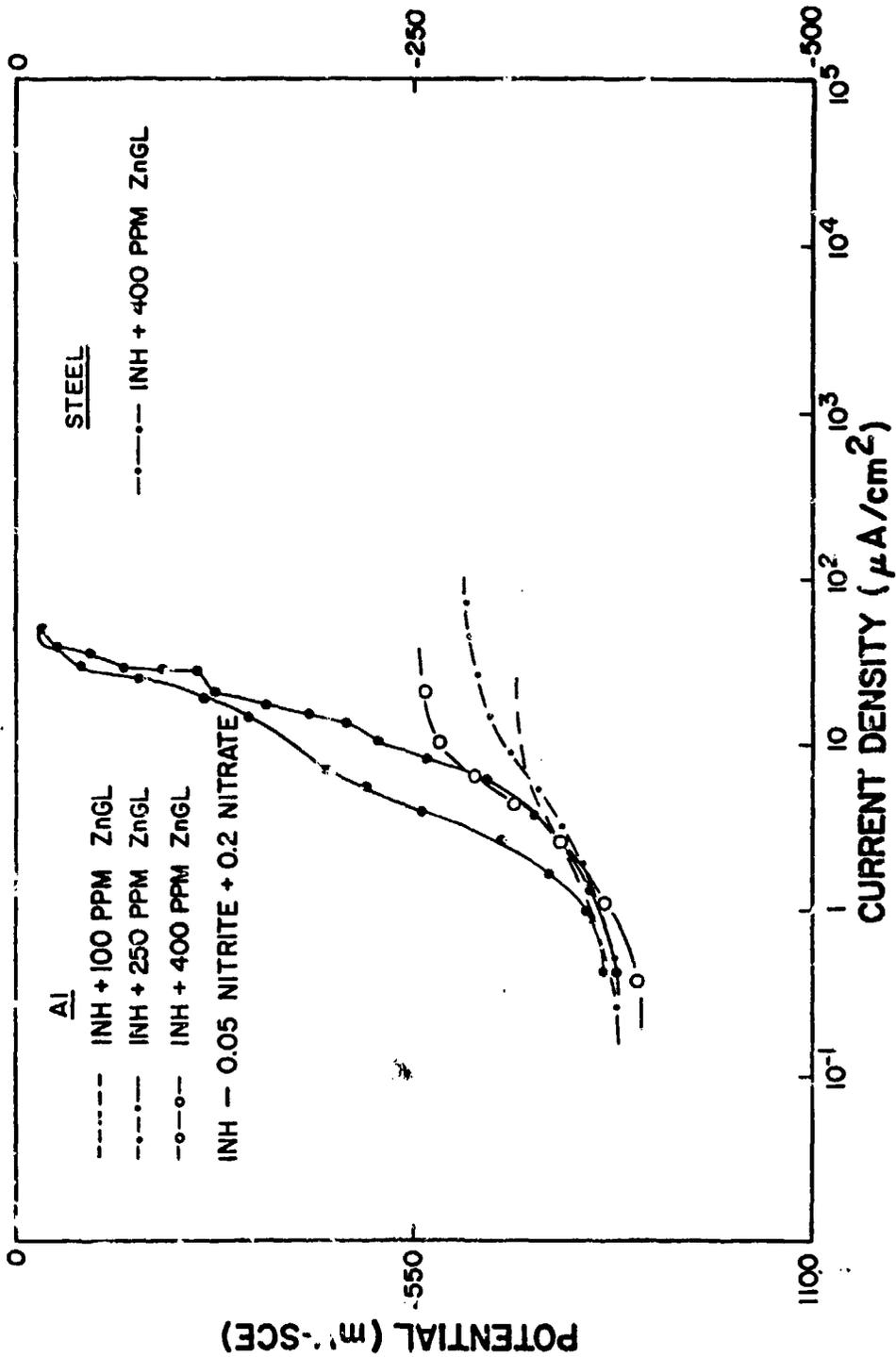


Figure 30. Effect of Zinc Gluconate Addition upon the Polarization Behavior of Al and Steel in Synthetic Urine.

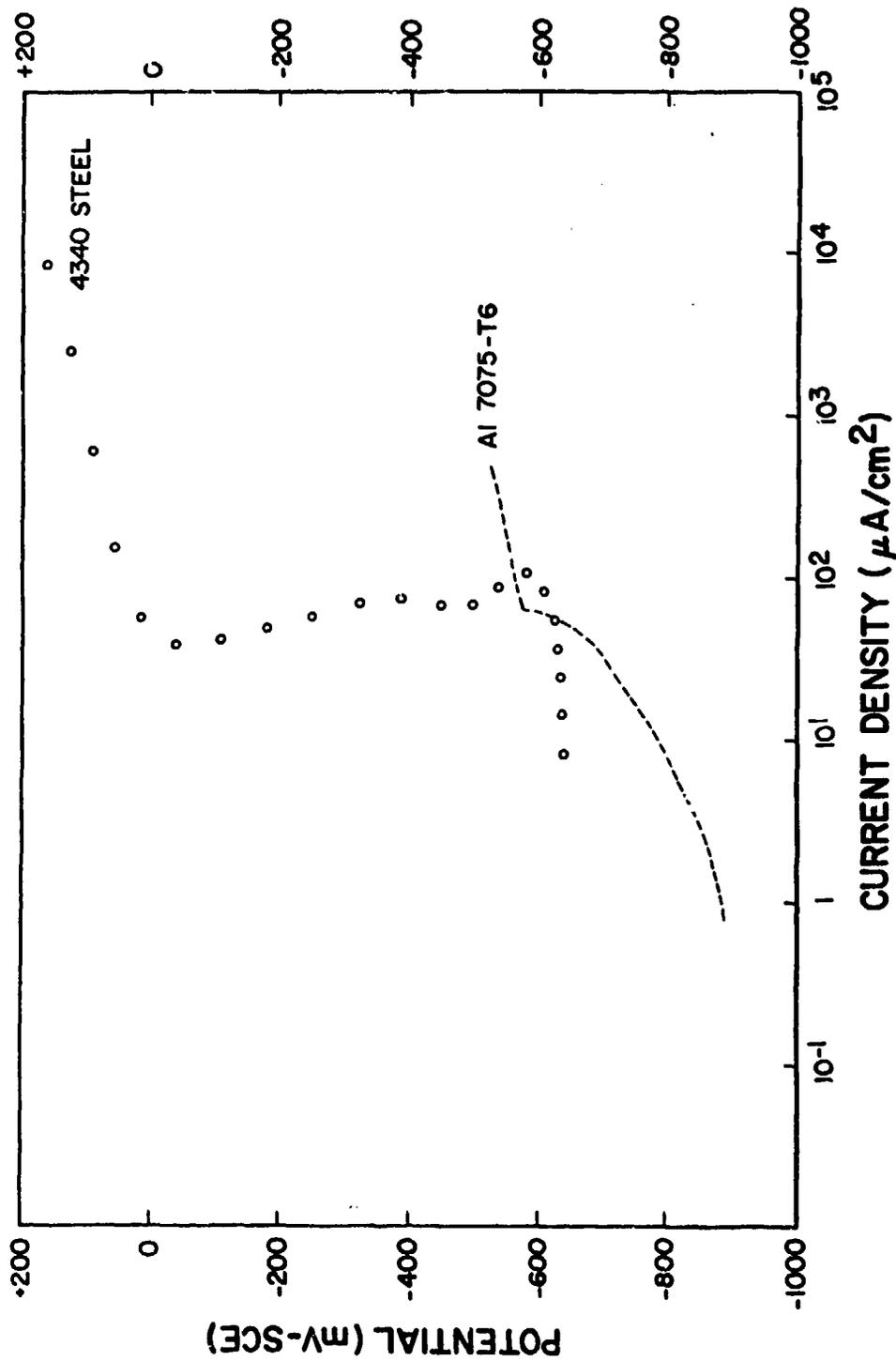


Figure 31. Effect of Sarcosine Addition upon the Polarization Behavior of Al and Steel in Synthetic Urine.

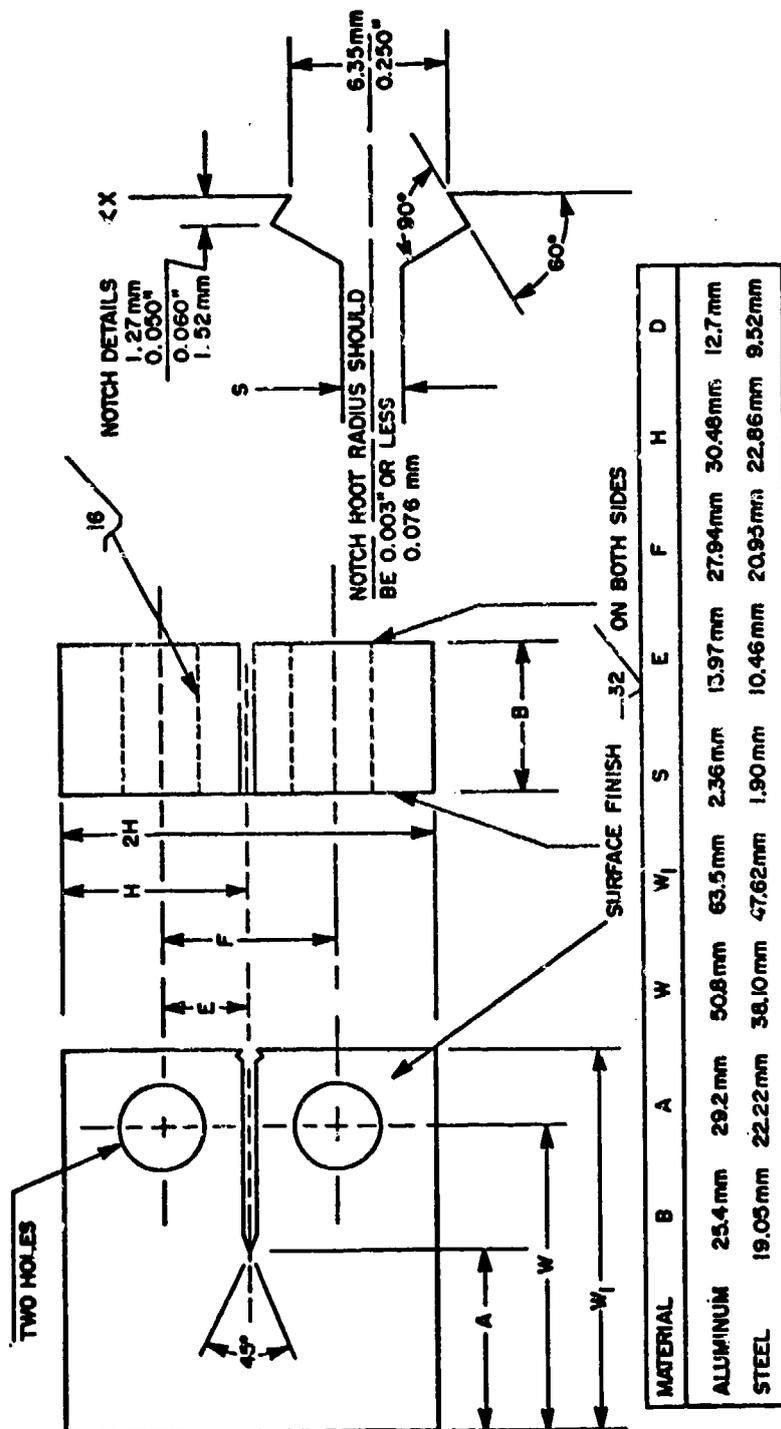


Figure 32. Compact-Tension Specimen.

No significant differences were found in the COD/load and crack-length/load curves. The crack length,  $a$ , was calculated from the analytical compliance relationship.<sup>14</sup>

$$a/W = 1.001 - 4.6695 U + 18.460 U^2 - 236.82 U^3 + 1214.94 U^4 - 2143.6 U^5$$

where

$$U = \frac{1}{\sqrt{\frac{EB (COD_{Max} - COD_{Min})}{P_{Max} - P_{Min}} + 1}}$$

$E$  is the Young's modulus and  $P$  the stress.  $W$  and  $B$  are the dimensions indicated in Fig. 30. The stress-intensity values were calculated from<sup>14</sup>

$$K = \frac{P}{BW^{1/2}} \frac{(2+a/w)(0.886+4.64 a/w) - 13.32(a/w)^2 + 14.72(a/w)^3 - 5.6(a/w)^4}{(1-a/w)^{3/2}}$$

where  $B$  and  $W$  are the dimensions indicated in Fig. 32 such that  $B$  and  $a$  are greater than  $2.5 (K_{IC}/YS)^2$ ,<sup>15</sup> with  $K_{IC}$  being the fracture toughness and  $YS$  the tensile yield strength. The crack-length-versus-number-of-cycles data were converted to fatigue-crack-growth rates ( $da/dN$ ) using a computer program.<sup>14</sup> Seven to eleven data points were fitted to a second-order polynomial, and the derivative ( $da/dN$ ) was then obtained from the middle data point. This process was then repeated over the range of data.

All fracture surfaces were examined visually and then by light microscopy. The specimens were ultrasonically cleaned in acetone, deionized water, and methyl alcohol. The light-microscopic observation was followed by scanning electron microscopy (SEM) for detailed examination of the fracture surfaces.

#### PHASE V - FIELD-APPLICATION TESTS

Several formulations investigated in Phases II to IV showed promising results, which made recommendation of a specific formulation for field application very difficult. The decision was made to conduct linear-polarization tests on these formulations to distinguish small differences

in performance. Some of the results obtained are shown in Table X. Representative linear polarization scans are shown in Figs. 33-36.

Based upon the results obtained during the development of a multifunctional inhibitor, a formulation consisting of borax, nitrite, nitrate, phosphate, silicate, and Richonate was recommended for field application. After discussion of alternatives with the Government personnel involved in the program, it was decided to package this formulation in the form of small cakes (1/2-oz. size). Nearly 30 lb of inhibitor has been packaged in cake form for field application. During this time the possibility of having the inhibitor formulation encapsulated was also pursued. Different types and sizes of capsules were prepared by Capsulated, Inc., of Yellow Springs, Ohio. The performance of these capsules in terms of life (leaching out) was tested by measuring the conductivity over several time intervals. The results are given in Table XI.

TABLE X  
TAFEL SLOPES AND CORROSION CURRENTS  
IN DIFFERENT ELECTROLYTES  
FOR Al 7075-T6

MATERIAL	ELECTROLYTE (wt%)	SOAK TIME	TAFEL SLOPES (mV/decade)		$i_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )
			ba	bc	
Al 7075-T6	synthetic urine	1 hr	100	135	6.25
Al 7075-T6	synthetic urine + rinse inhibitor	1 hr	120	160	3.42
Al 7075-T6	synthetic urine + rine inhibitor + 0.15 nitrite + 0.1 nitrate (1NH)	1 hr	160	130	2.44
Al 7075-T6	synthetic urine + 1NH + 75 ppm Triton X-114	1 hr	100	150	0.78
Al 7075-T6	synthetic urine + 1NH + 100 ppm Estersulf	1 hr	120	90	1.08
Al 7075-T6	synthetic urine + 1NH + 100 ppm Isopropylamine	1 hr	120	80	1.41
Al 7075-T6	synthetic urine + 1NH + 125 ppm Richonate 1850	1 hr	100	125	0.544
Al 7075-T6	synthetic urine + 1NH + 125 ppm Richo- nate + 500 ppm $\text{ZnSO}_4$ + 50 ppm MBT	1 hr	120	135	0.63
Al 7075-T6 + 4340 steel + brass	synthetic urine + 1NH + 250 ppm Isopropylamine	1 week	95	115	13.78
		2 weeks			5.3
		3 weeks			24.5
		4 weeks			30.0
		5 weeks			44.36
		6 weeks			46.6

TABLE X (Continued)

MATERIAL	ELECTROLYTE (wt%)	SOAK TIME	TAFEL SLOPES (mV/decade)		$i_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )
			ba	bc	
Al 7075-T6 + 4340 steel + brass	synthetic urine + INH +125 ppm Ridionate 1850	1 hour	85	105	24.66
		1 week			27.32
		2 weeks			-
		3 weeks			-
		4 weeks			-
		5 weeks			1.9
		6 weeks			0.8

TABLE XI  
RESULTS OF CONDUCTIVITY MEASUREMENTS ON ENCAPSULATED INHIBITOR

SAMPLE NO.	CAPSULE WALL CORE	CONDUCTIVITY NUMBERS ( $\times 1000$ )	pH	TIME OF EXPOSURE	COMMENTS
87-20	Cellulosic Pure Inhibitor	0.45	8.9	0.5 hour	Almost all into solution within 20 days.
		3.2	9.2	48 hours	
		3.6	9.2	10 days	
87-27	Cellulosic Pure Inhibitor	1.02	9.0	0.5 hour	Almost all into solution within one hour.
		2.3	9.15	48 hours	
		2.6	9.25	72 hours	
		2.5	9.25	10 days	
87-24	(OH) Polymer 1:1 Mannitol Complex	.8	8.95	0.5 hour	Almost all into solution within one hour.
		1.1	9.00	48 hours	
		1.4	9.15	72 hours	
		1.2	9.30	10 days	
87-36	(OH) Polymer 1:1 PVA Complex	0.9	8.7	0.5 hour	Almost all into solution within one hour
		1.1	9.4	48 hours	
		1.3	9.3	72 hours	
		1.3	9.3	10 days	
87-37	(OH) Polymer 1:1 PVA Complex	1.25	9.1	0.5 hour	Almost all into solution within one-half hour.
		1.25	9.40	48 hours	
		1.6	9.40	72 hours	
		1.2	9.30	10 days	
91-4	Cellulosic 1:1 PVA Complex	2.1	9.25	0.5 hour	Almost all into solution within one-half hour.
		2.3	9.35	48 hours	
		2.5	9.30	72 hours	
		2.2	9.30	10 days	

TABLE XI (Continued)

SAMPLE NO.	CAPSULE WALL CORE	CONDUCTIVITY NUMBERS ( $\times 1000$ )	pH	TIME OF EXPOSURE	COMMENTS
91-6	(OH) Polymer 1:1 PVA Complex	1.0	8.50	0.5 hour	Almost all into solution within two days.
		1.5	9.35	48 hours	
		1.8	9.30	72 hours	
		1.5	9.30	10 days	
91-9	(OH) Polymer 1:1 PVA Complex	1.1	9.25	0.5 hour	Almost all into solution within one hour.
		1.1	9.35	48 hours	
		1.4	9.35	72 hours	
		1.3	9.35	10 days	
91-10	(OH) Polymer 1:1 PVA Complex	0.8	8.10	0.5 hour	Almost all into solution within two days.
		1.4	9.25	48 hours	
		1.8	9.20	72 hours	
		1.4	9.25	10 days	
91-14	(OH) Polymer 1:1 Mannitol Complex	1.1	8.65	0.5 hour	Almost all into solution within two days.
		1.5	8.50	48 hours	
		1.8	8.50	72 hours	
		1.7	8.40	10 days	
91-15	(OH) Polymer 2:1 Mannitol Complex	0.6	8.30	0.5 hour	Almost all into solution within ten days.
		0.9	8.00	48 hours	
		1.25	7.8	72 hours	
		1.7	7.7	10 days	

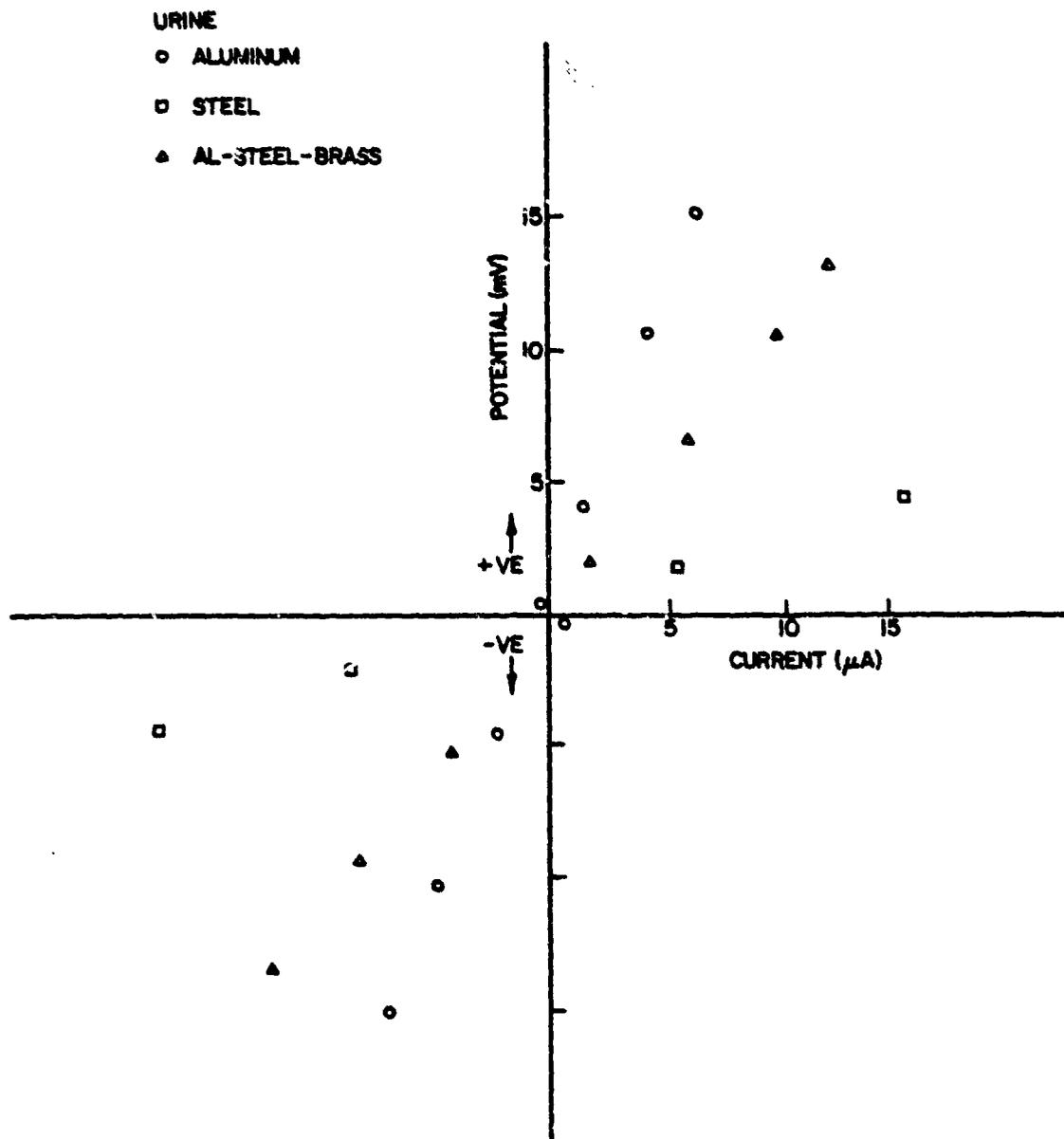


Figure 33. Linear-Polarization Curves of Al, Steel, and Aluminum-Steel-Brass in Natural Urine.

AML GUARD  
○ 1 HOUR SOAK  
△ 1 WEEK SOAK  
● 4 WEEKS SOAK

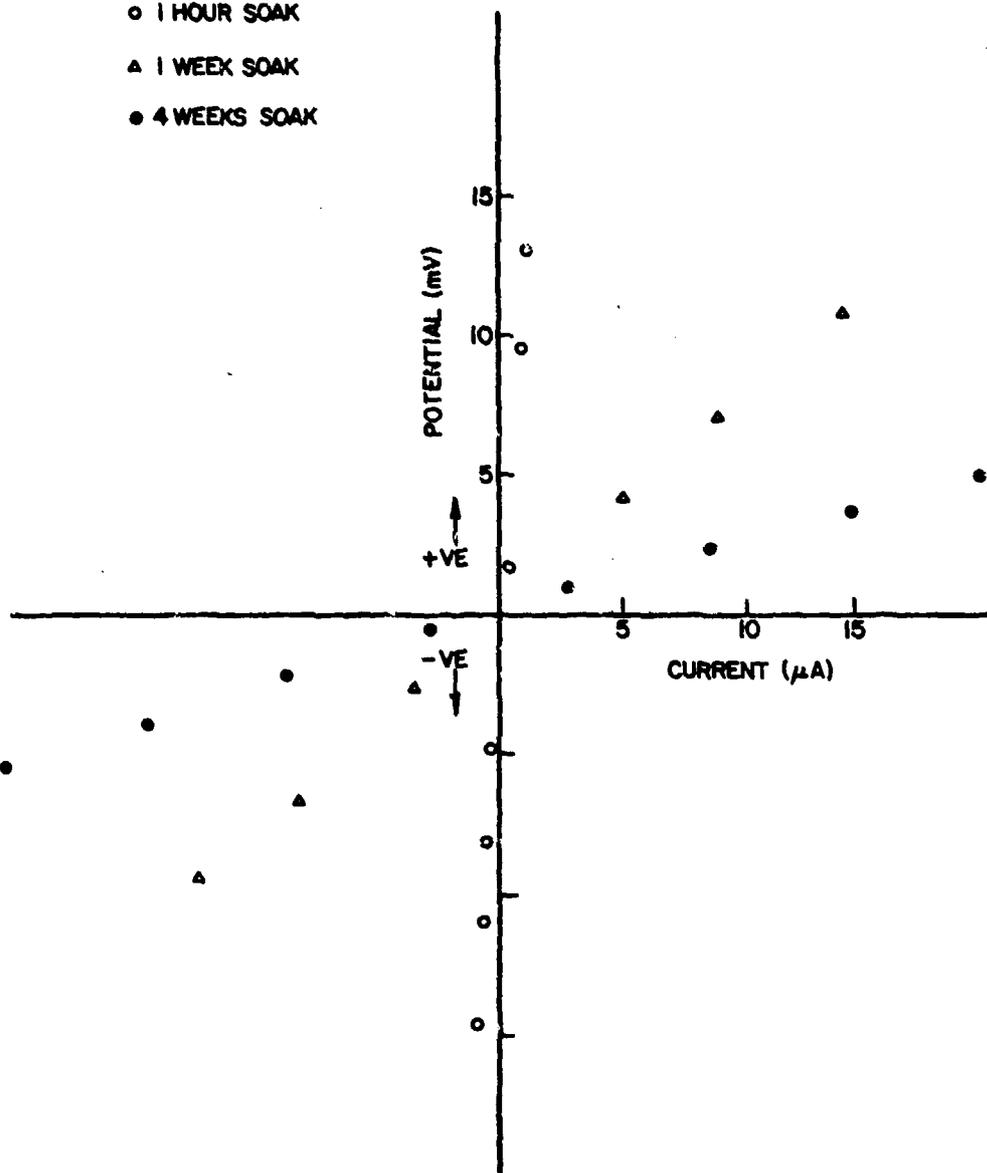


Figure 34. Linear-Polarization Curves of Al Inhibited by AML Guard.

NNH + RICHONATE 1850

▲ RUN NO. 1

□ RUN NO. 2

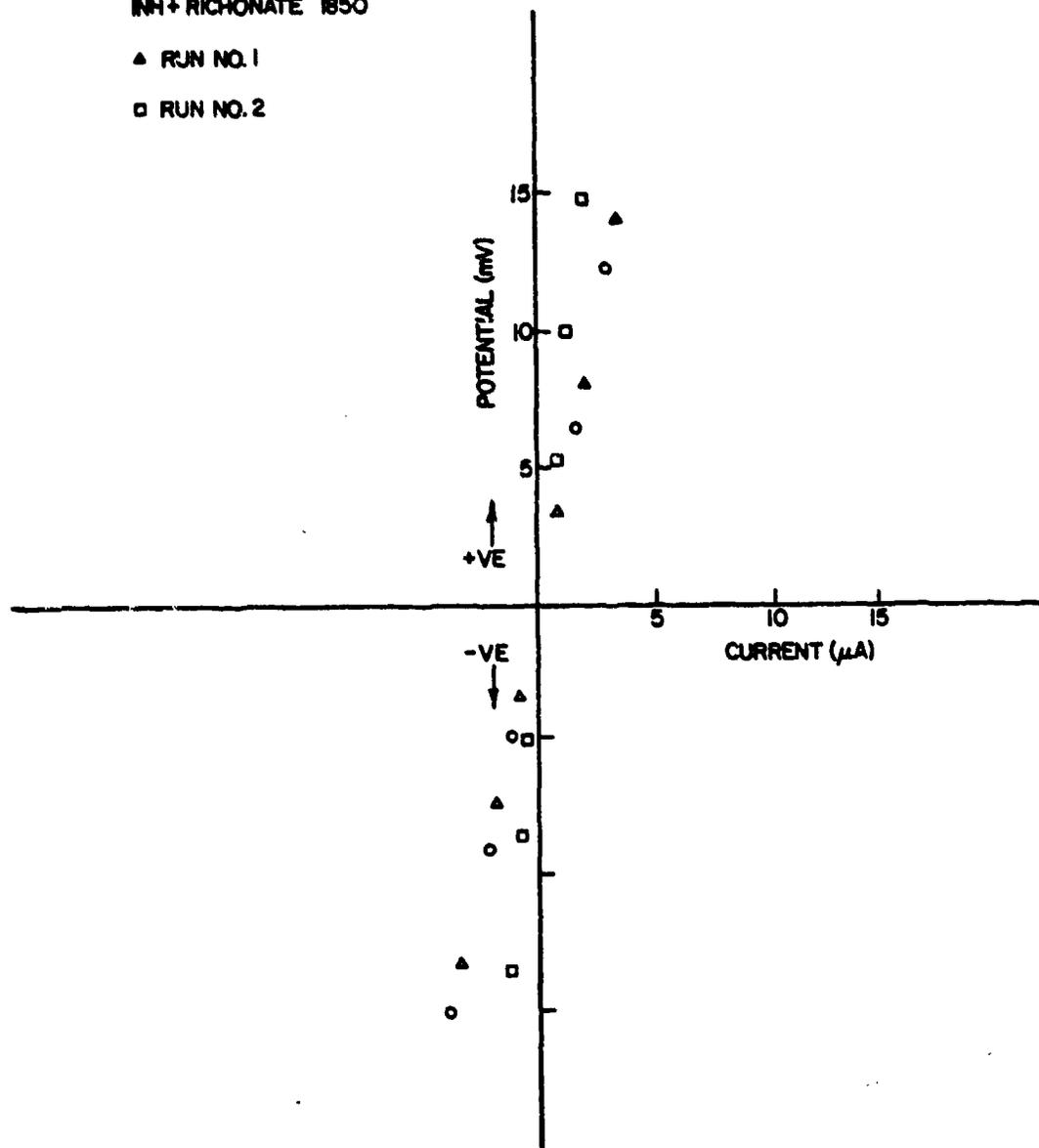


Figure 35. Linear-Polarization Curves of Al in Synthetic Urine Inhibited by Richonate 1850.

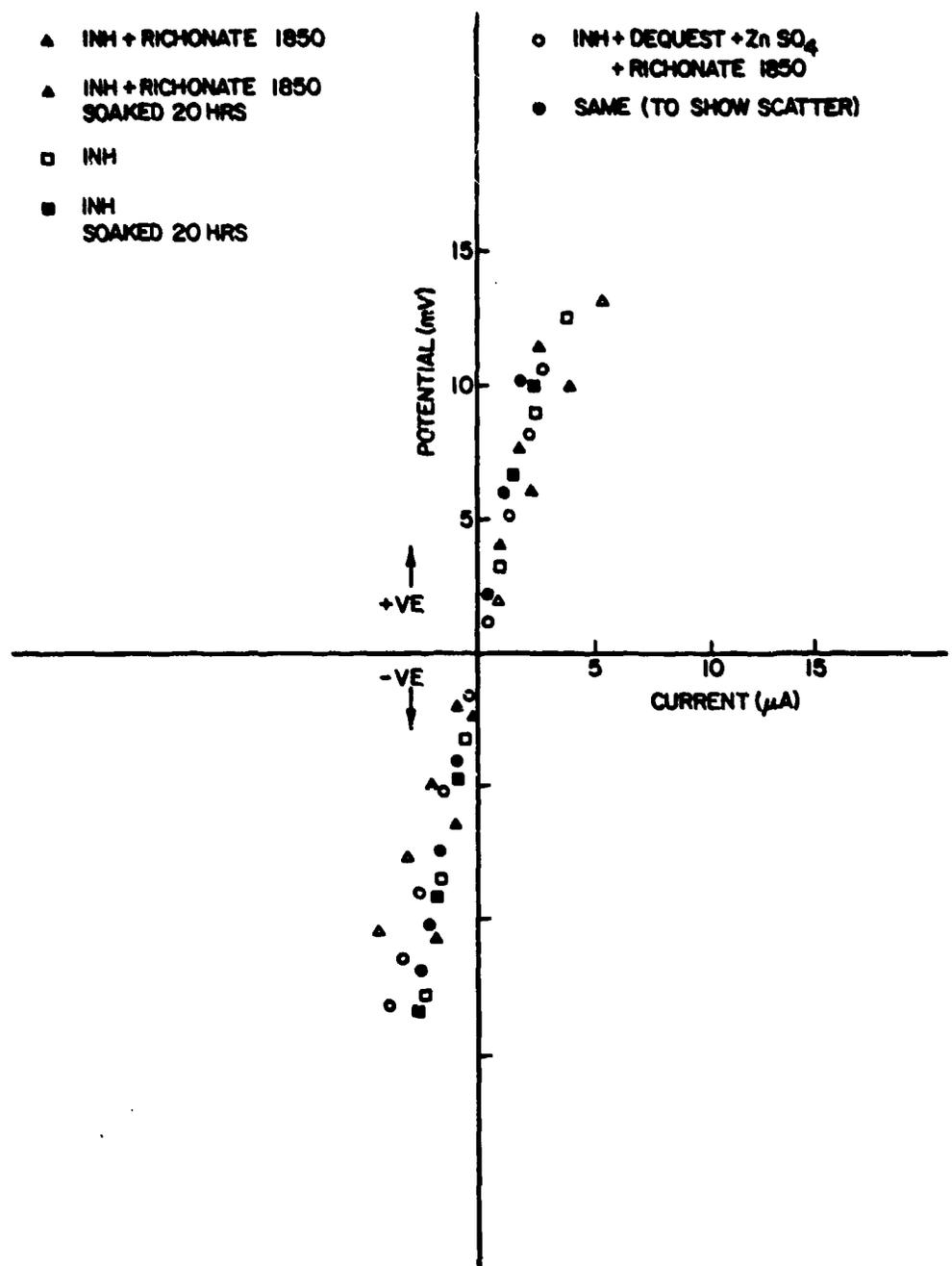


Figure 36. Linear-Polarization Curves of Al in Synthetic Urine Inhibited by Richonate and Dequest Additions.

## SECTION IV

### RESULTS

The immersion test results are shown in Tables VII to IX. Most of the results represent the average of at least five separate tests. In Figs. 17-31 the anodic polarization behavior of Al 7075-T6, 4340 steel, and copper is shown in inhibited and uninhibited synthetic and natural urine solutions. Representative linear polarization results are shown in Figs. 33-36. The corrosion-fatigue data on both high-strength steel and aluminum alloys are given in Figs. 37-47.

Some of the representative fractographic features of an uninhibited and inhibited Al 7075-T6 are shown in Figs. 48-51. Figure 48 is a low-magnification fractograph taken from a sample tested in an environment of natural urine. It shows a mixed mode of failure. The river patterns are very obvious in certain areas. Figure 49 is a high-magnification fractograph showing striations. Figure 50 shows the influence of inhibition in terms of the degree of embrittlement. Although there is evidence of mixed-mode failure, it is of a more ductile nature, as compared to that in Fig. 48. Figure 51 shows the striations. Figure 52 is a fractograph taken from the air sample for the sake of comparison. The steel samples were not preserved carefully and, as a result, a great deal of corrosion product was present on their surface. Figure 53 shows the general features of 4340 steel tested in a natural-urine environment. Figure 54 is a fractograph taken from the steel specimen tested in inhibited natural urine.

#### IMMERSION TESTS

Several formulations of borate-nitrite-base inhibitors showed promising results. From these, two combinations have been found to be the most effective. A formulation of sodium borate, sodium nitrate, sodium nitrite, sodium phosphate, sodium metasilicate, Richonate 1850, and sodium salts of MBT and BT inhibited urine corrosion of aluminum

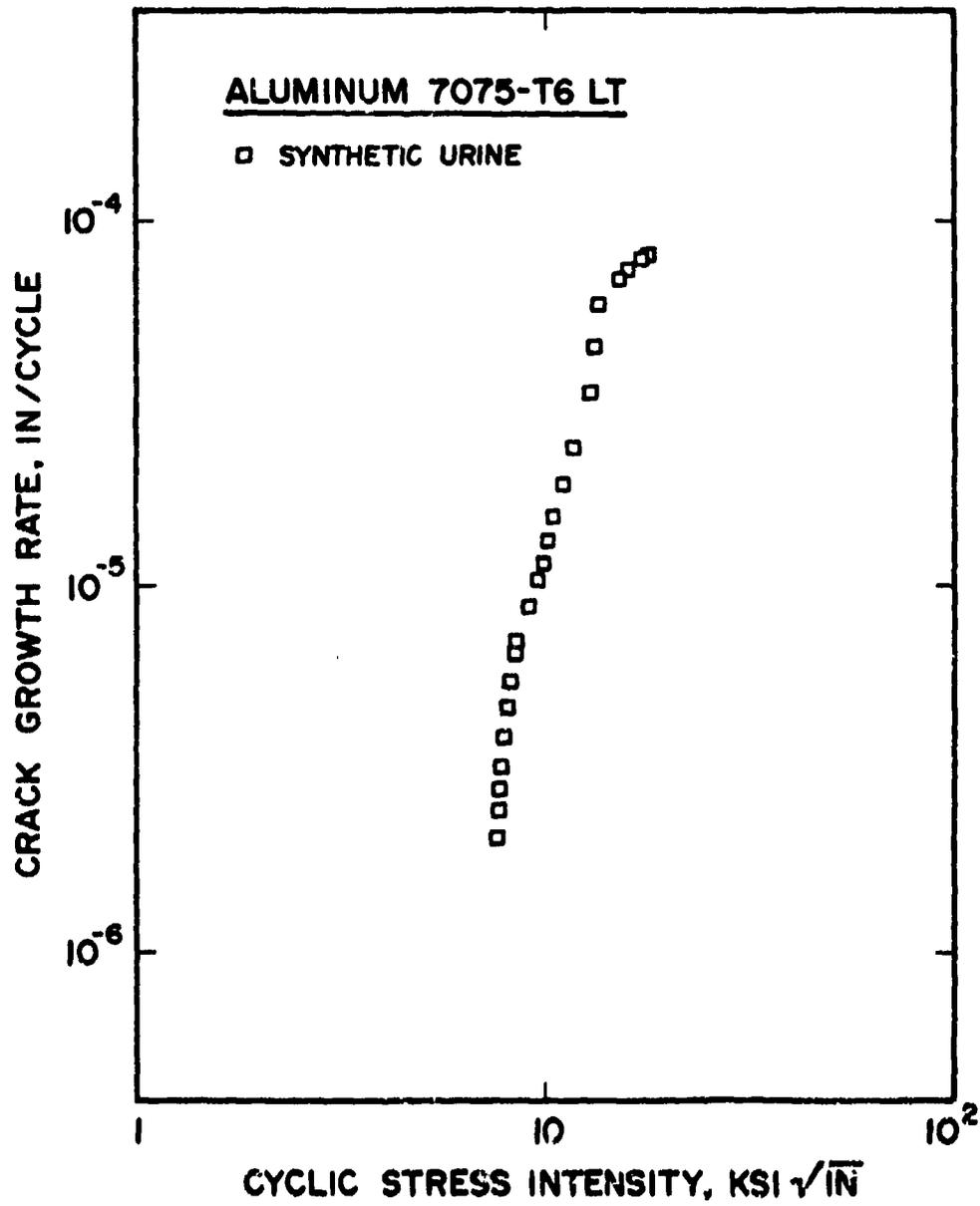


Figure 37. Corrosion-Fatigue Curve of Al 7075-T6 Tested in Synthetic Urine.

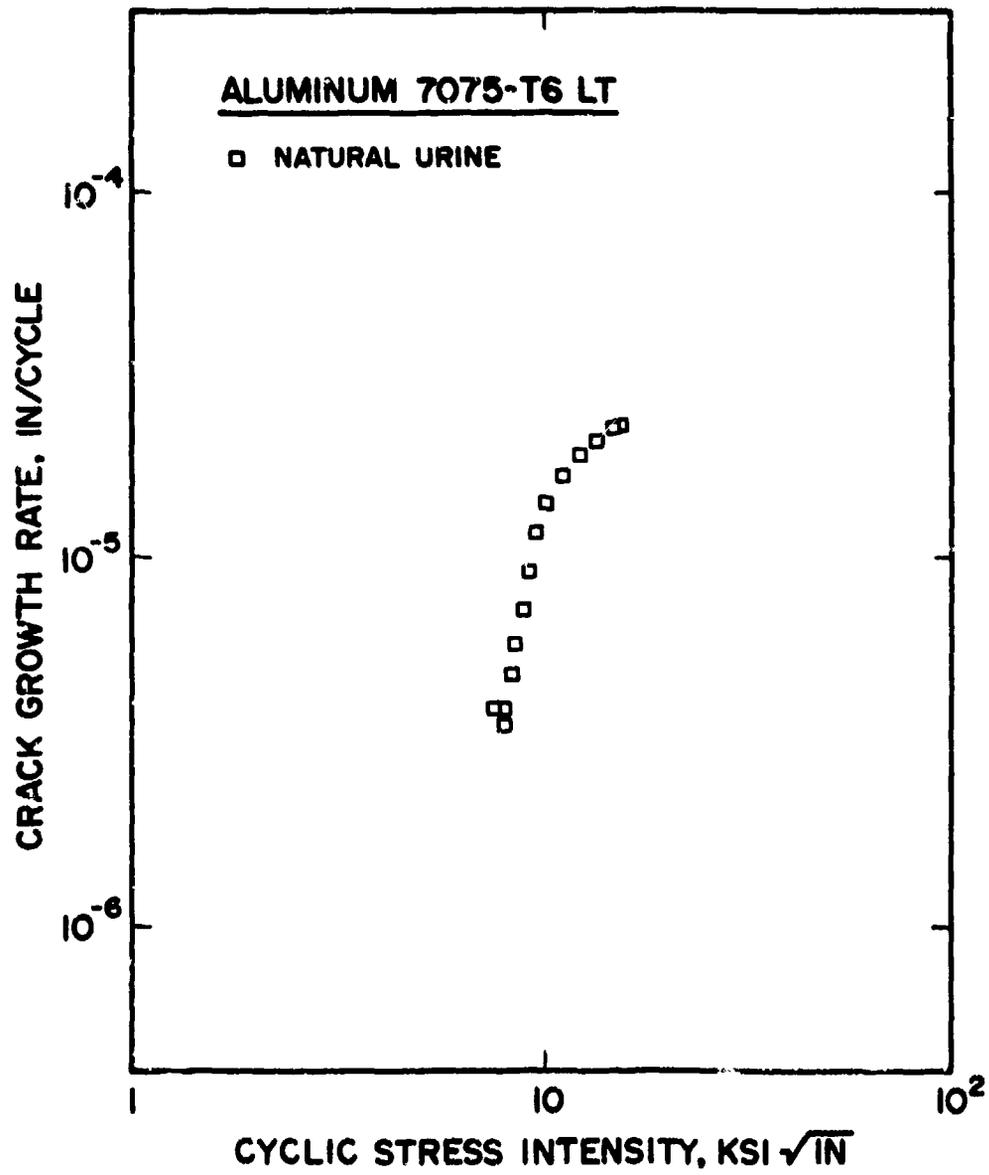


Figure 38. Corrosion-Fatigue Curve of Al 7075-T6 Tested in Natural Urine.

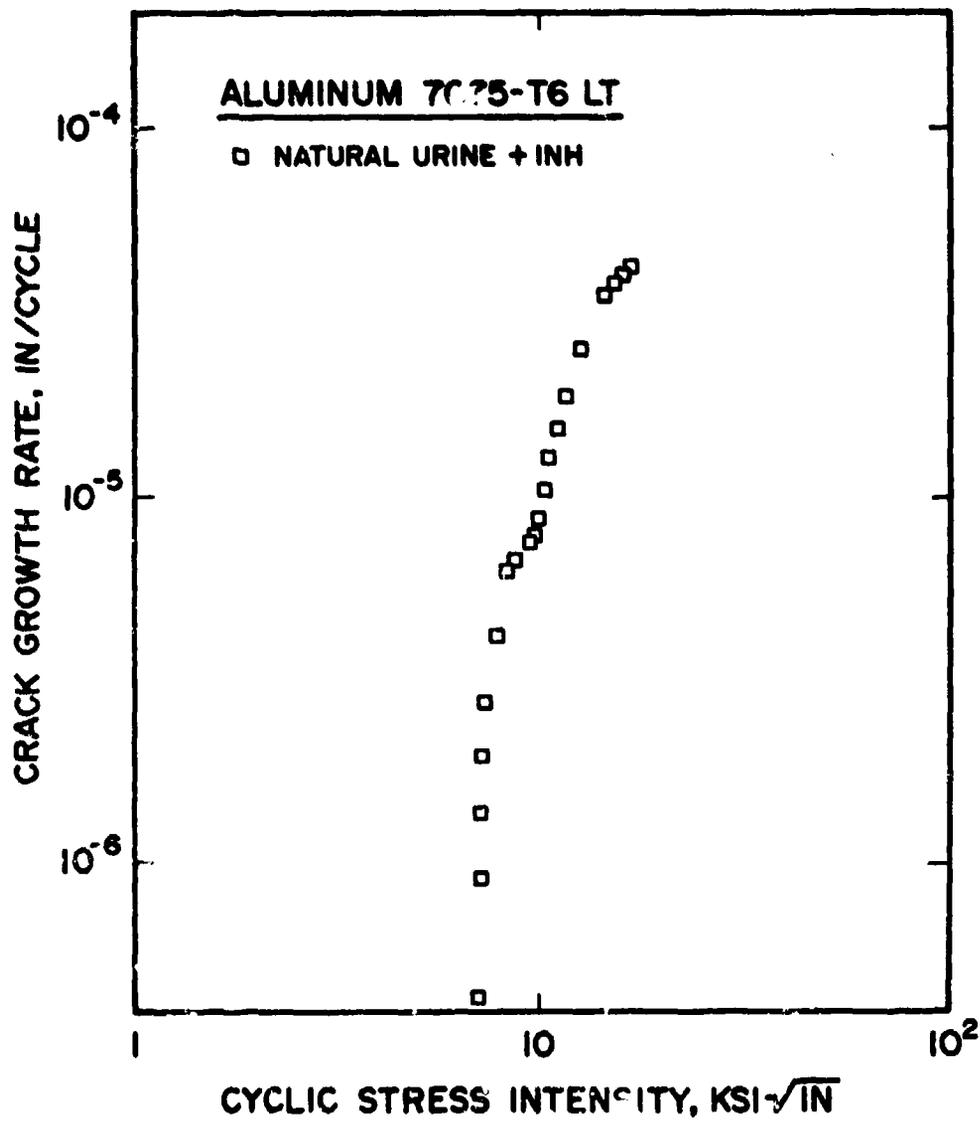


Figure 39. Corrosion-Fatigue Curve of Al 7075-T6 Tested in Inhibited Natural Urine.

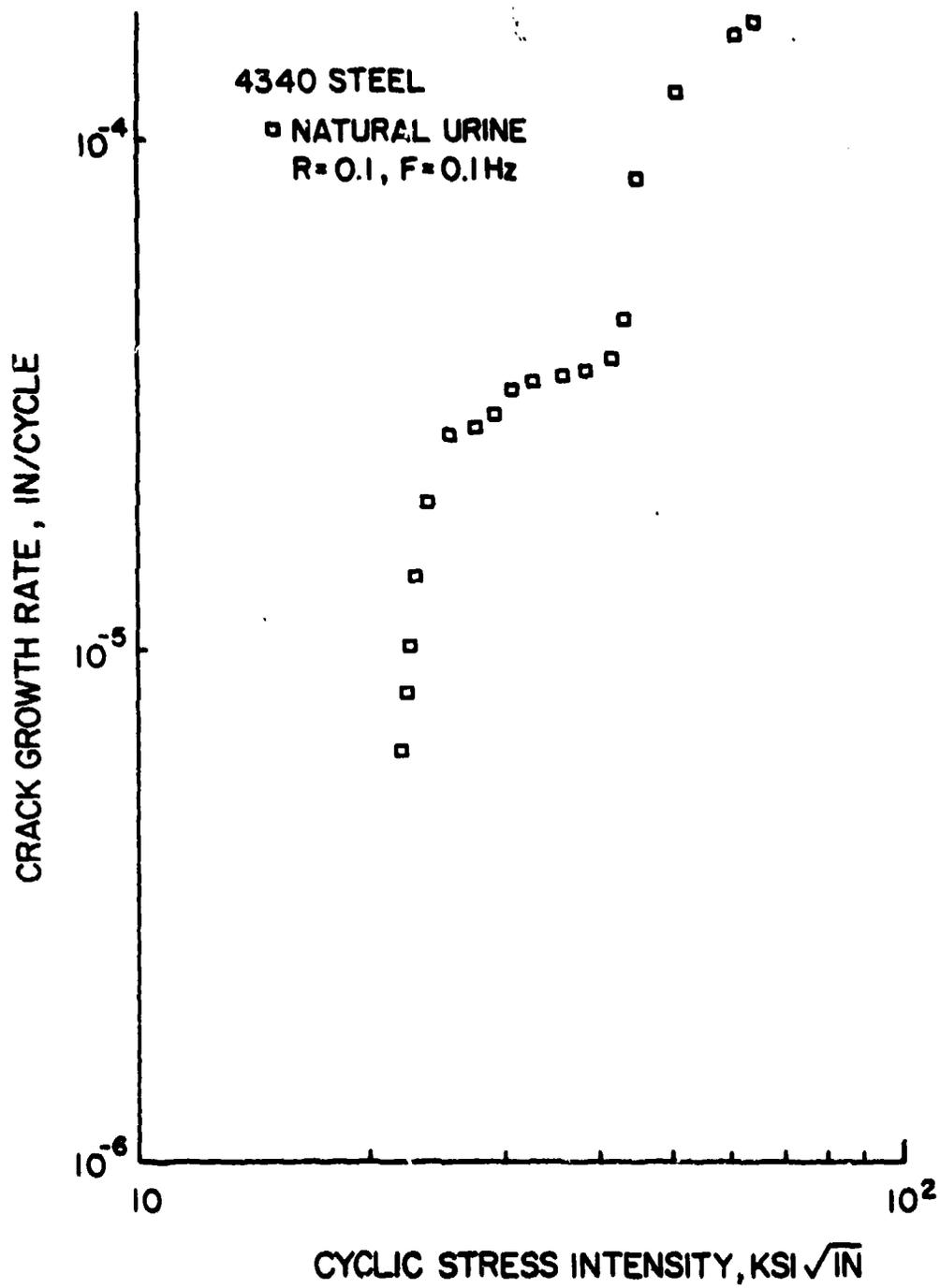


Figure 40. Corrosion-Fatigue Curve of 4340 Steel Tested in Natural Urine.

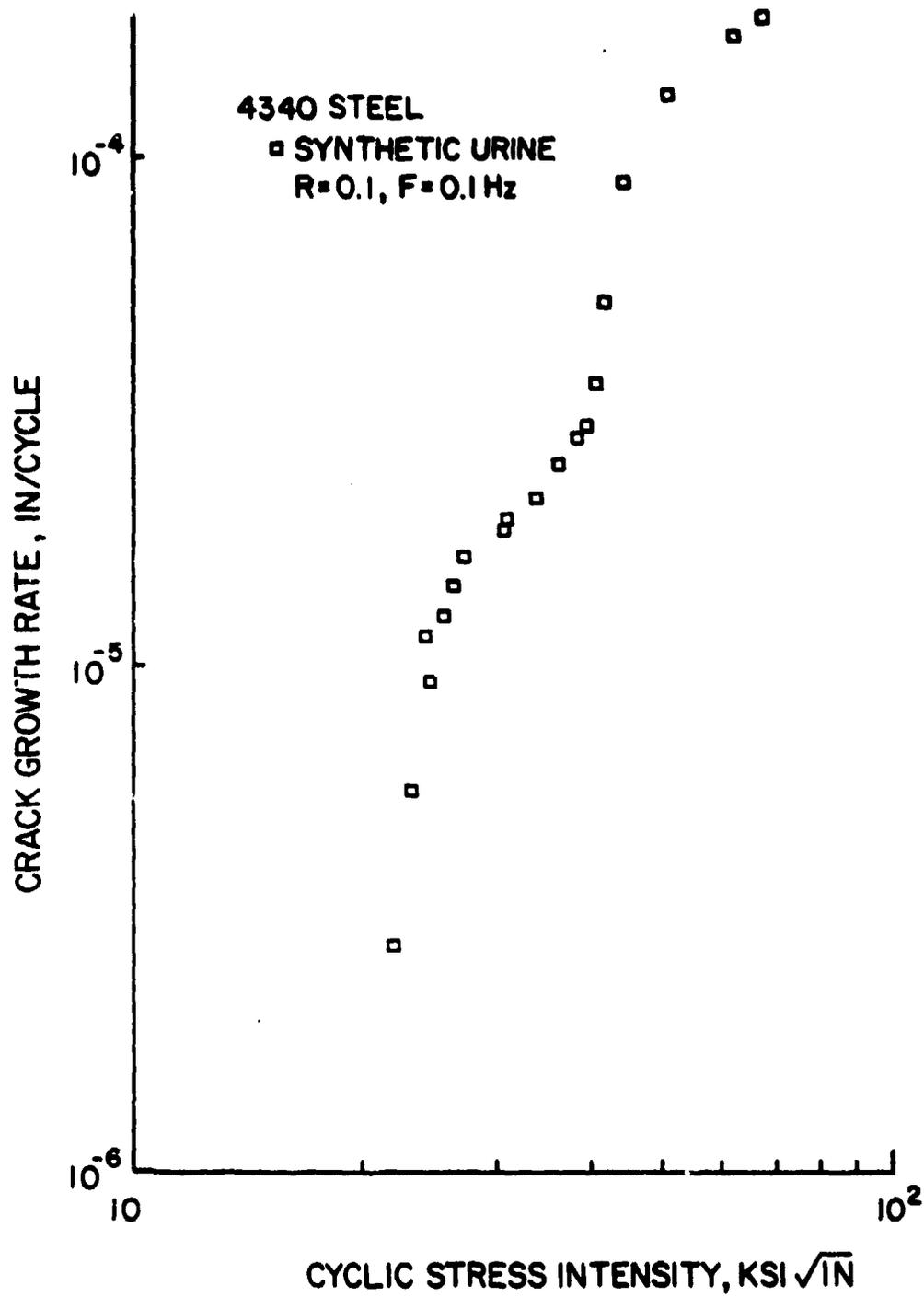


Figure 41. Corrosion-Fatigue Curve of 4340 Steel Tested in Synthetic Urine.

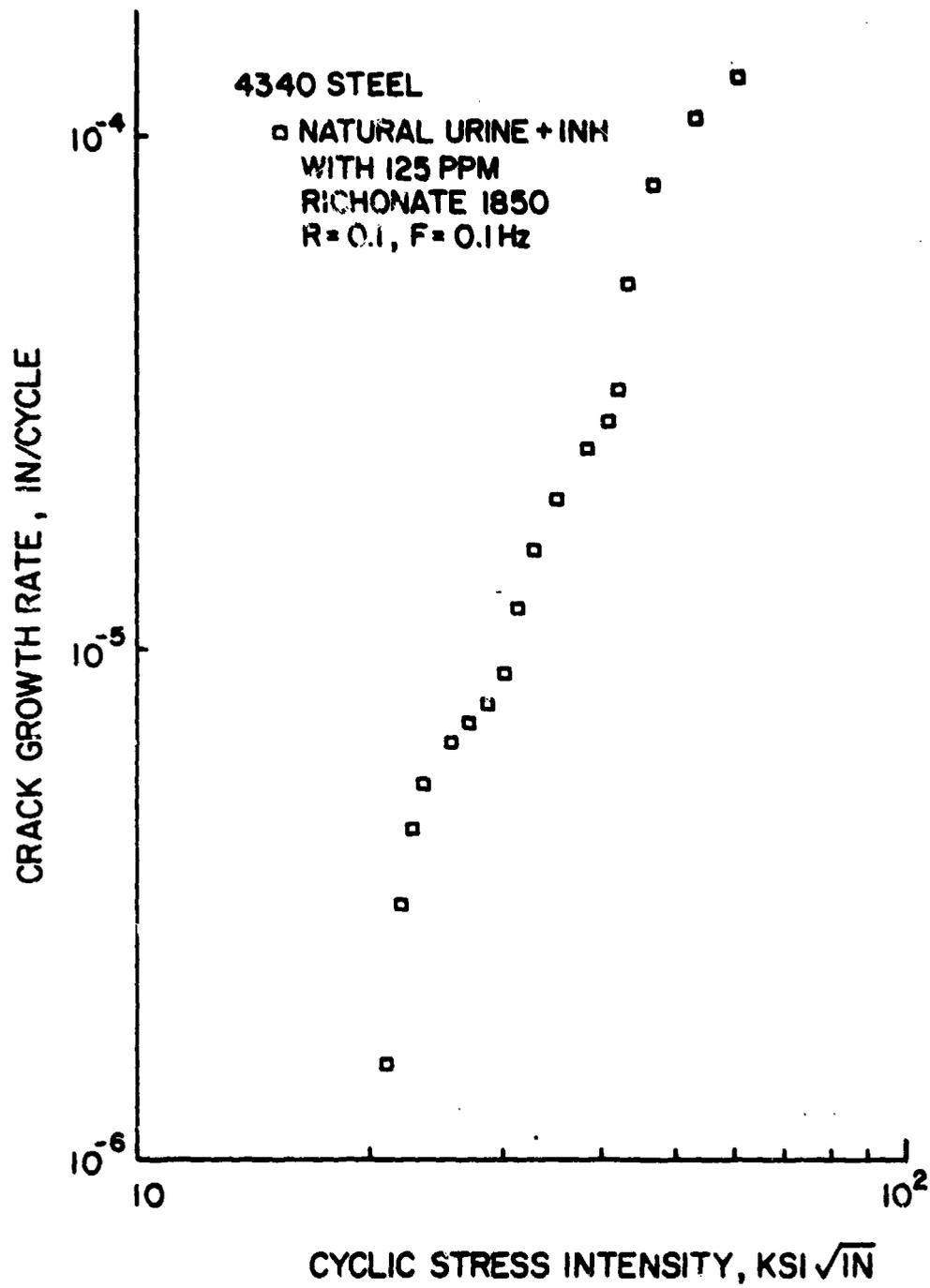


Figure 42. Corrosion-Fatigue Curve of 4340 Steel Tested in Inhibited Natural Urine.

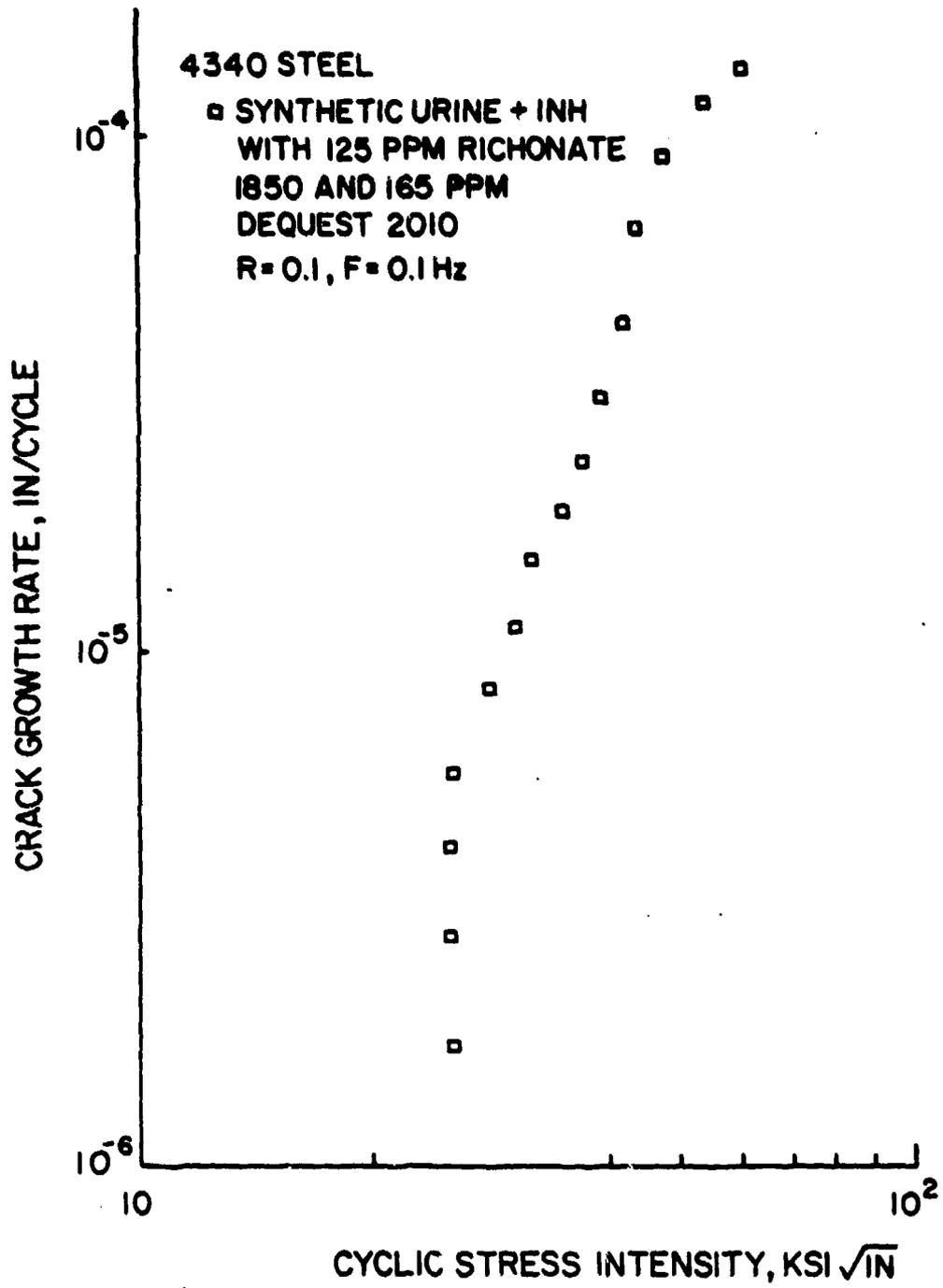


Figure 43. Corrosion-Fatigue Curve of 4340 Steel Tested in Synthetic Urine Inhibited with Dequest Formulation.

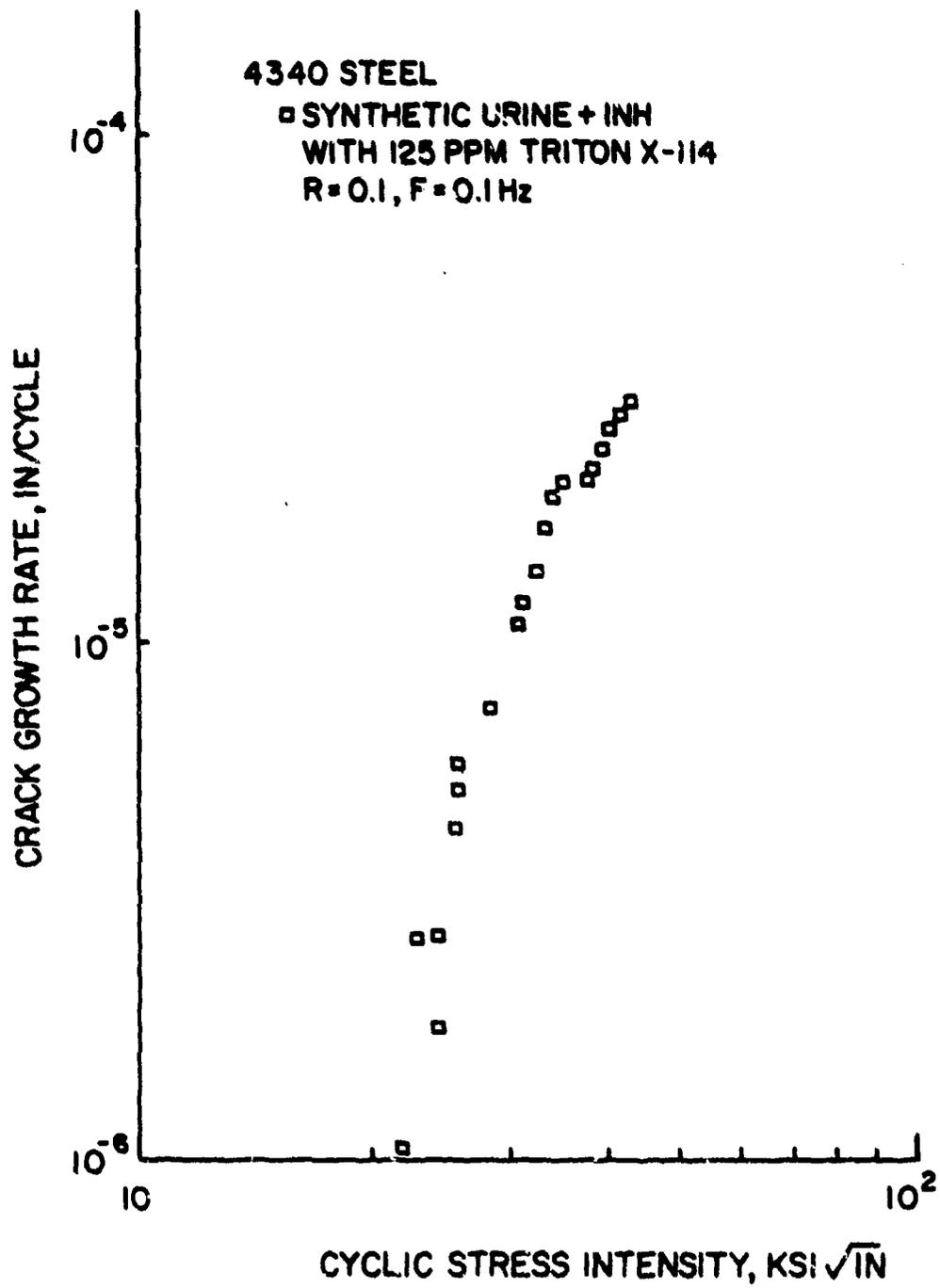


Figure 44. Corrosion-Fatigue Curve of 4340 Steel Tested in Synthetic Urine Inhibited with Triton X-114 Formulation.

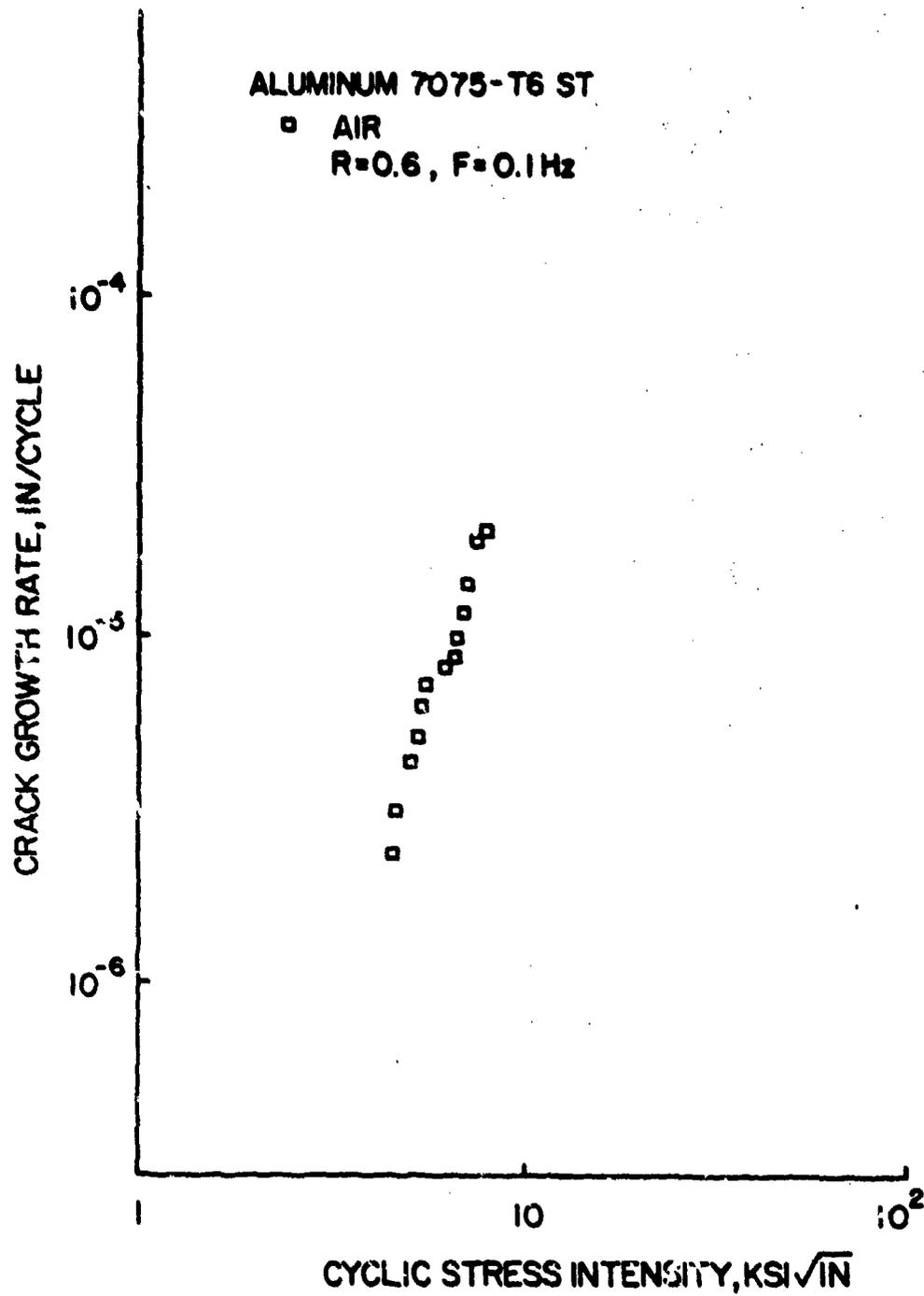


Figure 45. Corrosion-Fatigue Curve of Al 7075-T6 Tested in Air at R = 0.6 and F = 0.1 Hz.

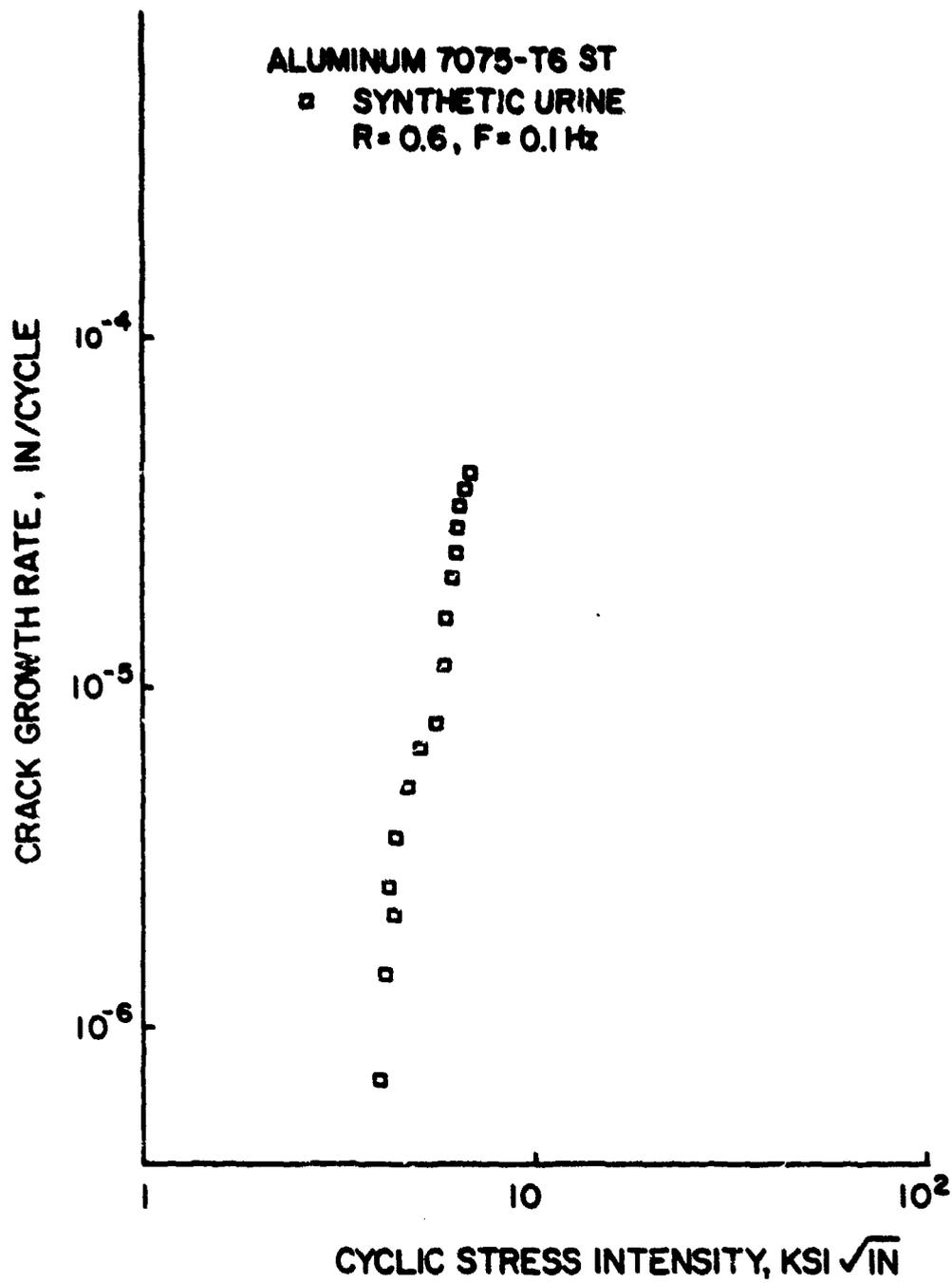


Figure 46. Corrosion-Fatigue Curve of Al 7075-T6 in Synthetic Urine Tested at R = 0.6 and F = 0.1 Hz.





Figure 48. General Features of Fracture Surface of Al 7075-T6 Tested in Natural Urine.



Figure 49. Fracture Surface of Al 7075-T6 Tested in Natural Urine Showing Fatigue Striations.



Figure 50. General Features of Fracture Surface of AL 7075-T6 Tested in Inhibited Urine.

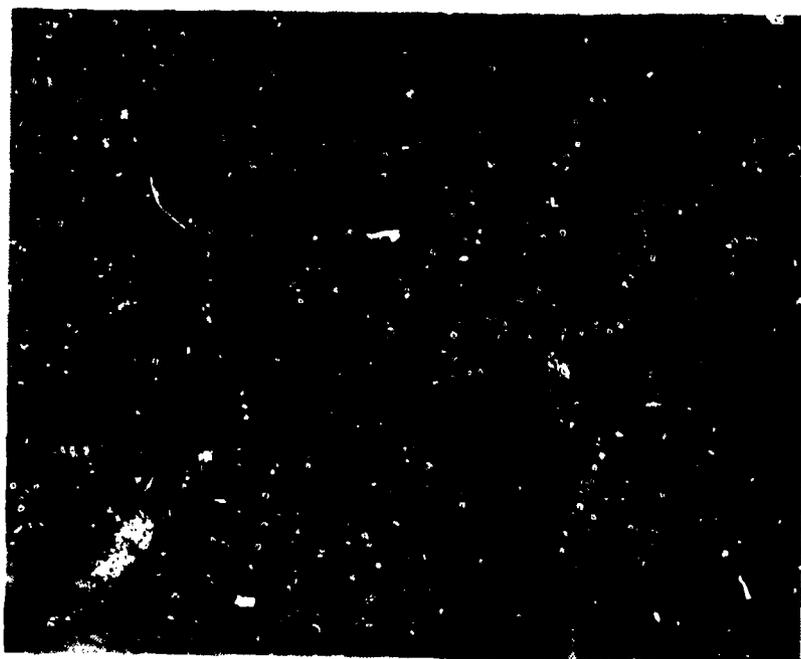


Figure 51. Fracture Surface of Al 7075-T6 Tested in Inhibited Natural Urine Showing Fatigue Striations.

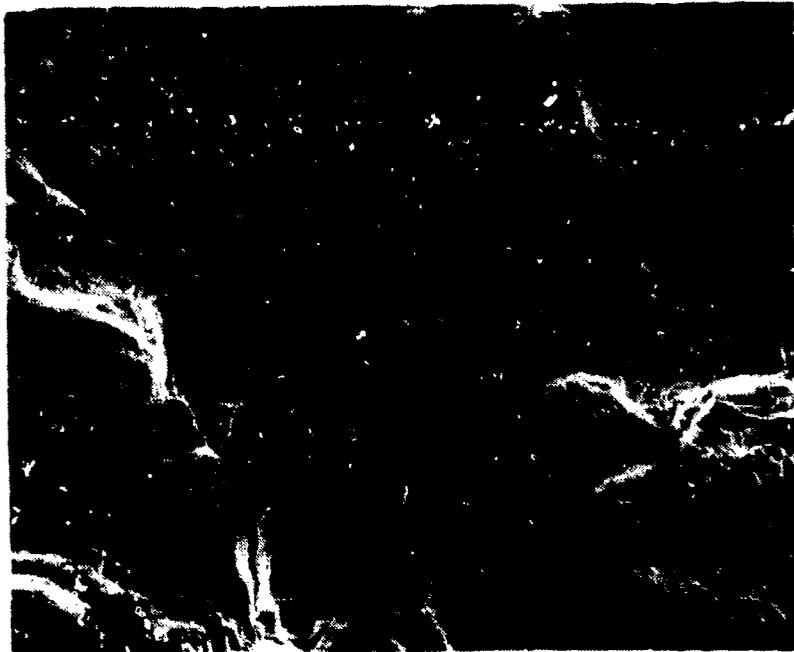


Figure 52. General Features of Fracture Surface of Al 7075-T6 Tested in Air at  $R = 0.6$  and  $F = 0.1$  Hz.

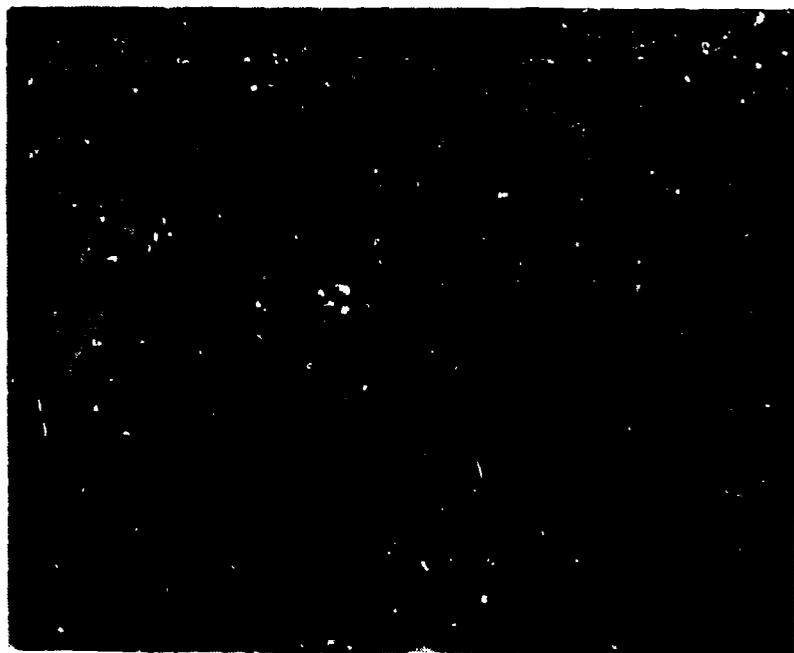


Figure 53. General Features of Fracture Surface of 4340 Steel Tested in Natural Urine.

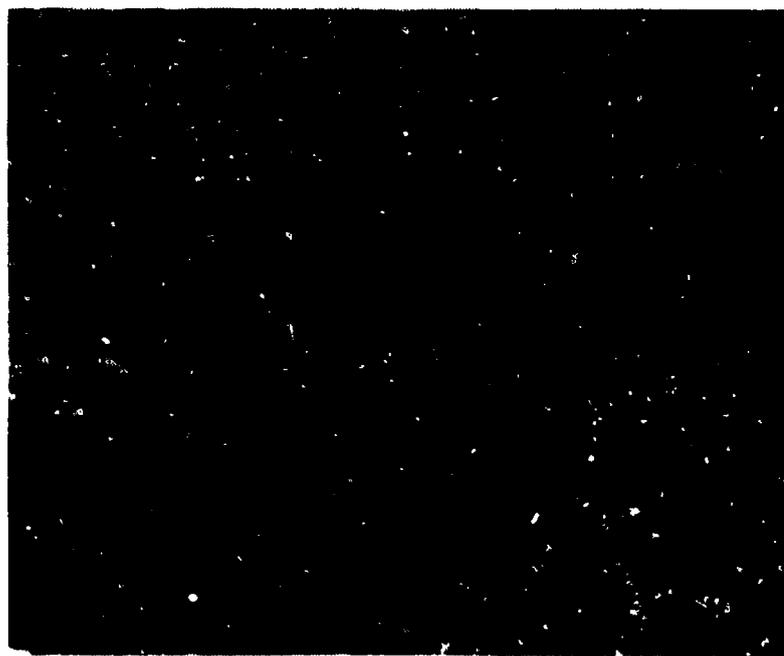


Figure 54. General Features of Fracture Surface  
of 4340 Steel Tested in Inhibited  
Natural Urine.

alloys, high-strength steels, and copper very effectively. The optimum concentration level was found to be 0.35% sodium borate, 0.2% sodium nitrite, 0.2% sodium nitrate, 0.01% sodium metasilicate pentahydrate, 50 ppm sodium meta-hexaphosphate, 150 ppm Richonate 1850, 50 ppm sodium salts of MBT, and 50 ppm sodium salts of BT. The second combination which yielded good results consisted of sodium borate, sodium nitrite, sodium nitrate, sodium metasilicate, sodium phosphate, Dequest 2010, zinc sulfate, and sodium salts of MBT and BT. The optimum concentration level is given in Table IX. Dequest may be replaced by Triton X-114.

Some of the non-borate formulations also yielded good results. In one combination, borate was replaced by 250 ppm potassium oleate. The other formulation consisted of a combination of benzoate and piperazine, but only very high concentrations were found to be effective.

The results for some of the screened commercial inhibitors are given in Table VII. Unfortunately, none of these yielded promising results. However, when used in combination with the borate-nitrite-base inhibitor, Boeshield showed excellent results. AML Guard performed very well in short-duration tests (two-weeks immersion) but lost its effectiveness after long (four-weeks) exposure. Some results of inhibitor performance in the presence of coffee spills, etc., are also included in Table IX.

#### POLARIZATION TESTS

The anodic-polarization behavior of Al 7075-T6 in synthetic and natural urine is shown in Fig. 1. The polarization curves obtained for Al 7075-T6, Cu, brass, and steel inhibited by a formulation of 0.35% sodium borate, 0.2% sodium nitrite, 0.2% sodium nitrate, 0.01% sodium silicate, 50 ppm phosphate, 125 ppm Richonate 1850, 50 ppm sodium salt of MBT and 50 ppm sodium salt of BT are shown in Fig. 24.

Of the several non-borate formulations investigated, the oleate compound (potassium soap) yielded the most promising results, as evidenced by Fig. 27. The results obtained with the benzoate-nitrite formulation, as

shown in Fig. 28, were poor. However, benzoate nitrite in higher concentrations offered good inhibition in tap water.

When the urine solution was diluted with tap water or distilled water (which might be closer to a realistic situation in the urinal and bilge areas of an aircraft), the inhibitor performance was more than adequate. As a matter of fact, a lower concentration of inhibitor was found to be effective, depending upon the amount of dilution. Some of the results are shown in Fig. 14.

Of the several commercial inhibitors studied, Dearborn 537 showed the most promise. The anodic polarization curves of some of the commercial inhibitors are displayed in Figs. 2-3.

Water-displacing compounds, such as WD-40, UM, and LPS, were also found to be ineffective in inhibiting corrosion attack on aluminum by the urine solution, as shown in Figs. 6-8. The anodic polarization behavior of Boeshield T-9 and AML guard is shown in Figs. 4-5.

#### CORROSION FATIGUE

The low-cycle corrosion-fatigue results on Al 7075-T6 are shown in Figs. 37-39. These tests were conducted in inhibited and uninhibited synthetic as well as natural urine. Figures 40-44 contain the crack-growth data on high-strength 4340 steel. These tests were also conducted to determine the influence of the inhibitor upon the crack-growth behavior of high-strength steel in an aggressive medium such as natural urine.

SECTION V  
DISCUSSION OF RESULTS AND CONCLUSION

Formulation of the synthetic urine was a difficult task because of the more than twenty aggressive ingredients involved. The corrosion behavior of the synthetic-urine formulation has been compared with that of several specimens of natural urine. Anodic- and cathodic-polarization and immersion test results have shown the corrosion behavior of the synthetic urine to be quantitatively comparable to that of natural urine. The similarity in the corrosion behavior can be seen in Fig. 1.

Initially the development work was based upon a previous investigation<sup>2</sup> of a borax-nitrite-base rinse formulation. This formulation performed poorly in the aggressive urine medium (natural or synthetic). This may be due to the breakdown of the passive layer by the chloride ion. The synthetic (or natural) urine is made up of nearly 1% sodium chloride. As shown earlier<sup>2</sup> the rinse formulation begins to lose its effectiveness or the breakdown of passivity approaches as the sodium-chloride concentration increases. The acceptable sodium-chloride concentration was found to be nearly 1000 ppm. The rinse formulation was modified to solve this problem. The concentration of sodium nitrite and sodium nitrate was increased, and the results were encouraging as can be seen from the immersion data shown in Table IX. Addition of silicate or phosphate to the rinse inhibitor had very little effect. The nitrite is known to increase the passivity of steels and aluminum.<sup>2</sup>

Due to the high concentration (~1%) of NaCl in the urine solution, corrosion attack on aluminum is quite severe. Some film formers, chelating agents, and wetting agents were studied for their ability to inhibit the chloride-ion penetration into the aluminum surface. Isopropylamine produced excellent results, as shown in Fig. 15. However, this was true only when aluminum alone was to be protected. When pieces of aluminum, copper, and steel were immersed together, severe pitting of the aluminum

occurred after long exposure which could not be prevented even by the addition of  $\text{MB}^-$  (to inhibit the copper ions) or  $\text{ZnSO}_4$  (to inhibit the Fe ions).

It was found to be much easier to inhibit Al in a diluted solution of urine. When the urine solution was diluted to one-half its concentration by the addition of water, the rinse inhibitor produced a passive region on the polarization curve, as shown by Fig. 14.

Sulfonates were found to be effective in improving the passive layer on the surface of aluminum. 100 oil, which is a calcium-sulfonate compound, and Triton X-114 yielded favorable results, as shown in Figs. 18 and 23. With Triton X-114 difficulty was experienced in inhibiting aluminum corrosion in the presence of copper and steel. However, this situation was improved by the addition of  $\text{ZnSO}_4$ . Similar results could not be achieved with 100 oil or other surfactants. Richonate 60-B showed more favorable results than Triton X-114 in a similar situation as can be seen from the immersion results in Table IX.

Richonate 1850 and Estersulf separately, when added in small concentrations to the borax-nitrite-base inhibitor provided a similar degree of passivity to aluminum, steel, and copper. However, in immersion tests Richonate 1850 showed superior results when compared to Estersulf, as shown in Table IX. In a continuing development process, the addition of Dequest 2010 along with a small concentration of  $\text{ZnSO}_4$  also provided excellent inhibition to aluminum, copper, and steel. The higher concentration of Dequest 2010 resulted in pitting, and, therefore, this formulation is not being recommended at present. More work is needed to improve this formulation.

It was discovered that molybdate nitrite offers the same level of protection as borate nitrite, but the addition of borate to the molybdate-nitrite formulation definitely has a synergistic effect. A combination of borate molybdate and nitrite offers inhibition for aluminum in

urine solution which is far superior to that achievable with molybdate nitrite or borate nitrite alone. This may be verified by the immersion results shown by #6, Table VIII. On the other hand, benzoate had either a damaging effect or little effect upon the inhibiting properties of the rinse inhibitor. Several formulations of benzoate and nitrite, other than borate-nitrite, were studied. Concentrated mixtures of benzoate, piperazine, and silicate showed promising results. All of the immersion results are not included in Table IX.

The oleate compound--potassium soap--offered the best results, in comparison with molybdate and benzoate. The passive region was increased more than 200 mV over the rinse inhibitor, as shown in Fig. 27. The immersion results showed almost no visible corrosion after a period of three months. In several tests borate was completely replaced by potassium soap. The results obtained are comparable to those obtained with borate, but more work is needed in this direction.

Of the several commercial inhibitors studied, Dearborn 537 showed some degree of promise. When this inhibitor, or some other such as Cortec 317, were used to protect aluminum only, the performance was very satisfactory, as shown by results in Table VIII. The inhibiting property was reduced when pieces of aluminum, copper, and steel were immersed in the same beaker containing the synthetic urine. Apparently, the individual ions have interfering effects, and their influence upon each other is not eliminated by these inhibitors.

The water-displacing compounds such as WD 40, UM, and the LPS's also were found to be ineffective in inhibiting corrosion attack by urine solution upon aluminum (see the results in Table VII and the polarization curves in Figs. 6-8). Boeshield T-9 showed promise when used with the rinse inhibitor, as shown in Fig. 4. The performance of AML Guard was excellent in inhibiting aluminum corrosion in the urine solution, as shown by Fig. 5. This is further supported by the linear-polarization results shown in Fig. 34. However, when pieces of aluminum, steel, and copper

were immersed together, severe pitting occurred after two weeks of exposure. This was later confirmed by linear-polarization results on a specimen which was soaked for different time intervals. The amount of corrosion increased with time. This is evidenced by the corrosion currents obtained through linear polarization tests, as shown in Table X.

As a result of these investigations, a formulation of 0.35% sodium borate, 0.2% sodium nitrite, 0.2% sodium nitrate, 0.01% sodium silicate, 125 ppm Richonate 1850, 50 ppm sodium phosphate, and 50 ppm sodium salts of MBT and BT is recommended for use in the bilge, urinal, and related areas of aircraft.

The corrosion-fatigue results are interesting in the sense that the synthetic or natural urine has little effect upon the crack-growth behavior of Al 7075-T6. However, the crack-growth rate is reduced five to eight times in the second region by introduction of the inhibitor. This is quite a large difference and indicates the improved performance of the inhibitor. At the same time the results demonstrate the ability of the inhibitor to nullify (almost) the effect of an aggressive environment.

The fracture surfaces of uninhibited and inhibited specimens in general have a similar appearance. Both show mixed-mode failures. However, the striation morphology appears to be very clearly defined in the inhibited sample, as seen in Fig. 49, while there was more evidence of cleavage fracture (as seen in Fig. 50) for the specimen tested in natural urine. In the case of steel specimens, the striations could not be traced. Figure 53 is a low-magnification fractograph but still shows evidence of mixed failures. The fractograph (Fig. 54) taken from the inhibited 4340 steel sample also shows mixed-mode failure. Apparently the fractographic studies are not conclusive, and further work is needed. One point should be made here: in the case of Al 7075-T6, the light-microscopic observations revealed some differences in the fracture surfaces of the inhibited and uninhibited specimens. The fractured samples tested in natural urine showed a greater amount of intergranular cracking than the sample tested in inhibited urine.

SECTION VI  
NEW DIRECTIONS FOR RESEARCH

The successful modification of the rinse formulation to provide inhibition of the corrosion attack of an aggressive solution such as natural urine suggests the need for further work to develop it into a nonchromate, widely applicable inhibitor. This inhibitor exhibits good properties, in preventing saline-water corrosion also.

Some non-borate formulations have shown promise. More work should be done in this area because borate formulations are difficult to encapsulate. Potassium soap-nitrite and benzoate with additions of small concentrations of silicates, phosphates, etc., and piperazine are examples. Piperazine alone has exhibited good inhibiting properties against general corrosion attack on high-strength steel and has shown interesting crack-growth results on Al 7075-T6. The crack-growth behavior of Al 7075-T6 in piperazine solution warrants further investigation.

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