

SELECTING AN ALGICIDE FOR USE WITH ALUMINUM ALLOYS

bу

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SELECTING AN ALGICIDE FOR USE WITH ALUMINUM ALLOYS

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ABSTRACT

Six commercially available algicidal compounds were evaluated for (1) relative toxicity to various concentrations of seven species of algae and (2) potential for causing pitting corrosion of aluminum alloys. Diuron (a common herbicide) and the acetic acid salt of a technical grade of dehydroabietylamine were the two compounds moxt toxic to algae. A filming amine corrosion inhibitor ranked third in toxicity. Potassium permanganate, which ranked fourth in algicidal effectiveness, was least corrosive and was the only compound for which no pitting corrosion was measurable. Hydrogen peroxide ranked fifth in toxicity. The chlorine-liberating algicide sodium hypochlorite was found to be substantially inferior to the other five compounds in both toxicity and corrosiveness. New techniques for the evaluation of algicides are described.

- Fig. 1 Percentages of algal cultures which required each of four minumum lethal algicidal concentrations. Comparisons between 84 cultures containing the lowest and highest initial cell densities of seven species are shown.
- Fig. 2 Cyclic potentiodynamic polarization curve for 6063-Al in air-saturated 0.01M KMnO4.
- Fig. 3 Pits on 6063-Al after cyclic potentiodynamic polarization in air-saturated 0.01M NaOC1.
- Fig. 4 Pit on 6063-Al after cyclic potentiodynamic polarization in air-saturated 2 g/L DCMU.
- Fig. 5 Crystallographic etching on 6063-Al after cyclic potentiodynamic polarization in air-saturated 2 mL/L ADA.
- Fig. 6 Pit on 6063-Al after potentiostatic anodic polarization in air-saturated 2 g/L DCMU.
- Fig. 7 Crystallographic etching on 6063-Al after potentiostatic anodic polarization in air-saturated 0.01M H_2O_2 .

Introduction

Aluminum alloys are particularly susceptible to localized corrosion attack. Algicides to be used in a system constructed wholly or partially of aluminum alloys should be evaluated for their ability to cause localized corrosion. For example, copper sulfate, a common algicide, severely pits most aluminum alloys. Little information has been published about (1) the susceptibility of aluminum alloys to pitting when these alloys are exposed to aqueous solutions of algicides or (2) the effectiveness of inexpensive, commercially available algicidal chemicals except for the corrosive copper sulfate and chlorine-liberating products.

A chlorine-liberating algicide, sodium hypochlorite (NaOC1), was found to be responsible for localized corrosion of aluminum in water basins at the Savannah River Plant near Aiken, S.C. Based on a comprehensive literature search, five commercially available chemicals were selected for evaluation and comparison with NaOCl for effectiveness as algicides and tendency to cause pitting corrosion of aluminum alloys: (1) hydrogen peroxide (H₂O₂), (2) potassium permanganate (KMnO4), (3) a filming amine corrosion inhibitor* (PRAD), (4) the acetic acid salt of dehydroabietylamine † (ADA), and (5) Diuron weed killer (DCMU). PRAD and ADA are synthesized by reacting a technical grade of dehydroabietylamine with ethylene oxide and acetic acid, respectively. Diuron is 3(3,4-dichlorophenyl) 1,1-dimethylurea and, in this investigation. was obtained by using a commercial weed killer which is a wettable powder containing 80% Diuron. ††

^{*} Polyrad® 1110A (Hercules Co.)
+ Amine D acetate 50S (Hercules Co.)
++ Karmex® (Du Pont)

Methods and Materials

Algicidal effectiveness. Many authors 1-6 have pointed out the large number of variables that determine the actual concentration of a chemical necessary to kill algae in a particular field situation. Experiments were thus directed toward comparing the six selected algicidal chemicals rather than determining a specific minimum lethal concentration of a specific chemical that would be applicable under all conditions.

Nonaxenic unialgal cultures of seven species representing three major algal divisions were tested. Sources of original algal material and culturing conditions for the experiments are listed in Table 1. The sixteen experiments included at least two with different initial cell densities for each algal species.

All seven species had been subcultured for several months and had previously demonstrated excellent growth under the experimental conditions.

Experiments were initiated by placing 12.5-mL of medium into each of 21 cotton-plugged 50-mL Erlenmeyer flasks. These flasks were then sterilized and 12.5-mL aliquots of an algal culture in early to mid-exponential stage of growth were added. A 1 mL aliquot was microscopically analyzed to estimate the initial cell density. The six algicidal compounds were tested as received. Algicides were prepared at 1, 10, and 100 ppm by adding chemicals to the flasks; final concentrations were 1, 10, and 100 mg/L of KMnO $_4$ and DCMU and 1, 10, and 100 μ L/L of 30% $\rm H_2O_2$, PRAD, ADA and 15% NaOC1. Three untreated flasks

served as controls in each experiment. Flasks were placed in a temperature-controlled greenhouse (first ten experiments) or an environmental chamber equipped with a light programmer set for a 12 hr light/12 hr dark cycle (last six experiments). Assessments of mortality were primarily based on fluorescence microscopical examinations of samples after treatment times of 24 hr, 48 hr, 1 wk, and 2 wk. This microscopical technique facilitated the differentiation between live cells containing chlorophyll (red fluorescence emission) and recently killed cells containing chlorophyll degradation products (yellow fluorescence emission). The degree of mortality of cells treated for 24 hr and 48 hr with DCMU, which inhibits photosynthesis rather than causing direct cell destruction, was questionable in the microscopical examinations; consequently the subculturing technique described by Fitzgerald and Faust 10 was employed at - these two time intervals. Determinations of complete mortality based on the growth of algae in subcultures were identical to the determinations made by fluorescence microscopy in all other cases.

Aluminum alloy pitting. This part of the study was to rank the six algicides according to their tendency to cause pitting of aluminum alloys. None of the generally accepted approaches to such a study precisely duplicate the phenomena observed in actual service. In theory, the best approach is to rank the algicides according to pitting potentials measured using some alloy of interest. In practice, pitting potentials cannot be reliably measured. 11

The approach chosen for this investigation is based on three different types of tests: (1) coupon, (2) cyclic potentiodynamic polarization, and (3) potentiostatic anodic polarization. In general, the probability that a test specimen will undergo pitting corrosion in a particular algicide solution increases progressively from the coupon test to the potentiostatic test. The algicide that causes pitting in the greatest number of tests is the most aggressive pitting agent.

The solutions used in these tests were at least ten times more concentrated than would be required from an algicidal standpoint. Concentrated solutions were used in order to magnify any aggressive tendency. The concentrations used throughout were 0.01 M solutions of KMnO₄, H_2O_2 , and NaOC1; 2 mL/L solutions of PRAD and ADA; and a 2 g/L solution of DCMU.

Preliminary testing with a variety of alloys (1100, 6063, 8001, and pure Al) indicated that 6063-Al is the most susceptible to pitting corrosion. For this reason, 6063-Al was used in all pitting tests, although the coupon and cyclic potentiodynamic polarization tests were repeated with 1100-Al and pure Al. These duplicate tests were consistent.

All specimens were 4 by 4 by 0.1 cm cold-rolled 6063-Al polished with 600-grit paper. After polishing, the specimens used in the potentiostatic test were dipped in hot phosphoric-nitric solution to further remove surface blemishes.

Coupon test. Six specimens were placed in ~250 mL of the six algicides. The solutions were changed every two weeks.

After 128 days, the specimens were removed and examined by scanning electron microscopy (SEM).

Cyclic potentiodynamic polarization test. Polarization curves were obtained by (1) immersing a specimen in ~500 mL of test solution contained in an electrochemical cell, (2) allowing the specimen to stand on open-circuit for one hour, and (3) performing cyclic polarization starting at the open-circuit potential and proceeding with descending cathodic, ascending cathodic, ascending anodic, and descending anodic scans. The extent of scan was two volts on both sides of the open-circuit potential, and the scan rate was 1 mv/sec. The solutions were air saturated. Polarization curves were obtained using a PAR 173 potentiostat with logarithmic current converter, a PAR 175 universal programmer, and a PAR 9002A X-Y recorder. After polarization, each specimen was examined by SEM.

Potentiostatic anodic polarization test. Curves of opencircuit potential vs. time and applied current vs. time were obtained by (1) immersing a specimen in ~500 mL of test solution contained in an electrochemical cell, (2) recording open-circuit potential vs. time until a steady state was achieved, (3) anodically polarizing the specimen and recording current vs. time at least until a steady state was achieved, and (4) re-establishing open circuit and repeating Step 2. The solutions were air saturated. Data were obtained with a Wenking LB75M potentiostat and an HP 7100BM recorder. After the post-polarization open-circuit potential measurement, each specimen was examined by SEM.

Results and Discussion

Algicidal effectiveness. Table 2 shows the relative toxicity ranking of the six algicides in each of the 16 experiments. A relative value of 1 (most effective) through 6 was given to the algicides. DCMU and ADA were consistently more effective. These two were followed in order of decreasing toxicity by PRAD, KMmO4, H2O2, and NaOC1. The variation in ranking attributable to differential responses of the compounds to different algal species was not substantial. In fact, the variability in relative toxicity observed in two or three experiments with the same species was generally as great. Variability in results from experiments with a single species is attributed to the use of different initial cell densities and the lack of identical environmental conditions for all experiments.

The overall ranking of the six algicides was the same for all four treatment times, and 24 hours of treatment was as effective as 2 weeks of treatment for more than 50% of the samples. However, comparison of treatment times of 24 hr and 2 wk by algicide and by taxon (Table 3), shows that all algicides became more effective over time in at least one experiment. PRAD increased the most in algicidal effectiveness during the two-week treatment periods. Among taxa, the diatom *Nitzschia* required the longest

treatment time to be killed, probably because diatom cells contain a siliceous frustule, or shell, which may reduce the speed at which toxic chemicals can penetrate the cells.

The necessary concentration of all six algicides appeared to be directly proportional to the density of algae subjected to treatment (Fig. 1). The amount of toxicant per cell is undoubtedly an important criterion in the determination of the minimum lethal concentration of any algicide. 4

Aluminum alloy pitting. The appearance of each of the coupon test specimens is described in Table 4. The precipitate on the specimen exposed to KMnO₄ solution was probably MnO₂ formed during the spontaneous reduction of MnO₄. The complementary oxidation process was the oxidation of aluminum with no contribution from the oxidation of water because the open-circuit potential of 6063-Al in KMnO₄ is more negative than the reversible potential for oxygen evolution (see Table 5). The precipitate on the specimen exposed to PRAD solution resulted because PRAD is a filming amine. A film was also observed on the specimen exposed to ADA solution. In the coupon test, pitting occurred only on the specimen exposed to NaOC1 solution.

A typical cyclic potentiodynamic polarization curve is shown in Fig. 2. The cathodic portion of a cyclic potentiodynamic scan is useful as a final cleaning step, but it provides no information concerning pitting susceptibility. However, pitting susceptibility can be predicted fairly reliably from the anodic

portion of a scan. If the descending anodic curve is shifted to lower currents (positive hysteresis) or if the descending curve essentially retraces the ascending curve (neutral hysteresis), the solution is not an aggressive pitting agent and no pitting is expected. However, if the descending curve is shifted to higher currents than the ascending curve (negative hysteresis), the solution is probably an aggressive pitting agent and pitting is expected. Figure 2 shows an example of positive hysteresis. For this study, anodic hysteresis was measured by subtracting the descending current density from the ascending current density measured at a potential 1000 mV more noble than the open-circuit. potential. Another approach would be to determine the area enclosed between ascending and descending curves. The concept of anodic hysteresis can assist in the determination of pitting susceptibility; particularly when well defined pits do not develop during cyclic polarization.

Anodic hysteresis values are given in Table 6. Hysteresis was positive with KMnO₄ solution, with no pitting. Hysteresis was also positive with PRAD, with no pitting. With H₂O₂ solution, hysteresis was nearly neutral with no observable pitting. With NaOCl solution, hysteresis was strongly negative, and the test specimen was speckled with well defined pits (Fig. 3). Hysteresis was also negative with DCMU solution and pitting was extensive (Fig. 4). ADA solution produced a fairly strong negative hysteresis, but not pitting. Isolated regions of surface damage were apparent

however, and this damage took the form of superficial crystallographic etching (Fig. 5). In this instance, crystallographic etching may logically be viewed as a precursor to pitting because (1) substantial negative hysteresis was observed during cyclic polarization in ADA solution and (2) crystallographic etching of the type shown in Fig. 5 is nearly identical to the structure observed in the interior of pits produced in 6063-Al by either potentiodynamic or potentiostatic anodic polarization.

In the cyclic potentiodynamic polarization test, specimens exposed to NaOCl solution and DCMU solution were pitted. Surface damage, in the form of crystallographic etching (a precursor to pitting), was observed on the specimen exposed to ADA solution.

In the potentiostatic anodic polarization test, 6063-Al was anodically polarized at potentials near 1000 mv more noble than the steady-state pre-polarization open-circuit potentials. Well-established pitting was observed with solutions of NaOCl, DCMU, ADA, and PRAD. The interior of each pit possessed a crystallographic structure similar to that shown in Fig. 5. Figure 6 shows a typical pit. Pitting was not observed with H_2O_2 solution, but the specimen surface was characterized by etched regions (Fig. 7). The structure in Fig. 7 is not as well defined as that in Fig. 5, but its crystallographic nature is still apparent. In this instance, crystallographic etching may not be a precursor to pitting because both surface damage and substantial negative hysteresis were absent in the cyclic potentiodynamic polarization

test. No pitting or surface damage was observed on the specimen exposed to $KMmO_{\,4}$ solution.

Additional results of the potentiostatic anodic polarization test are contained in Table 5. For each algicide, the steadystate pre-polarization open-circuit potential was more positive than the steady-state post-polarization open-circuit potential. The decrease in open-circuit potential was most pronounced for those algicides that did not cause pitting. Also, for each algicide, the pre-polarization and post-polarization open-circuit potentials were more negative than the reversible potential for oxygen evolution. Because the solutions were saturated in air, oxygen was probably reduced under open-circuit conditions in all six algicidal solutions. Reduction of oxygen was probably the dominant open-circuit reduction process in solutions of the three organic materials. In solutions of KMnO₄, H₂O₂, and NaOC1, the reduction of oxygen was supplemented by the reduction of MnO₄ to MnO₂, H₂O₂ to H₂O, and ClO⁻ to Cl⁻, respectively.

In the potentiostatic anodic polarization test, pitting occurred on the specimens exposed to NaOC1, DCMU, ADA, and PRAD solutions. Surface damage, in the form of crystallographic etching, was observed on the specimen exposed to $\rm H_2O_2$ solution.

The results of the pitting study are summarized in Table 7. The algicides may be ranked in the following order (starting with the least aggressive): $KMnO_4$, H_2O_2 , PRAD, ADA, DCMU, and NaOC1. The average steady-state current densities, obtained during

potentiostatic anodic polarization, reflect essentially the same order, with the least aggressive pitting agent producing the lowest current density (see Table 5). Thus, during potentiostatic anodic polarization, the oxidation process is dominated by anodic dissolution in pits, with other processes (such as the oxidation of water) proceeding at a substantially slower rate.

Conclusions

Five relatively noncorrosive commercially available compounds were compared with one another and with sodium hypochlorite for their potential applicability as algicides in water systems containing aluminum alloys. Potassium permanganate (KMnO₄) appeared to be the most suitable compound when corrosion prevention is of prime concern. This algicide ranked fourth in terms of algicidal effectiveness, but was the only compound for which no pitting corrosion or surface damage of any type was observed in the most sensitive (potentiostatic anodic polarization) corrosion test.

Use of KMnO₄ as an algicide has previously been reported. 12-18

Hydrogen peroxide (H_2O_2) and PRAD, which ranked fifth and third, respectively, in toxicity tests, showed very slight corrosion potential and would probably be suitable in situations where trivial corrosion could be tolerated. H_2O_2 has been recommended for use in cooling towers in Czechoslovakia. ¹⁹ PRAD is a corrosion inhibitor when used in systems containing stainless steel. Its effectiveness as an algicide has not previously been reported.

The herbicide diuron (DCMU) and ADA were the two most effective compounds for killing algae. Corrosion testing, however, indicated that some pitting of aluminum could be expected from repeated use of either of these compounds. Sodium hypochlorite was substantially inferior to the other five compounds both in terms of toxicity to algae and aluminum corrosion.

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TABLE 1

Algal Species and Environmental Conditions for Experiments

		Culture Conditions		
Taxon	Source	Temp.,	Light, ft-C*	Media
Cyanophyta (Blue-green algae)				
Mastigocladus laminosus Cohn	UTEX ⁺	45	50	D 7
Chlorophyta (Green algae)	•			
Coelastrum cambricum Archer	z-usc [‡]	20	100	F/2 ⁸
Selenastrum capricornutum Printz	EPA-C [§]	20	100	F/2
Chlamydomonas reinhardtii Dang.	Z-USC	20	100	F/2
Cosmarium subcostatum Nordst	UTEX	20	100	F/2
Chlorella sp.	Z-USC	20	100	F/2
Bacillariophyta (Diatoms)				
Nitzschia palea (Kutz.) W.Smith	U3RC**	20	100	F/2

^{*} Environmental chamber experiments only (12 hr per day)

⁺ UTEX = University of Texas culture collection at Austin.

[‡] Z-USC = Dr. Richard G. Zingmark, Univ. of S.C., Columbia.

[§] EPA-C = Environmental Protection Agency, Corvallis, Ore.

^{**} U3RC = Isolated from Upper Three Runs Creek, Aiken, County, S.C.

TABLE 2

Toxicity Ranking of Six Algicidal Compounds (Two-week Treatment)

Algal Species	<pre>Initial Cell Density, cells/mL</pre>	DCMU	ADA	PRAD	KMn04	H202	Na OC 1
Selenastrum capricornutum	1.2×10^5	2.5	2.5	2.5	2.5	5.5	5.5
Selenastrum capricornutum	2.0 x 10 ⁵	2.5	2.5	2.5	2.5	5.0	6.0
Selenastrum capricornutum	9.1×10^{5}	1.5	1.5	4.0	4.0	4.0	6.0
Chlamydomonas reinhardtii	1.0 x 10 ⁴	1.0	2.5	2.5	5.0	5.0	5.0
Chlamydomonas reinhardtii	5.5×10^4	2.0	2.0	2.0	5.0	5.0	5.0
Cosmarium subcostatum	4.2×10^{2}	1.5	1.5	3.0	4.5	4.5	6.0
Cosmarium subcostatum	1.2 x 10 ⁴	1.5	1.5	3.0	4.5	4.5	6.0
Chlorella sp.	9.3×10^4	2.5	1.0	2.5	4.5	4.5	6.0
Chlorella sp.	1.0×10^6	2.0	2.0	2.0	4.5	4.5	6.0
Coelastrum cambricum	4.3×10^4	2.0	2.0	2.0	4.5	4.5	6.0
Coelastrum cambricum	2.0×10^{5}	1.0	2.0	3.5	3.5	5.5	5.5
Mastigocladus laminosus	2.5×10^3	2.0	2.0	2.0	4.5	4.5	6.0
Mastigocladus laminosus	1.5 x 10 ⁴	1.5	1.5	3.5	3.5	5.5	5.5
Mastigocladus laminosus	4.0×10^6	2.0	2.0	2.0	5.0	5.0	5.0
Nitzschia palea	7.5×10^3	1.5	1.5	3.0	4.5	4.5	6.0
Nitzschia palea	2.0×10^{5}	1.0	2.5	2.5	4.5	4.5	6.0
Total		28.0	30.5	42.5	67.0	76.5	91.5

TABLE 3

Percent of Samples in which a Two-Week Treatment was more Effective than a 24-Hour Treatment

By Alg	<u>icide</u>	By Algal Taxon	
PRAD	68.8%	Nitzschia	66.7%
ADA	37.5%	Chlamydomonas	50.0%
DCMU	25.0%	Chlorella	25.0%
H ₂ O ₂	18.8%	Mastigocladus	22.2%
KMn04	12.5%	Cosmarium	16.7%
NaOC1	12.5%	Coelastrum	16.7%
		Selenastrum	11.1%

TABLE 4
Coupon Tests (128 days in solution)

Algicide	Concentration of Test Solution	Appearance of Test Specimen
KMn0 ₄	10 ⁻² M	Light brown; surface partially covered by particles of hemispherical precipitate
H ₂ O ₂	10 ⁻² M	Coated with aluminum oxide; speckled but no pits
PRAD	2 mL/L	Dull gray; coated with a thin, non-oxide, continuous film
ADA	2 mL/L	Dull gray; coated with a thin, non-oxide film
DCMU	2 g/L	Slight blue; no evidence of coating detectable using SEM
NaOC1	10 ⁻² M	Coated with aluminum oxide; speckled with pits

TABLE 5
Potentiostatic Anodic Polarization Test Information

Current ation, Density, A/cm ²
.28
1.3
52.0
110.0
62
3100
5

^{*} Calculated from E = $(401 - 59.1 \log [OH^-] + 14.7 \log Po_2) - 242$ using Po₂ = 0.2 ATM and log [OH⁻] = pH-14 and the tabulated pH values.

TABLE 6
Cyclic Potentiodynamic Polarization Tests

Algicide	Concentration of Test Solution	Pre-Polarization Open Circuit Potential After One Hour, mV vs. SCE	Hysteresis at Pre-Polarization Open Circuit Potential Plus One Volt,
KMn04	10 ⁻² M	+279	+ 7.5
H ₂ O ₂	10 ⁻² M	-254	- 0.09
PRAD	2 mL/L	-937	+ 4.3
ADA	2 mL/L	-579	-125
DCMU	2 g/L	-501	- 15.6
NaOC1	10 ⁻² M	-666	-500

TABLE 7

Results of SEM Examination for Pitting of Test Specimens

Algicide	Coupon Test	Cyclic Potentiodynamic Polarization Test	Potentiostatic Anodic Polarization Test
KMn04	NP	NP	NP
H ₂ O ₂	NP	NP	NP/SD
PRAD	NP	NP	P
ADA	NP	NP/SD	P
DCMU	NP	Р	P
NaOC1	P	Р	P

P Pitted

NP Not Pitted

SD Surface damage in the form of crystallographic etching

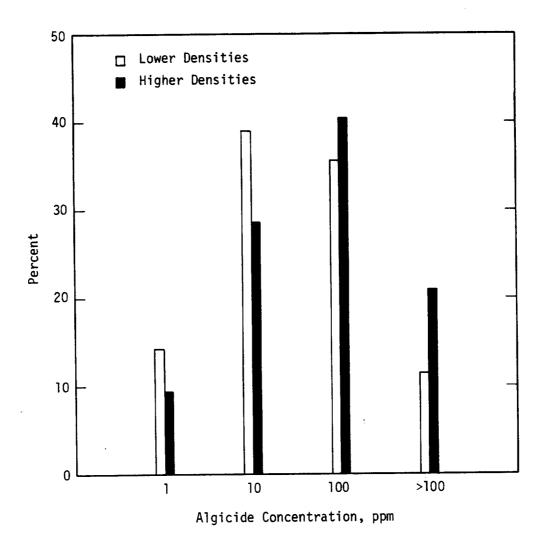


FIGURE 1. Percentages of algal cultures which required each of four minimum lethal algicidal concentrations. Comparisons between 84 cultures containing the lowest and highest initial cell densities of seven species are shown.

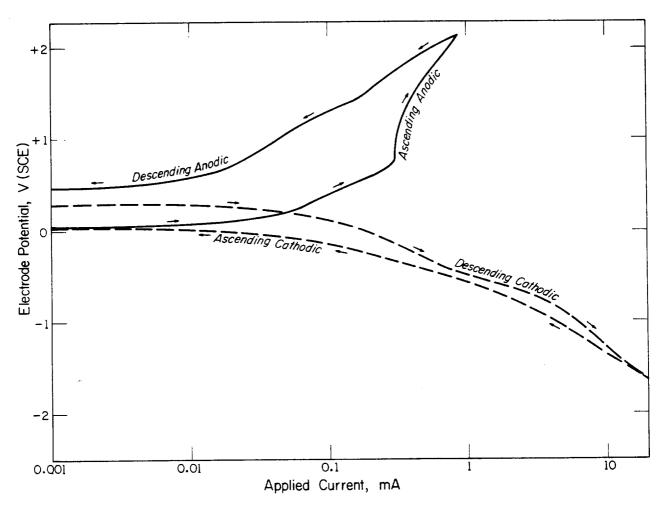


Fig. 2. Cyclic Potentiodynamic Polarization Curve for 6063-Al in Air Saturated 0.01M $KMnO_4$



Fig. 3. Pits on 6063-Al After Cyclic Potentiodynamic Polarization in Air Saturated 0.01M NaOCl

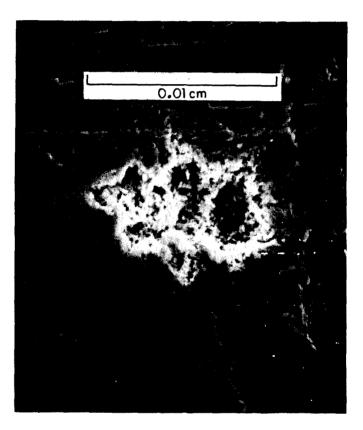


Fig. 4. Pit on 6063-Al After Cyclic Potentiodynamic Polarization in Air Saturated 2 g/L DCMU

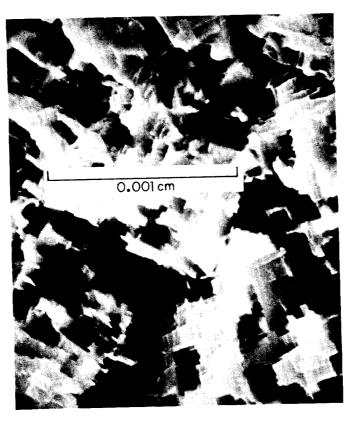


Fig. 5. Crystallographic Etching on 6063-Al After Cyclic Potentiodynamic Polarization in Air Saturated 2 mL/L ADA

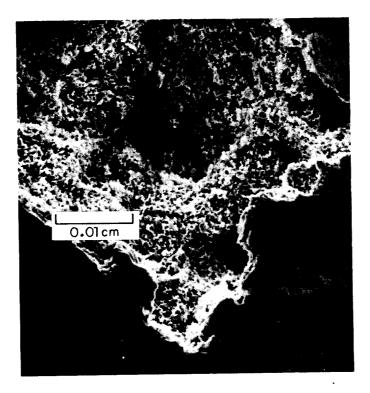


Fig. 6. Pit on 6063-Al After Potentiostatic Anodic Polarization in Air Saturated 2 g/L DCMU

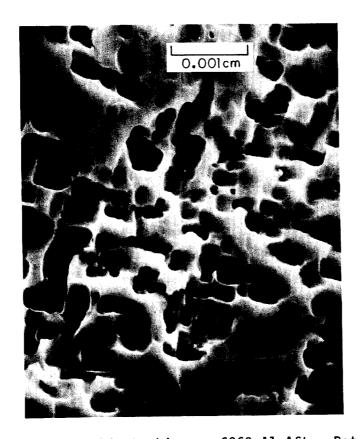


Fig. 7. Crystallographic Etching on 6063-Al After Potentiostatic Anodic Polarization in Air Saturated 0.01M $\rm H_2O_2$