

THE DEVELOPMENT OF MULTIFUNCTIONAL CORROSION
INHIBITORS FOR AEROSPACE APPLICATIONS

M. Khobaib
Systems Research Laboratories, Inc.
2800 Indian Ripple Road
Dayton, OH 45440

F. W. Vahldiek
and
C. T. Lynch
Air Force Wright Aeronautical Laboratories
Materials Laboratory (AFWAL/MLLN)
Wright-Patterson Air Force Base, OH 45433

ABSTRACT

The development of inhibitors for aerospace applications such as automated rinsing of aircraft requires systems of high solubility, low toxicity, and reasonable cost which are effective on a wide variety of high-strength corrosion-susceptible alloys. Chromate-based products, in combination with polyphosphates, have been reasonably effective against corrosion of ferrous and nonferrous metals and alloys and are presently the most widely used inhibitors. The use of chromates, however, has been the subject of ecological concern, and the present investigation involves the development of non-toxic, multifunctional water-soluble inhibitors. The performance of a large number of nonchromate inhibitors has been studied and a borax-nitrite-based formulation developed which inhibits the corrosion of both ferrous and nonferrous alloys. This formulation consists of a combination of low-toxicity components and is effective in preventing localized corrosion and accelerated crack growth as well as general corrosion. Effectiveness in aggressive environments including synthetic urine has been demonstrated. Applications include lower-bay, galley, and related areas of large aircraft and automated aircraft rinse facilities. Field evaluations are underway.

INTRODUCTION

During the past four years, a considerable number of studies have been conducted in the United States regarding the total cost of corrosion prevention and control for aircraft. The inescapable conclusion is that total corrosion costs in terms of life-cycle management and maintenance of aircraft represent an intolerable burden to the U. S. Air Force in maintaining force effectiveness at a reasonable cost to the taxpayer. A recent study conducted by NBS [1] has indicated that the total corrosion cost for one year (1976) was more than 70 billion dollars nationally, with costs to the USAF estimated to exceed one billion dollars. In order to minimize these costs, the USAF has been searching for ways to combat corrosion in all its forms. Several years ago a study [2] conducted by the U.S. Navy on corrosion prevention in carrier-based aircraft revealed that by merely rinsing the aircraft with water to remove detrimental particles such as salt and ash, a considerable savings could be realized in terms of corrosion maintenance. By late 1975, the USAF had made a decision to build a rinse facility for the F-4 aircraft and to install it under AFLC/WRALC and TAC at MacDill Air Force Base, FL. At the corrosion managers conference at WRALC in the fall of 1975, questions concerning hard-water rinsing as opposed to inhibited or demineralized-water rinsing were discussed [3]. In the rinsing of aircraft, the possibility exists that water will be trapped in crevices or so-called dry-bay areas and that trapped hard water will cause serious corrosion problems and hence completely jeopardize any advantage of hard-water rinsing as a corrosion-control method. Therefore, the incorporation of a low concentration of a non-toxic water-soluble inhibitor into the rinse facility was suggested.

The use of inhibitors to reduce costs also received impetus as a result of the conclusions reached at the 1975 AFML-AFOSR Corrosion Workshop [4]. The expanded use of inhibitors to reduce the costs and problems associated with corrosion in aerospace systems was recommended as a cost-effective, flexible, and widely applicable approach. In this regard one of the major cost items for depot repair has been due to corrosion in the lower surfaces of particularly larger aircraft, such as the C-130 and C-141A. Generally inaccessible and hard to inspect, these areas (referred to as "bilge" areas) act as traps for dirt and moisture which accelerate corrosion and result in major corrosion damage that requires large-scale structural repair. In addition to lower cargo bay areas, hot spots for corrosion are found in the galley and latrine areas. Warner Robins Air Logistics Center Corrosion Management Office, GA, has often cited the need to investigate the development of corrosion inhibitors for this type of application that would be simple to apply or use. Bilge inhibitors in package form have already been reported in use by the Royal Air Force in Great Britain [3], but they are reported to contain chromates which would not be satisfactory from a toxicity standpoint for the Air Force. Some commercial use has been made of water-displacement compounds, but these have limited life, are difficult to apply, and are toxic in application. The magnitude of the cost of bilge-area rework is indicated from recent figures for depot work on the C-141A, on which 1182 hours were required per aircraft for a cost in excess of two million dollars per year for the entire C-141A force.

Although chromate-based [5,6] corrosion inhibitors have been widely used to combat corrosion of ferrous and nonferrous metals and alloys, the use of chromates has recently been the subject of ecological concern. The present investigation was carried out to search for alternatives to chromates, one such

alternative being a borax-nitrite-based inhibitor. The value of borax nitrite as a corrosion inhibitor has long been recognized [7,8]. Earlier work [9] has shown a borax-nitrite combination to be very effective in controlling general corrosion as well as crevice corrosion of high-strength steels. However, this combination was not found to be effective against the corrosion of other ferrous and nonferrous metals and alloys. The present study was conducted first to develop a nontoxic multifunctional corrosion inhibitor (which would be effective against corrosion of ferrous and nonferrous metals and alloys--mainly aluminum and copper alloys) to be incorporated into the USAF Automated Rinse Facility at MacDill Air Force Base in Tampa, FL. The second objective was to use this system as the basis for the further development of a nontoxic, multifunctional corrosion inhibitor system which would be applicable to incorporation into hot-spot corrosion-prone areas such as the lower bay areas of large aircraft.

Several hundred inhibitor compounds and formulations were surveyed with regard to their effect upon electrochemical behavior, general corrosion, galvanic corrosion, crevice corrosion, and corrosion fatigue. As a result a borax-nitrite-based inhibitor was developed and is currently being evaluated in the Automated Rinse Facility at MacDill Air Force Base. This solution contains no chromate, is biodegradable, and offers other important advantages over chromate-based combinations which will be discussed. The Rinse Facility was placed in operation in 1978; and in tests begun in late 1979, inhibitors were added. Efforts have been initiated to track corrosion maintenance costs of F-4 aircraft undergoing the inhibited rinse operation.

In the follow-on effort new formulations have been developed for use in the lower cargo bay, galley, and latrine areas of large aircraft. These inhibitors

have proven effective in laboratory tests in extremely aggressive environments over long periods of time.

GENERAL CONSIDERATIONS FOR INHIBITORS

Several commercial inhibitors are available for various service applications such as cooling-tower circuits, central-heating systems, and automotive radiators. These formulations are normally combinations of several classes of inhibitor compounds, some functioning as anodic inhibitors and others as cathodic inhibitors. Commercial experience has shown that such combinations are often more effective due to some synergistic [10] effect. Unfortunately, most of them are optimized for a specific application. The results of work conducted at the Air Force Wright Aeronautical Laboratories/Materials Laboratory have demonstrated an encouraging inhibition effect of borax-nitrite upon high-strength steels [11]; chromates have not been found to be so effective in the presence of chloride ions [12]. The promising results of the borax-nitrite combination were observed in crack-growth experiments--both in static test and cyclic corrosion-fatigue tests--but this combination per se was not effective in inhibiting the corrosion of high-strength aluminum alloys, copper, and other alloys used in aircraft structures and in the Rinse Facility. However, the encouraging results obtained on high-strength steels served as the impetus for further exploration.

A substantial number of corrosion-preventive compounds (called CPC's) are also available commercially. These are based upon the use of water displacing compounds, protective organic films, and surfactant agents in a solvent vehicle. Their chief disadvantages appear to be limited effective life, the requirement of clean and uncorroded surfaces, cost, and toxicity of the carrier solvents.

In order to systematize the development of new inhibitor formulations and current commercial products, it is desirable to establish some guidelines for selection of inhibitors for further experimental screening. In Table 1 some of the more important considerations and possible compound types are listed. Most of these are obvious considerations, with a few being particularly important for aerospace or other applications where high-strength alloys are utilized. These considerations require effectiveness to retard or eliminate hydrogen embrittlement, stress-corrosion cracking, and corrosion fatigue which can lead to catastrophic cracking failure in high-strength alloys [11].

The first and foremost task in the screening of the inhibitors was the question of toxicity. All the inhibitor formulations which were obviously toxic (based upon information in the literature [13]) were eliminated first--chromates, aniline, and arsenic additions being obvious examples. It is also important that the materials used be cost effective and readily available. They should be economical and have long-term effectiveness. For bilge areas of aircraft, effectiveness should last between major field maintenance operations and ideally between programmed depot maintenance intervals.

The use of the other guidelines delineated in Table 1 is discussed in more detail in a previous report on the development of the rinse inhibitors [14]. These guidelines led to a selected list of inhibitor compounds and formulations for subsequent experimental screening. Special solutions were employed, as discussed in the experimental section, to reproduce the rinse water used at the Automated Rinse Facility and to reproduce more aggressive media based upon possible high-chloride contamination of the rinse water upon recycling after use

on the aircraft. For bilge environments it was necessary to develop special solutions for synthetically reproducing the most aggressive media expected to be present in the lower-bay areas of large aircraft. This included the use of a synthetic-urine solution which simulated natural urine in corrosive action as subsequently described.

EXPERIMENTAL

Since the inhibitor was being developed for aircraft rinsing and for aircraft galley and dry-bay areas, the materials chosen to be tested were those commonly used in aircraft structures and in the Rinse Facility. Three high-strength aluminum alloys--2024-T3, 7075-T6, and 7050--along with high-strength steel, 4130, 4340, cast iron, and 70-30 brass were obtained from a local supplier (Jorgenson Steel, Dayton, OH).

Standard 60 × 30 × 3.125 mm test coupons were used for immersion tests on aluminum alloys. Smaller rectangular sheets with dimensions 75 × 25 × 3.125 mm were used for high-strength steel, brass, and cast iron. These were mechanically polished with emery paper up to 400, cleaned thoroughly in acetone and alcohol, and in several instances finally degreased with petroleum ether. A hole, nearly 5 mm in diam., was made close to one end; and the specimens were suspended by means of a fish line (nylon thread). The maximum duration of these tests has been up to 30 months, but most of the test specimens were immersed in the respective electrolytes for 90 days.

The working electrodes for the electrochemical tests were 25-mm-square pieces which were carefully mounted in resin and were tapped with 3-48 thread for attaching to the electrode holder. All electrochemical tests were carried out in accordance with ASTM Standard G5-72, "Standard Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Standardization Measurements." The measurements were conducted using an automated PAR unit consisting of a corrosion cell, potentiostat/galvanostat, log converter, programmer, and X-Y recorder.

A series of systematic tests were conducted which involved the screening of 1) anodic inhibitors (single component, multicomponent), 2) cathodic inhibitors (single component, multicomponent), 3) a combination of anodic and cathodic inhibitors, and 4) multifunctional systems containing the anodic-cathodic inhibitors. The screening of a large number of combinations was conducted by the potentiodynamic polarization technique and weight-loss methods.

In the immersion tests, the weight loss per unit of surface area of the specimens in different electrolytes was converted to mpy (mils per year). The percentage inhibitive efficiencies were not calculated because the final selection of the inhibitor was based upon the visual observation (where there was no change in surface appearance) and polarization results. In some cases, pieces of aluminum, high-strength steels, brass, and cast iron were suspended together in one electrolyte to check the effectiveness of inhibitors against interfering ions. Finally, the effectiveness of the inhibitor for metallic

parts prone to galvanically coupled conditions was also examined. Galvanic couples were prepared as shown in Fig. 1. Pieces of aluminum, steel, brass, and cast iron were connected through a stainless-steel rod and individually bolted with stainless-steel nuts.

Low-cycle corrosion-fatigue tests [15] were conducted to determine the effectiveness of the inhibitor formulations in retarding crack growth. The rinse inhibitor containing 0.35% (w/o) borate + 0.05% nitrite + 0.1% nitrate + 0.01% silicate + 50 ppm phosphate + 30 ppm MBT and a modified formulation for bilge solution inhibition containing 0.35% (w/o) borate + 0.2% nitrite + 0.2% nitrate + 0.01% silicate + 50 ppm phosphate + 50 ppm MBT + 125 ppm Richonate 1850 were used for this purpose. Compact-tension plane-strain fracture-toughness specimens, (A1 7075-T6) as shown in Fig. 2, were used to determine the crack-growth rate in the presence of uninhibited and inhibited tap water and saline solution and in uninhibited and inhibited natural and synthetic urine. A detailed description of the corrosion-fatigue tests on high-strength aluminum alloys is given in Ref. [15]. Sinusoidal tension-tension cycling was used at a frequency of 0.1 Hz. All tests were performed at a maximum load of 5328N (1200 lbs.) 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. 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 [16].

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

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. 2. The stress-intensity values were calculated from

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

where B and W are the dimensions indicated in Fig. 2 such that B and $a > 2.5 (K_{IC}/YS)^2$, with K_{IC} being the fracture toughness and YS is the tensile yield strength. The crack-length-vs.-number-of-cycles data were converted to fatigue-crack-growth rates (da/dN) using a computer program [16]. Seven to eleven data points were fitted to a second-order polynomial, and the derivative (da/dN) was then obtained for the middle data point. This process was then repeated over the range of data. The da/dN -vs.- ΔK curves were then constructed based upon test data of uninhibited and inhibited solutions.

Commercial inhibitor solutions and aerosols were obtained from the manufacturers or commercial vendors. Reagent-grade chemicals and distilled water were used to make solutions, with the exception of the use of tap water for typical hard-water simulation. The most aggressive solutions used were an aqueous solution containing 0.1M sodium chloride to represent a highly contaminated rinse solution after multiple recycling in the Rinse Facility and the synthetic urine used to simulate the corrosive behavior of natural urine. Most of the tests were conducted in tap water (Wright-Patterson Air Force Base, Dayton, OH). Several tests were performed in the water obtained from the Automated Rinse Facility at MacDill Air Force Base in Tampa, FL. The analysis of the rinse water at MacDill is shown in Table 2. The composition of the synthetic solution, consisting of the most aggressive components of natural urine, is given in Table 3. The corrosive behavior of the synthetic urine was found to closely approximate that of natural urine and was used in most subsequent testing. The polarization behavior of synthetic urine is found to be almost identical to that of natural urine on Al 7075-T6, as shown in Fig. 3.

RESULTS AND DISCUSSION

From the hundreds of polarization and immersion tests that have been conducted in this investigation, a number of representative results have been selected for discussion in this paper. It is important to understand that optimizing inhibitor formulations for aggressive environments such as 0.1M sodium chloride in water and synthetic urine requires many more experiments than will be described here. Initially any new formulation was tested with Al 7075-T6; if the anodic-polarization curve looked encouraging (in terms of current density and the amount of passive region), the performance of the formulation was

checked with high-strength steel and brass. It was found that formulations for aggressive environmental effects that were inhibitive toward the corrosion of high-strength aluminum alloys were generally protective toward other aerospace alloys such as high-strength steels. The converse of this, however, was generally not true.

Figure 4 shows the anodic and cathodic polarization of Al 7075-T6 and Al 2024-T3 in one of the inhibitor formulations. As expected, there is a small difference in the anodic current at the nose level. The difference is more apparent in the cathodic curve; although not clearly shown, the anodic part of the curve has a larger passive region for Al 2024-T3. These two results simply indicate that Al 2024-T3 is more effectively inhibited than Al 7075-T6, possibly due to the fact that Al 2024-T3 is more corrosion resistant than Al 7075-T6 under these conditions. The results of anodic polarization tests of Al 7075-T6 in Wright-Patterson Air Force Base tap water, distilled water, 0.1M NaCl, and one of the inhibitor formulations (0.35% sodium borate, 0.05% sodium nitrite, 0.1% sodium nitrate, 0.01% sodium metasilicate pentahydrate, 50 ppm sodium metaphosphate, and 30 ppm sodium salt of MBT) are shown in Fig. 5.

It is interesting to note that nearly the same level of current density is providing the passivity for aluminum in both distilled water and the inhibited solution. However, the results of the long-time immersion tests show the difference in the corrosion rates of aluminum in these solutions (see Table 3).

Figure 6 shows the performance of the borax-nitrite-base inhibitor as compared to that of sodium nitrate, 1% sodium dichromate, and one of the most promising

commercial inhibitors screened in this investigation. The corrosion current extrapolated against the passive region is least for the borax-nitrite-base inhibitor; at the same time, better passivity is achieved by this formulation. This formulation was found to be effective in inhibiting the corrosion of high-strength steels, aluminum alloys, and copper-bearing materials such as brass.

Borates alone are not particularly effective as inhibitors except for perhaps a limited number of ferrous alloys in mild environments. Nitrites provide a degree of protection to iron and carbon steel in tap water similar to that provided by the chromates; however, higher inhibitor concentrations are required with increasing chloride content to protect against local corrosion [17]. A mixture of borate and nitrite, however, was found to be very effective in the corrosion inhibition of high-strength steels. The borax-nitrite system does not provide satisfactory inhibition to aluminum. Silicates, phosphates, and nitrites are the most commonly known passivators of aluminum. In addition silicates and phosphates [18] provide corrosion inhibition to iron and high-strength steels. The nitrates [19] are known to provide protection to aluminum and its alloys against attack by chloride ions. Hence, a mixture of borate, nitrite, silicate, nitrate and phosphate in the proper concentrations should provide inhibition to iron, steel, and aluminum. Sodium mercaptobenzothiazole was added to the formulation due to the problems expected from the presence of copper ions in the Rinse Facility. The sodium salt of MBT is known [20] to provide inhibition to copper and its alloys. This explains the excellent inhibition provided to aluminum, brass, and steel by the rinse formulation developed in this study as shown by the anodic-polarization results in Fig. 6 and the immersion results in Table 3.

Generally the exact concentration of inhibitor needed depends upon the quality of the water, especially upon the chloride content. The breakdown of the passivity with increasing concentration of chloride ions is demonstrated in Fig. 7. The results show that up to 1000 ppm NaCl, the passive region still occupies nearly a 400-mV portion of the anodic curve and that the corrosion current remains the same. This establishes a conservative limit for effective use of this inhibitor in tap water, even in the presence of 500 - 600 ppm NaCl.

Extensive weight-loss tests were conducted to supplement the polarization experiments. Although these tests are time consuming, they have certain advantages over polarization tests, where small mistakes could result in erroneous conclusions. The results of several weight-loss tests are shown in Table 4, and the corrosion rates calculated represent the average values obtained from five to ten tests. The best results were obtained with the formulation of sodium borate, sodium nitrate, sodium nitrite, sodium metasilicate, sodium phosphate, and sodium salts of MBT which was found to be effective in inhibiting the corrosion of aluminum, copper, and steel in Tampa, FL, water (see Table 2). It is interesting to note the difference in corrosion rates of Al 2024-T3 and Al 7075-T6 when immersed in distilled water and inhibited tap water. According to the anodic-polarization curve, the passivity of aluminum is achieved both in distilled water and inhibited water at the same current-density level as that shown in Fig. 5. However, the long-time immersion test results show a corrosion rate of 0.34 - 0.57 mpy for Al 2024-T3 and 0.051 to 0.95 for Al 7075-T6 in distilled water from weight-loss measurements; no corrosion was detected in the borax-nitrite-base inhibitor solution. This illustrates the need for conducting weight-loss tests in parallel with fast screening polarization tests for adequate evaluation of inhibitor-formulation effectiveness. To

expand the experimental variables of importance, some immersion tests were conducted where a) the solution was stirred, b) only the lower-half portion of the specimen was immersed, c) the specimen was intermittently immersed and dried, and d) the specimen was sprayed with the inhibitor solution. The performance of the borax-nitrite-based inhibitor was excellent in all of these situations.

When the more aggressive synthetic urine environments were employed, it was necessary to improve the effectiveness of the inhibitor system. Figure 8 is the anodic polarization plot of Al 7075-T6 in the synthetic-urine solution with the rinse inhibitor [14] added. The values of Tafel slopes and corrosion current calculated from linear polarization tests are given in Table 5. Concurrent with the polarization tests, immersion experiments were conducted. These results are given in Table 6. These results show that only limited protection is provided by the rinse inhibitor in this aggressive environment. The anodic-polarization curve (Fig. 8) indicates a very small passive region. However, the current density corresponding to the break-down potential (pitting potential) has been lowered as compared to that in synthetic urine. Since the synthetic (and natural) urine contains nearly 1% sodium chloride and since sodium nitrate is known to provide inhibition against chloride ions, several formulations with higher concentrations of nitrites and nitrates were used in the development process. The immersion results in Table 6 suggest that better protection is provided by formulation Nos. 2 and 3. This is mainly the effect of higher nitrite and nitrate concentrations, as indicated earlier. Long-term immersion resulted, however, in the pitting of aluminum and steel. This is

thought to be due to the local breakdown of the passive layer by ions present in the complex chemistry of the synthetic urine. At the same time the corrosion rates as shown in Table 5 decreased only by a small amount and there was only slight improvement in the breakdown (of passivity) potential.

Several modifications of rinse-inhibitor formulations [14] by additions of small concentrations of film formers, chloride absorbers, and a number of chelating agents were tested. Figure 9 shows the effect of the addition of low concentrations of isopropylamine, Triton X-114, and Estersulf. The anodic polarization curves exhibit a large passive region, and the linear polarization results shown in Table 5 represent marked lowering of the corrosion current. The immersion test results on Al 7075-T6 were found to be excellent for some of these formulations. There was no visible corrosion, upon close inspection after six to ten months of immersion. No weight loss could be detected and was reported as negligible. This is consistent with the observation that amines, along with silicates and nitrites, [21,22] provide passivation for aluminum. Vermilyea, et al., [23] have also reported that satisfactory passivation is provided to aluminum by salts of organic acids (sulphonic acid, stearic acid, etc.).

Problems were encountered when pieces of aluminum, steel, and brass were immersed together in the synthetic urine. Some of the formulations which exhibited excellent inhibition to aluminum alloys failed to protect the metals under these conditions. Table 7 gives immersion results for selected formulations. There was evidence that copper ions were dissolving out from the brass and interfering with the inhibiting effect of these formulations. When different metallic materials are present simultaneously in one aggressive electrolyte, it becomes necessary to use a combination of different inhibitors in order to provide protection from the effect of interfering ions on all the materials

present. For the combination of steel and copper or copper and aluminum, in which the corrosion of steel--and particularly of aluminum--is frequently increased by copper ions, corrosion of the copper itself may not be significant. In view of this, the concentration of mercaptabenzothiazole or benzothiazole was increased in some formulations. $ZnSO_4$ was also included in several formulations to provide additional protection to steel. The immersion results of some of these combinations are shown in Table 7. Figure 10 contains the anodic polarization curves for aluminum, brass, and steel. The weight-loss measurements combined with the polarization results show that very effective inhibition is provided by 0.35 w/o borate + 0.2 w/o nitrite + 0.2 w/o nitrate + 0.01 w/o silicate + 50 ppm phosphate + 50 ppm MBT + 125 ppm Richonate 1850. Weight-loss results clearly demonstrate the much improved protection provided by this formulation.

Certain formulations which are effective for general corrosion inhibition actually accelerate corrosion in crevice situations and are crack accelerators. In order to evaluate the effectiveness of the inhibitors in all practical applications, low-cycle corrosion-fatigue tests were conducted. Figure 11 illustrates the corrosion-fatigue behavior of Al 7075-T6 in synthetic urine and synthetic urine inhibited by the formulation developed as a result of the present study. The air result is shown for comparison. The reduction in the fatigue-crack-growth rate due to the addition of the inhibitor can be clearly observed. It is interesting to note that the crack-growth rate is two to three times lower in Region II, as compared to the air value, and five to six times lower than that obtained in uninhibited synthetic urine. The difference in the crack-growth rates in air and inhibited synthetic urine may be due to the fact that the air value is not a vacuum value and, in general, is higher. This

Some problems have arisen with the maintenance of a discrete population of aircraft within the test group and the control group, since some aircraft have been transferred to other stations. It now appears, however, that at least one-half of both groups will be maintained at MacDill Air Force Base for a sufficient time to complete a two to three year test program. As far as the authors know, this is the first attempt to actually track maintenance costs in the use of aircraft rinsing facilities. The general observation has been that this practice is "beneficial," but no cost-effectiveness studies have been conducted.

A view of the Rinse Facility at MacDill Air Force Base is given in Fig. 13. The holding tanks for rinse water, major piping and pumping systems, return tanks, etc., are located underground. Only the control facilities are above ground. The inhibitors are added to a tank holding ~ 11,000 liters of water (~ 3,000 gallons). A forced-air system mixes the inhibitors to effect full dissolution within about 1 min. after addition, and a conductivity bridge is used to monitor inhibitor concentration in the rinse water. When an aircraft passes over an induction coil on the runway, it triggers the rinse system to deliver ~ 560 liters of rinse water in a 15 - 20 sec. time period, pumping at ~ 2,250 liters/min. at the maximum point after startup. Water jets below the runway/taxiway surface direct water to various parts of the aircraft. An F-4 aircraft as it taxis through the facility is shown in Fig. 14.

The method of monitoring the rinse-inhibitor concentration by following the change in conductivity is shown in Fig. 15. Laboratory experiments have shown this to be a reliable and accurate method. The Rinse Facility provides for discharge of the effluent water periodically as contaminants build up

suggests that the introduction of the inhibitor nearly eliminates the environmental influence upon the crack growth. For applications involving high-strength aerospace alloys, it is important to establish this inhibition or elimination of the environmental acceleration of crack-growth rates in the corrosion-inhibiting medium.

In a similar manner the rinse inhibitor has been found to eliminate the environmental effects on crack-growth rates. In Fig. 12 da/dN -vs.- ΔK is shown for Al 7075-T6 in the rinse inhibitor formulation.

RINSE-FACILITY APPLICATION

The borax-nitrite-based inhibitor with additions of nitrate, polyphosphate, metasilicate, and mercaptobenzothiazole was recommended for use in the Rinse Facility as a result of the research efforts in 1978. Experimental use commenced in the summer of 1978 with inhibitors added to the rinse water. In August of 1979 a full-scale test program to evaluate the use of an inhibited rinse was begun on F-4 aircraft stationed at MacDill Air Force Base, FL. The missions of these aircraft emphasize over-sea water exercises at low altitudes; MacDill Air Force Base itself is surrounded on three sides by salt water. In addition the Tampa industrial area contributes substantial suspended particulates and sulfur dioxide to the atmosphere. Thus, it is considered to be a prime area for conducting such tests for the use of automated rinsing to reduce contamination of surfaces and subsequent increased corrosion on operational aircraft. Twenty-five F-4 fighter aircraft were selected to use the Rinse Facility, and a second group of twenty-five F-4's not using the facility was designated as a control group. This test program is still underway, and it is planned that tracking of maintenance costs and corrosion damage will be completed within the next year.

and for the removal of oily water to appropriate disposal facilities. In actual practice, 100 - 200 liters of water are lost on the runway and not returned to the holding tanks after each aircraft rinse. Fresh water is added to the holding tank at this point, and tracking of the inhibitor concentration is essential in determining when additional inhibitors should be added. While this could be accomplished automatically, in the current test it is done manually. Recent experiments have indicated that the action of the rinse-inhibitor formulation may be improved by small additions of a surfactant material (in the parts-per-million level). This change in the rinse-inhibitor composition is planned for late spring of 1981.

CONCLUSIONS

Multifunctional nonchromate inhibitors have been developed for the USAF Automated Rinse Facility to reduce corrosion maintenance costs by removing corrosive contaminants from aircraft which operate in aggressive environments such as those encountered near the sea coast. These inhibitor systems are low cost, water soluble, nontoxic formulations which are effective against general corrosion, localized corrosion, and environmentally assisted crack growth under conditions of stress corrosion and corrosion fatigue.

A synthetic-urine solution has been formulated and found to experimentally reproduce the corrosion behavior of natural urine which is considered to be the most aggressive corrosive environment in the lower-cargo bay, galley, and comfort-station areas of large aircraft.

Extensive polarization and immersion experiments have been conducted to determine and optimize the effectiveness of various inhibitor systems in aggressive media.

A borax-nitrite-based inhibitor containing small additions of nitrate, silicate, phosphate, and mercaptobenzothiazole has been found to provide excellent corrosion protection for the high-strength aluminum and steel alloys used in aerospace applications and for the copper-bearing alloys used in electronic components and in parts of the Rinse Facility. For the bilge environments this inhibitor formulation was improved to provide long-term effectiveness in very aggressive environments. The new formulation is also a borax-nitrite-based inhibitor with 0.35% (w/o) borate, 0.2% nitrite, 0.2% nitrate, 0.01% silicate, 50 ppm phosphate, 50 ppm MBT, and 125 ppm Richonate 1850.

Environmental effects upon crack-growth rates of aluminum and high-strength steel alloys were eliminated--reducing the rates in corrosion fatigue as compared to those obtained in air.

A test program using these inhibitors is currently underway in the USAF Automated Rinse Facility at MacDill Air Force Base, FL. Tracking of maintenance costs and corrosion damage is being conducted to determine the effectiveness of the inhibited rinse in reducing corrosion costs.

REFERENCES

1. L. H. Bennett, J. Kruger, R. L. Parker, E. Passaglia, C. Reimann, A. W. Ruff, and H. Yakowitz, Economic Effects of Metallic Corrosion in the United States, Part I and II, NBS Special Publication 511-1,2 (U. S. Department of Commerce, National Bureau of Standards, Washington, D.C., May 1978).
2. J. DeLuccia, Naval Air Development Center, Warminster, PA, Private Communication, 1-2 December 1975.
3. Data presented at AFLC Corrosion Managers Conference, WRALC, Robins AFB, GA, October 1975.
4. "1975 AFML-AFOSR Corrosion Workshop." AFML-TR-77-175 (Air Force Materials Laboratory, Wright-Patterson AFB, OH, 1977).
5. Corrosion Inhibitors (C. C. Nathan, ed.) (National Association of Corrosion Engineers, Houston, TX, December 1974).
6. The Corrosion and Oxidation of Metals (Second Supplementary Volume) (U. R. Evans, ed.) (Edward Arnold Publishers, Ltd., Great Britain, 1976).
7. J. Green and D. B. Boies, "Corrosion-Inhibiting Compositions," U. S. Patent No. 2,815,328, 3 December 1957.
8. J. T. Bregman and D. B. Boies, Corrosion 14, 275 (1958).

9. K. Bhansali, C. T. Lynch, F. Vahldiek, and R. Summitt, "Effect of Multifunctional Inhibitors on Crack Propagation Rates of High Strength Steels in Corrosive Environments," Prepared discussion presented at the Conference on the Effect of Hydrogen on Mechanical Behavior of Materials, Moran, WY, 7-11 September 1975.
10. F. N. Speller, Discussion, Proc. ASTM 36 (Part 2), 695 (1936).
11. C. T. Lynch, F. Vahldiek, K. J. Bhansali, and R. Summitt, "Inhibition of Environmentally Enhanced Crack Growth Rates in High Strength Steels," Symposium on Environment Sensitive Fracture of Engineering Materials, AIME Meeting, Chicago, IL, 26 October 1977. Proceedings Volume, AIME, 1979, pp. 639-658.
12. C. T. Lynch, K. J. Bhansali, and P. A. Parrish, "Inhibition of Crack Propagation of High-Strength Steels through Single- and Multi-Functional Inhibitors," AFML-TR-76-120 (Air Force Materials Laboratory, Wright-Patterson AFB, OH, 1976).
13. N. I. Saz, Dangerous Properties of Industrial Materials (Second Edition) (Reinhold Publishing Corporation, NY, 1963).
14. M. Khobaib, "Development of Corrosion Inhibitors," AFML-TR-79-4127, Part II (Air Force Materials Laboratory, Wright-Patterson AFB, OH, September 1979).
15. M. Khobaib, C. T. Lynch, and F. W. Vahldiek, "Inhibition of Corrosion Fatigue in High-Strength Aluminum Alloys," To be published in Corrosion.

16. N. E. Ashbaugh, "Mechanical Property Testing and Materials Evaluation and Modeling," AFML-TR-79-4127, Part I (Air Force Materials Laboratory, Wright-Patterson AFB, OH, September 1979).
17. J. Weber, Br. Corr. J. 14(2), 69 (1979).
18. S. O. Lahandy and L. Kastelan, Proc. 4th European Symposium on Corrosion Inhibitors, Ferrara, Italy, 1975, p. 223.
19. H. Bohni and H. H. Uhlig, J. Electrochem Soc. 116, 906 (1969).
20. J. B. Cotton and I. R. Scholes, Br. Corr. J. 2, 1 (1967).
21. G. Schick, Mater. Perf. 23 (February 1975).
22. A. H. Roebuck and T. R. Pritchett, Mater. Perf. 16 (June 1966).
23. D. A. Vermilyea, J. F. Brown, and D. R. Ochaе, J. Electrochem. Soc. 783 (June 1970).

TABLE 1
INHIBITORS

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. GENERAL CONSIDERATIONS

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

TABLE 2

CITY OF TAMPA - WATER DEPARTMENT

AVERAGE DAILY ANALYSIS OF FINISHED WATER

	<u>Color</u> Units	<u>Total</u> <u>Hardness</u> CaCO ₃	<u>Total</u> <u>Alkalinity</u> CaCO ₃	<u>Calcium</u> <u>Hardness</u> CaCO ₃	<u>pH</u> Units	<u>Resid.</u> <u>Chlorine</u>	<u>Temp</u> °F
Max.	4	196	118	164	7.6	3.5	81
Min.	3	171	103	142	7.4	2.7	77
Average	3	181	110	154	7.5	3.2	79

JUNE MONTHLY COMPOSITE
COMPLETE ANALYSIS

(Results expressed in milligrams per liter)

Calcium	Ca	61.6
Magnesium	Mg	7.00
Sulfates	SO ₄	55.
Chlorides	Cl	57.
Fluorides	F	0.32
Sodium	Na	36.0
Potassium	K	3.2
Nitrates	NO ₃	0.08
Silica	SiO ₂	4.4
Manganese	Mn	0.0
Iron	Fe	0.08
Bicarbonates	HCO ₃	136
Phosphates	PO ₄	0.26
Aluminum	Al	0.30
Total Solids		350
Total Hardness	CaCO ₃	180
Total Alkalinity	CaCO ₃	112
Non-Carb. Hardness	CaCO ₃	68
Amonia-Nitrogen	NH ₃	ND
L.A.S.	MBAS	0.03
Copper	Cu	0.03
Color	Units	3
Turbidity	Units	0.7
pH	Units	7.6
Temperature	°F	76
Sp. Conductivity	MMhos	425
B.O.D. (5 days at 20°C)		0.2

TABLE 3
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

TABLE 4
IMMERSION TEST RESULTS

No. of Tests	Electrolyte	pH		Surface Appearance		Corrosion Rate (mpy)		Remarks
		Initial	Final	2024-T3	7075-T6	2024-T3	7075-T6	
5	Tap Water (WPAFB)	7.62	8.48	Stained; several pits.	Couple of oxide patches; several pits.	0.034 to 0.65	0.38 to 0.78	Should be inhibited.
5	0.1M NaCl in Distilled Water	6.95	7.50	Entire surface corroded; several pits.	Entire surface corroded; several pits.	1.38 to 1.98	1.54 to 2.4	Should be inhibited.
5	NALCO 39L (18cc/liter) in Tap Water	9.24	9.00	Looks as original.	Looks as original.	<10 ⁻⁴	<10 ⁻⁴	Very good.
3	Betz 545 (500 ppm) in Tap Water	8.83	8.42	Corners and edges badly pitted; surface fairly clean.	Entire surface dark; several pits.	0.017 to 0.063	0.028 to 0.054	Poor.
5	Calgon Inhibitor CS (4000 ppm) in Tap Water	8.90	8.80	Light tinted scale all over; no visible pits.	Light tinted scale all over; no visible pits.	0.067 to 0.088	0.083 to 0.092	Poor.
3	1% Sodium Dichromate in Tap Water	5.80	5.80	Surface looks as original.	Surface looks as original.	<10 ⁻⁴	<10 ⁻⁴	Very good.
3	0.1% (Sodium Metasilicate + Sodium Polyphosphate) in Tap Water	8.64	8.45	Surface looks as original.	Surface looks as original.	<10 ⁻⁴	<10 ⁻⁴	Very good.
8	0.35% Sodium Borate + 0.05 Sodium Nitrite + 0.1 Sodium Nitrate + 0.01 Sodium Silicate + 50 ppm Polyphosphate + 30 ppm MBT in Tap Water	8.78	8.84	Surface looks as original.	Surface looks as original.	<10 ⁻⁴	<10 ⁻⁴	Excellent.

TABLE 5
TAFEL SLOPES AND CORROSION CURRENTS
IN DIFFERENT ELECTROLYTES
OF Al 7075-T6

ELECTROLYTE (wt%)	TAFEL SLOPES (mV/decade)		i corr ₂ ($\mu\text{A}/\text{cm}^2$)
	ba	bc	
Synthetic Urine	100	135	6.24
Synthetic Urine + Rinse Inhibitor	120	160	3.42
Synthetic Urine + Rinse Inhibitor + 0.15 Nitrite + 0.1 Nitrate (INH)	160	130	2.44
Synthetic Urine + INH + 75 ppm Triton X-114	100	150	0.78
Synthetic Urine + INH + 100 ppm Estersulf	120	90	1.08
Synthetic Urine + INH + 100 ppm Isopropylamine	120	80	1.41
Synthetic Urine + INH + 125 ppm Richonate 1850	100	125	0.544
Synthetic Urine + INH + 125 ppm Richonate + 500 ppm ZnSO ₄ + 50 ppm MBT	120	135	0.63

TABLE 6
IMMERSION TEST RESULTS ON A1 7075-T6

TYPE NO.	ELECTROLYTE (wt%)	mpy	pH		TIME OF EXPOSURE	SURFACE APPEARANCE
			INITIAL	FINAL		
1	Synthetic Urine	0.23	5.6	5.8	3 Mo.	Nearly 20% surface area pitted.
2	Natural Urine	0.18	5.8	6.0	3 Mo.	Nearly 25% surface area pitted.
3	Synthetic Urine + Rinse Inhibitor	0.12	8.30	8.25	3 Mo.	Several pits on the surface.
4	Synthetic Urine + Rinse Inhibitor + 0.15 Nitrite + 0.1 Nitrate	0.078	8.35	8.35	3 Mo.	Surface clean, very light corrosion.
5	Synthetic Urine + Rinse Inhibitor + 0.25 Nitrite + 0.2 Nitrate	Negl.	8.40	8.35	3 Mo.	Clean as original. No sign of corrosion.
6	No. 4 + 25 ppm Triton X-114	Negl.	8.30	8.30	3 Mo.	Clean as original. No sign of corrosion.
7	No. 4 + 75 ppm Estersulf	Negl.	8.35	8.30	3 Mo.	Clean as original. No sign of corrosion.

TABLE 7

TEST RESULTS OF AL, BRASS, AND STEEL
SPECIMENS IMMERSSED TOGETHER

SPECIMEN	ELECTROLYTE (wt%)	pH		TIME OF EXPOSURE	SURFACE APPEARANCE
		INITIAL	FINAL		
Al 7075-T6	0.35 Borate + 0.2 Nitrite + 0.2 Nitrate + 0.01 Silicate + 50 ppm Phosphate + 25 ppm MBT (INH) + 250 ppm Isopropylamine in Synthetic Urine,	8.45	8.30	3 Mo.	50% area pitted.
Brass				3 Mo.	Slowly dissolv- ing into solution.
Steel				3 Mo.	Several pits.
Al 7075-T6	INH + 25 ppm Triton X-114 in Synthetic Urine.	7.75	7.60	3 Mo.	Several large pits.
Brass				3 Mo.	Clean but dull.
Steel				3 Mo.	Pitted - dull.
Al 7075-T6	INH + 25 ppm Triton X-114 + 100 ppm ZnSO ₄ in Synthetic Urine.	7.65	7.60	3 Mo.	Clean and shiny.
Brass				3 Mo.	Clean.
Steel				3 Mo.	One corner pitted.
Al 7075-T6	INH + 75 ppm MBT + 125 ppm Richonate 1850 in Synthetic Urine.	8.25	8.20	3 Mo.	Clean and shiny as original.
Brass				3 Mo.	Clean, as original.
Steel				3 Mo.	Clean, as original.
Al 7075-T6	INH + 50 ppm Estersulf in Synthetic Urine.	8.30	8.20	3 Mo.	Clean, few pits.
Brass				3 Mo.	Clean.
Steel				3 Mo.	Clean, but several fine pits.
Al 7075-T6	AML Guard in Synthetic Urine.	6.90	6.95	3 Mo.	Nearly 20% area badly pitted.
Brass				3 Mo.	Nearly 20% area badly pitted.
Steel				3 Mo.	More than 50% area badly pitted.
Al 7075-T6	1% Boeshield T-9 in Synthetic Urine.	5.10	5.15	3 Mo.	Several large pits and number of small pits.
Brass				3 Mo.	Dull, one pit.
Steel				3 Mo.	Several large pits and number of small dark pits.

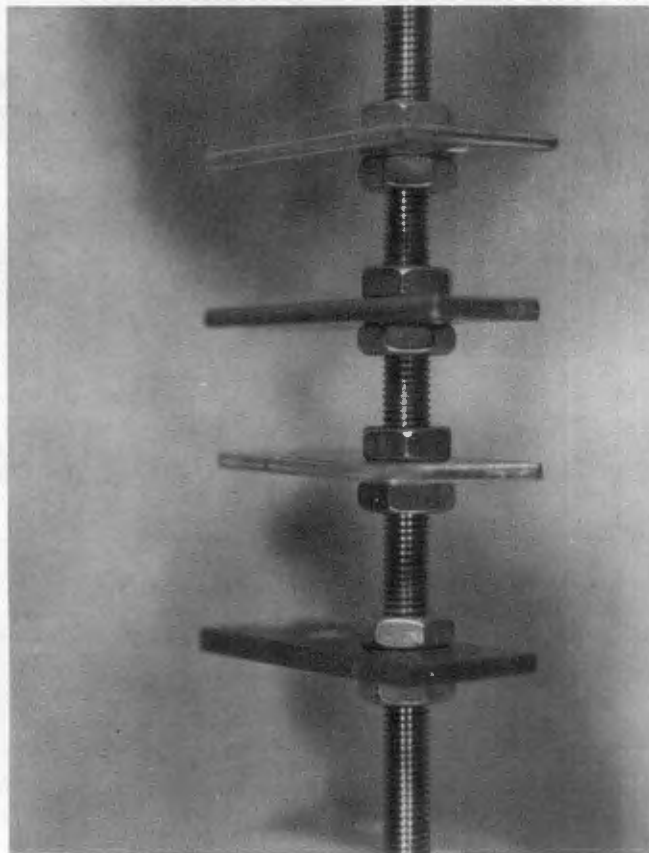


Figure 1. Galvanic Couple.

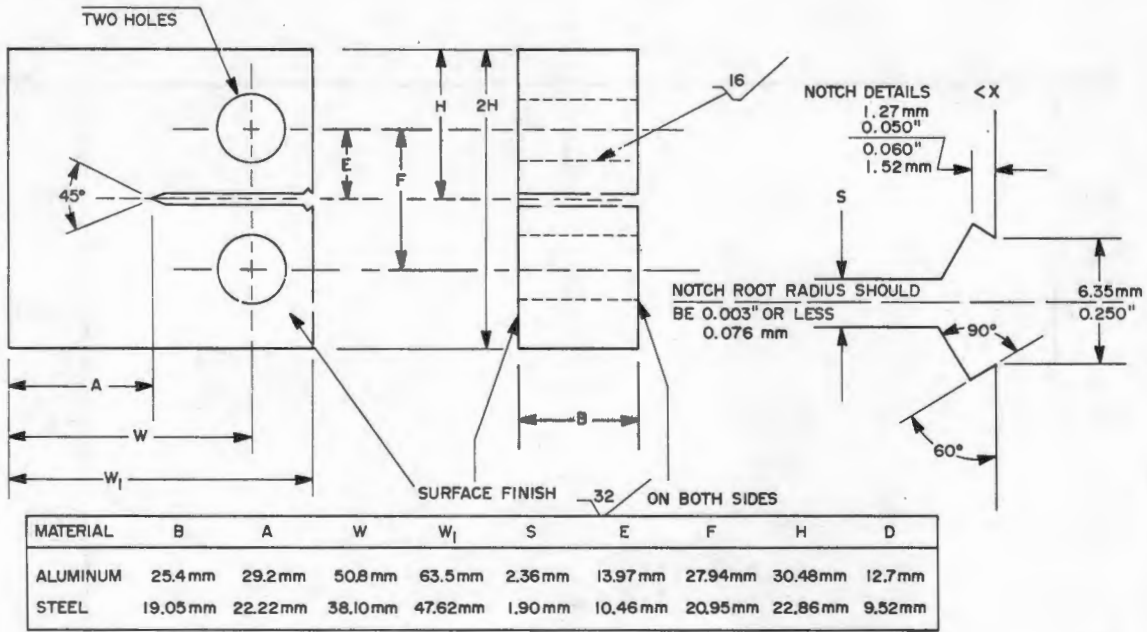


Figure 2. Compact-Tension Specimen.

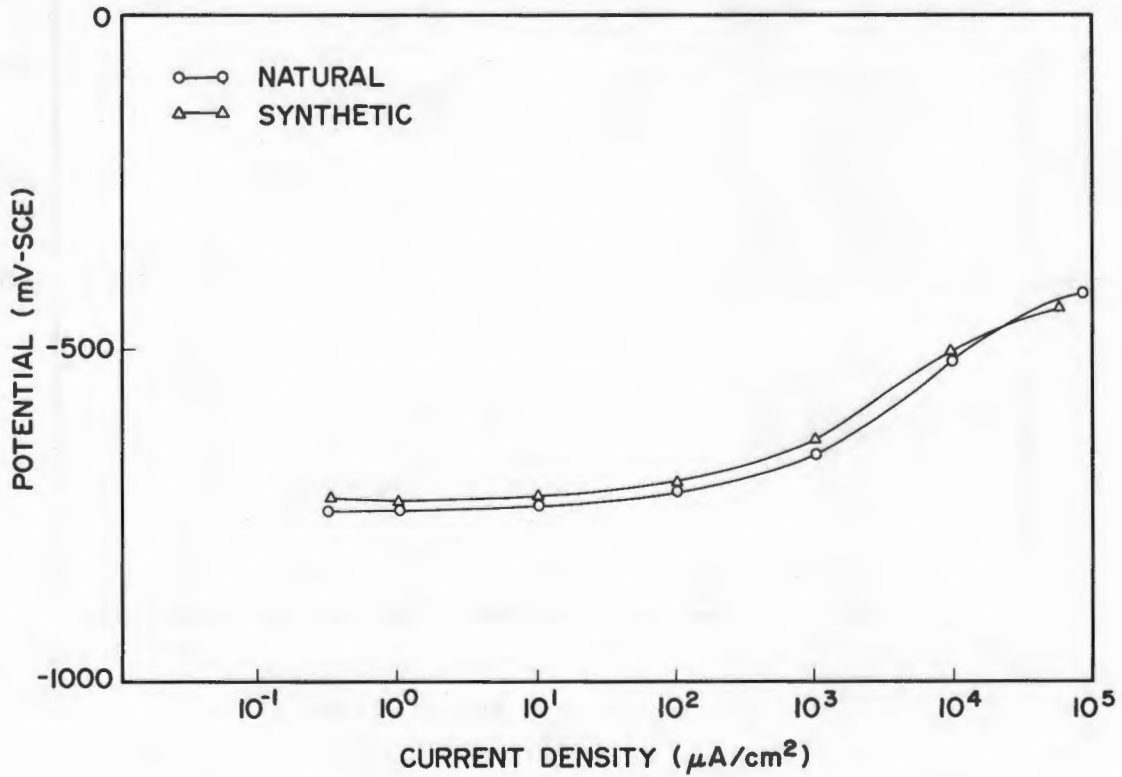


Figure 3. Comparison of Anodic Polarization Behavior of Al 7075-T6 in Synthetic and Natural Urine.

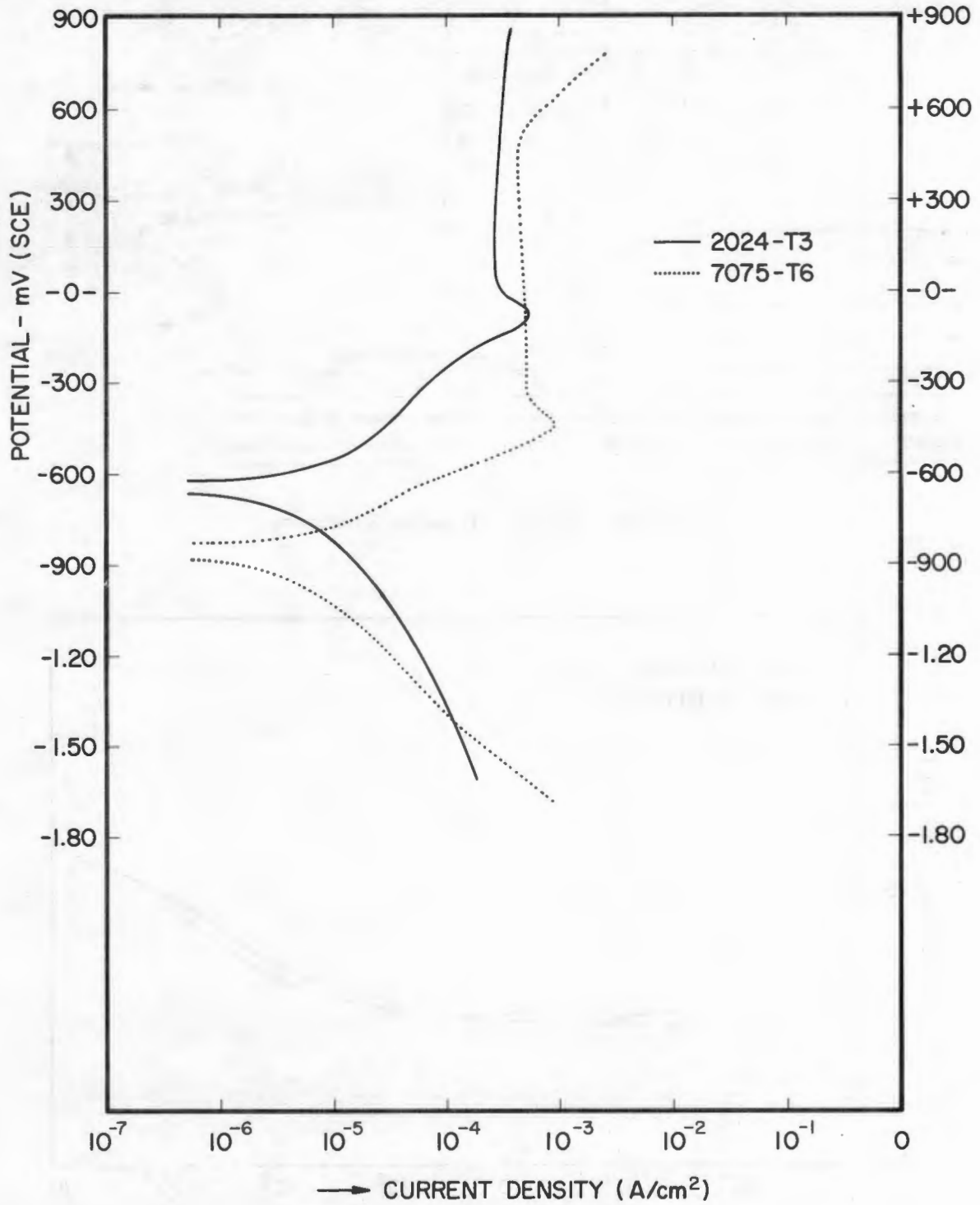


Figure 4. Anodic and Cathodic Polarization Curves for Al 2024-T3 and Al 7075-T6 in an Inhibited Solution.

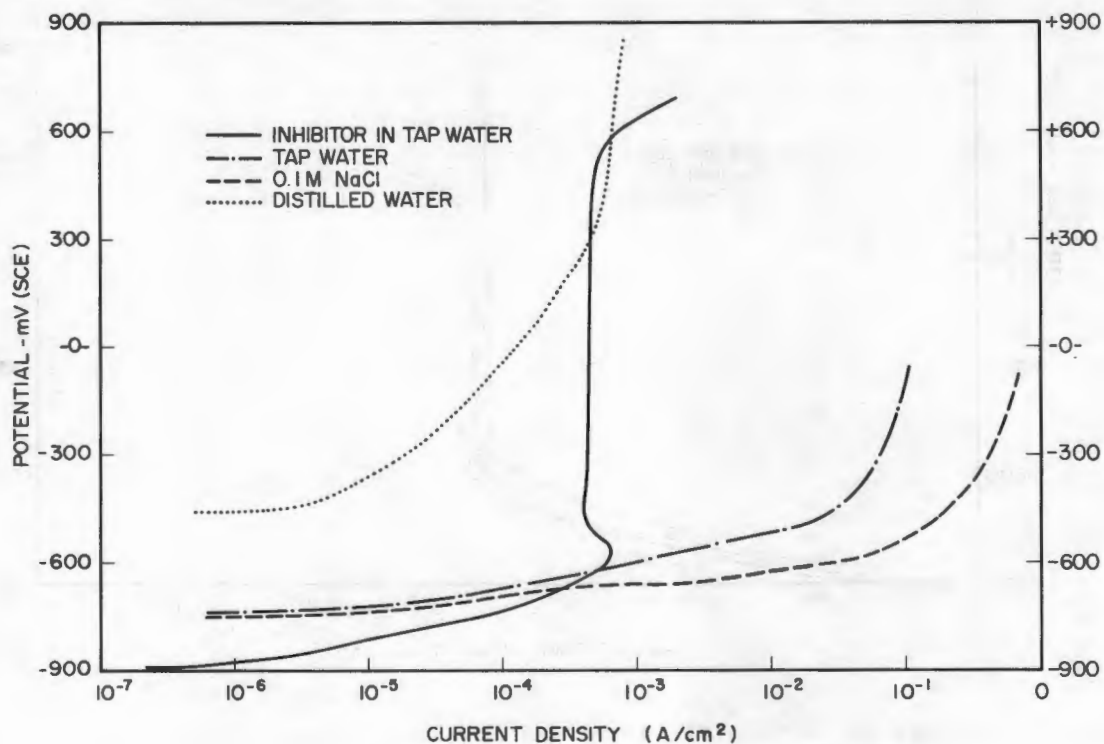


Figure 5. Anodic Polarization Curves for Al 7075-T6 in Tap Water, Distilled Water, 0.1M NaCl and Inhibitor.

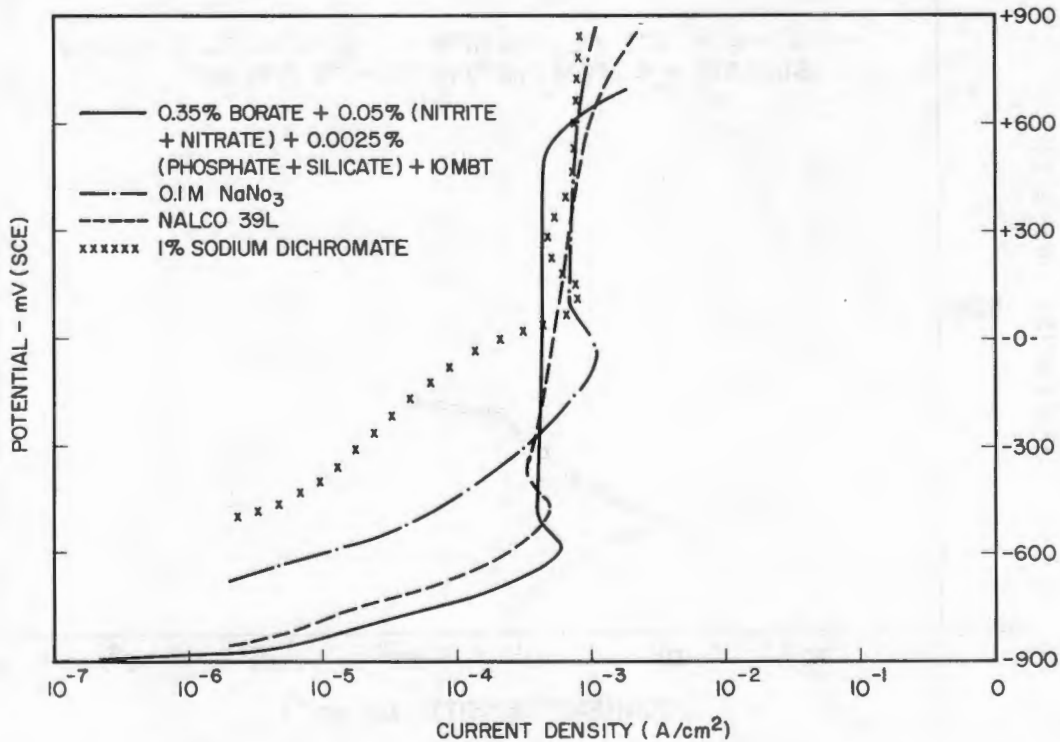


Figure 6. Anodic Polarization Behavior of Al 7075-T6 in Different Inhibitors.

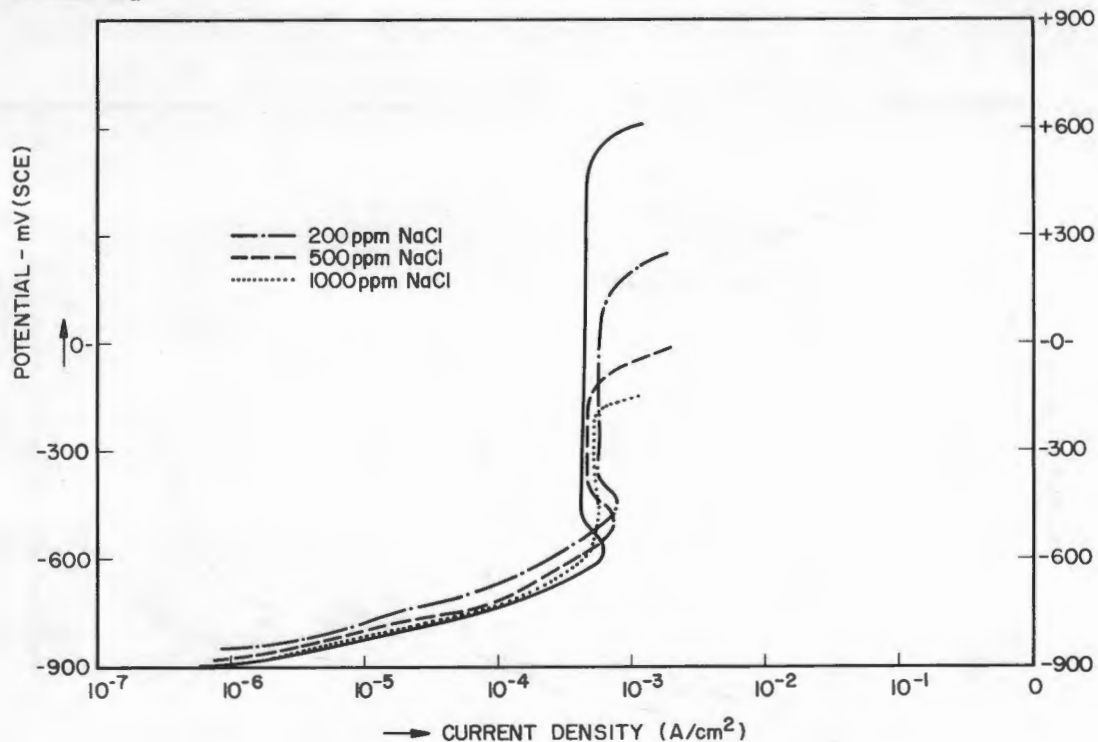


Figure 7. Effect of Increasing Chloride Concentration Upon the Pitting Behavior of Al 7075-T6 in an Inhibited Solution.

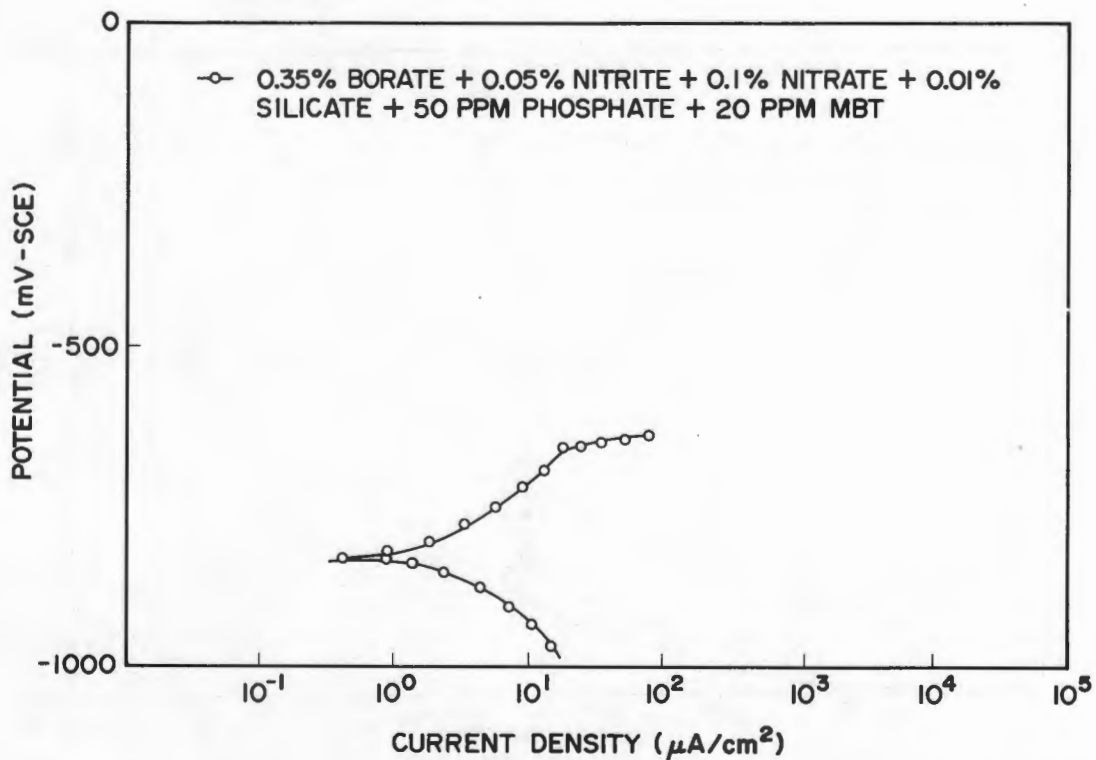


Figure 8. Anodic and Cathodic Polarization Behavior of Al 7075-T6 in Synthetic Urine Inhibited by Rinse Formulation.

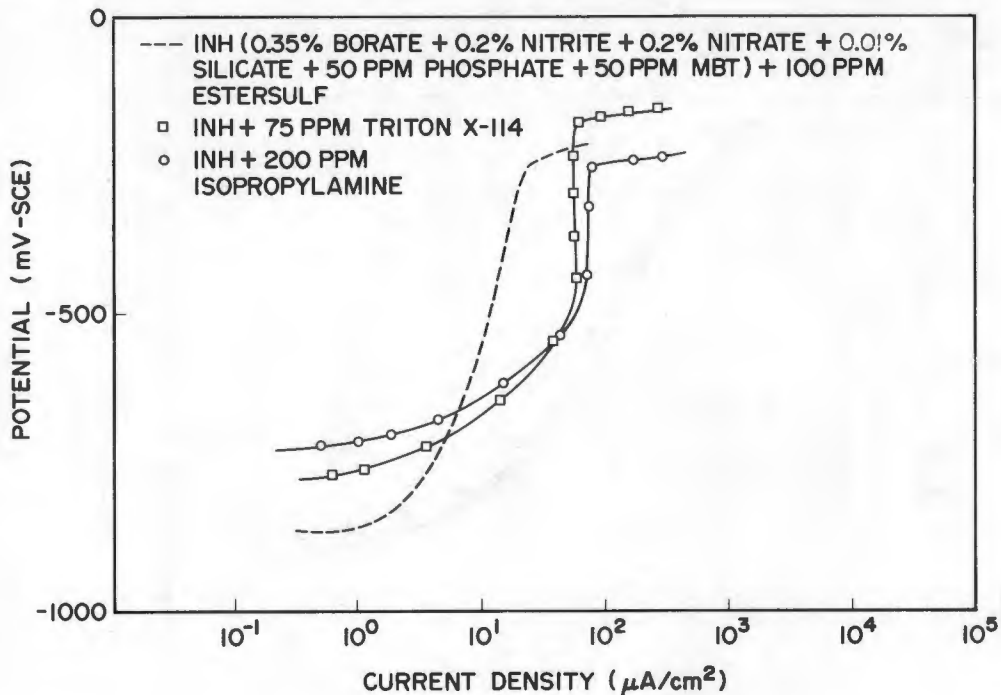


Figure 9. Effect of Addition of Estersulf, Triton X-114, and Isopropylamine Upon the Anodic Polarization of Al 7075-T6.

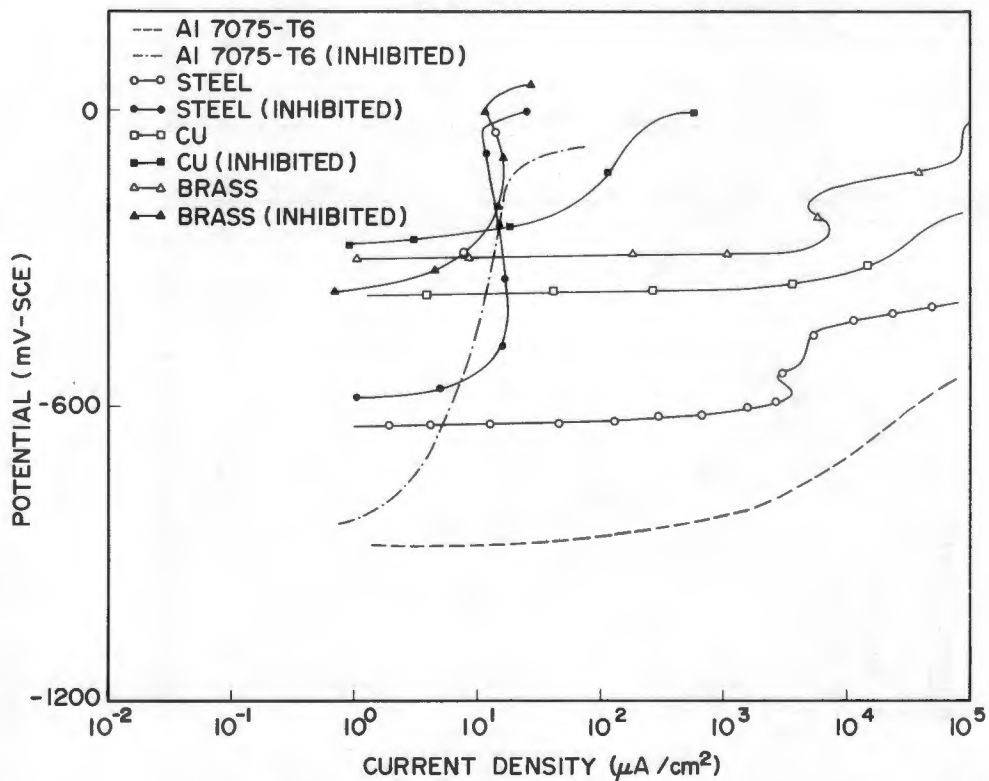


Figure 10. Anodic Polarization Behavior of Al 7075-T6, Steel, Copper, and Brass in Inhibited Synthetic Urine.

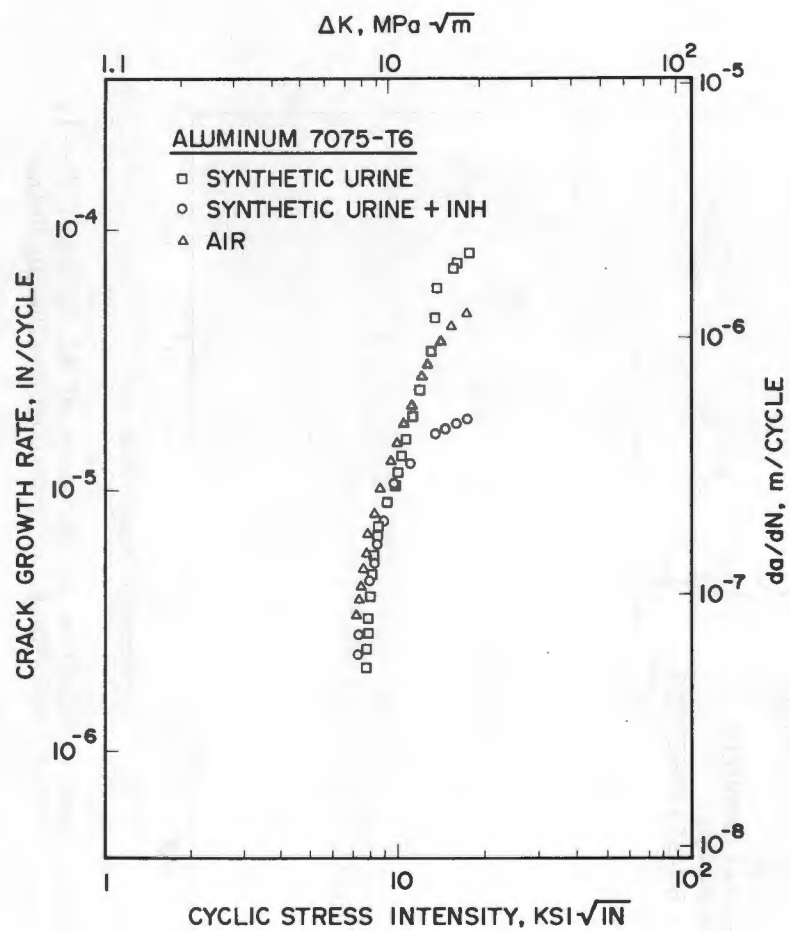


Figure 11. Comparison of Crack-Growth Rates of Al 7075-T6 in Air and Inhibited and Uninhibited Synthetic Urine.

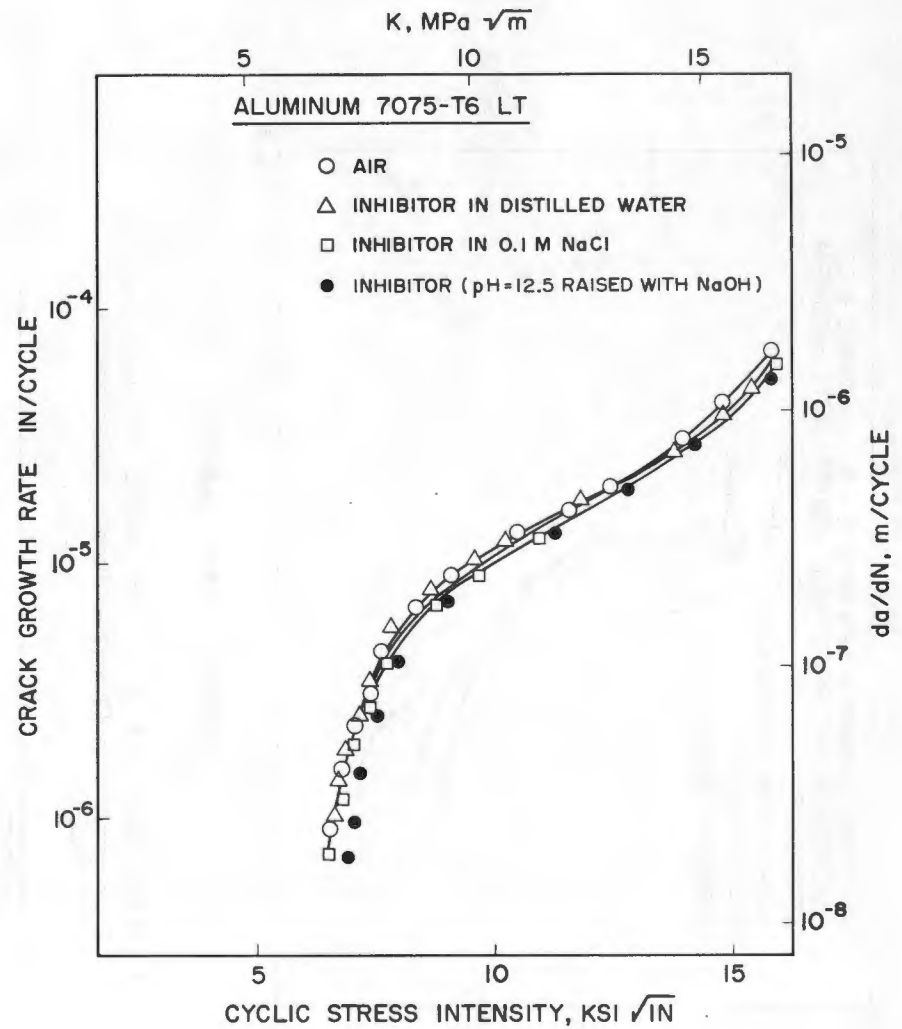


Figure 12. Effect of Rinse Inhibitor Upon Crack-Growth Rates of Al 7075-T6 LT.



Figure 13. View of the USAF Automated Rinse Facility.



Figure 14. F-4 Aircraft Taxiing Through the Rinse Facility.

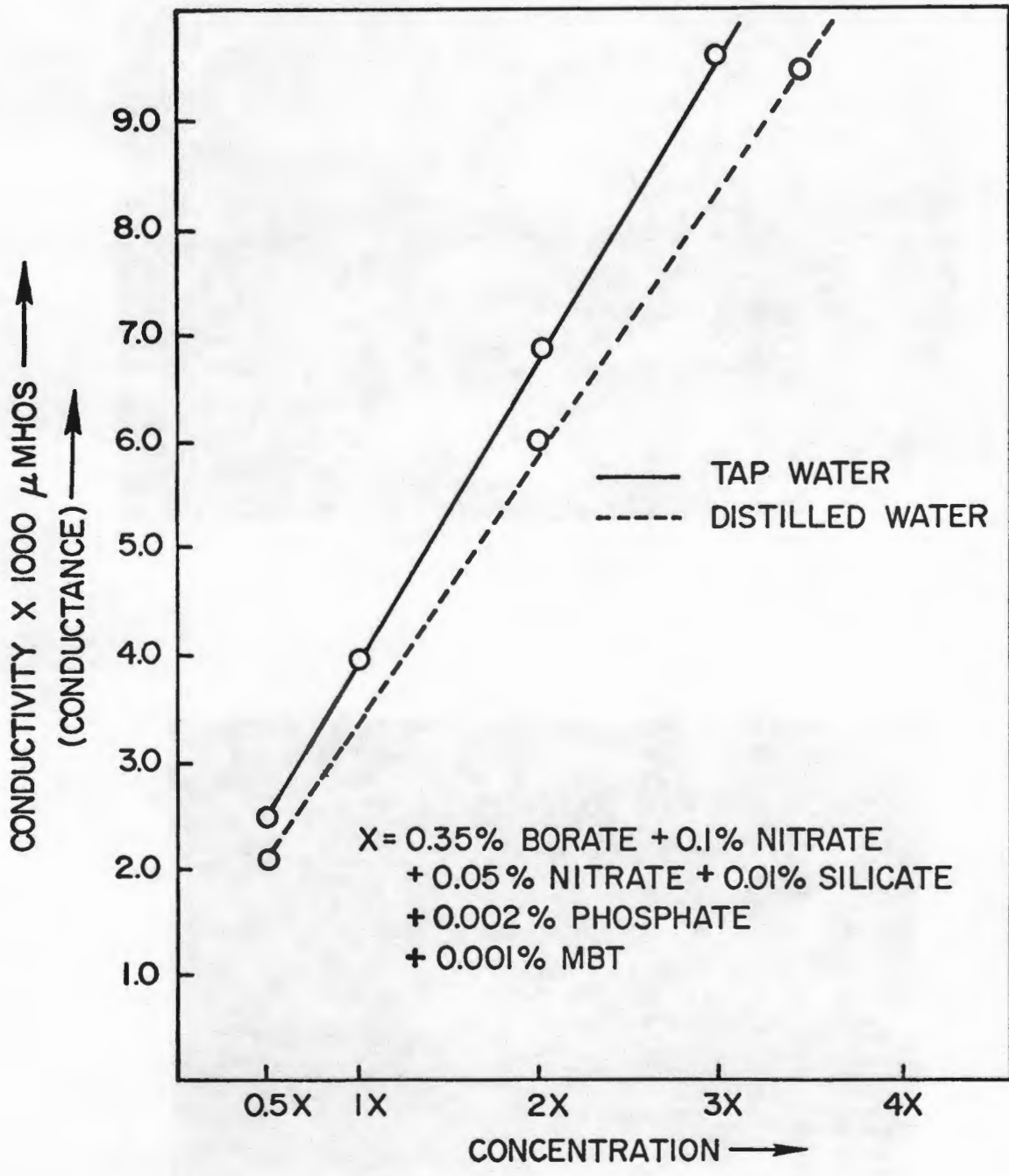


Figure 15. Calibration Chart of Conductivity as a Function of Inhibitor Concentration.