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Marine Corrosion Studies

The Corrosion Characteristics and Response to Cathodic Protection of Copper Alloys in Quiescent Seawater

(Eighth Interim Report of Progress)

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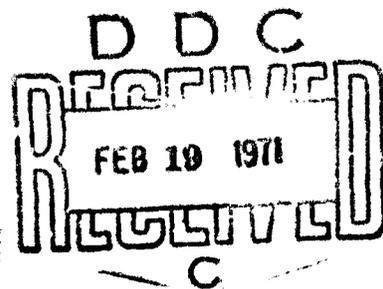
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ABSTRACT

The corrosion characteristics, dealloying susceptibility, marine fouling characteristics, and the response to cathodic protection of seventeen copper alloys and unalloyed copper, which served as a control, were studied in quiescent seawater.

Detailed examination after 735 days showed that several alloys in the unprotected condition had severely corroded either by deep localized attack or by dealloying. The corrosion rates were determined; on the unprotected specimens a maximum rate of 0.74 mils per year was observed.

Cathodic protection from zinc anodes reduced the corrosion rate to essentially zero and prevented localized corrosion except in Naval brass and Muntz metal where metallurgical studies indicated that dealloying was not completely prevented.

Histograms have been presented for the electrochemical potentials of each specimen, and a galvanic series for the copper alloys has been included. There was no correlation between the electrochemical potentials and the type or severity of corrosion.

The resistance of the copper alloys to marine fouling varied widely. All unprotected specimens fouled to some extent, whereas the cathodically protected specimens were heavily fouled.

Status

This report completes one phase of the task; work is continuing on other phases.

Authorization

NRL Proben No. 63M04-02.201
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INTRODUCTION

There has always existed a continuing need for information on the corrosion technology of various metals in seawater for use by designers of marine equipment for ocean engineering applications. Copper alloys have been considered for seawater applications because of their generally low corrosion rate and their history of inherent resistance to marine fouling. Some of the copper alloys, however, have been known to dealloy in seawater, a corrosion phenomenon not readily detected in service. Detection of dealloying can usually be made only by metallographic examination.

Numerous investigators have reported data on the corrosion characteristics of copper and its alloys in seawater (1-12). Considerable data have been obtained at relatively high seawater velocities, high temperatures, and low oxygen concentrations because of the importance of copper alloys in the construction of piping and pump components for heat exchangers (13-20). The electrochemical potential data previously reported for copper and its alloys have been obtained at seawater velocities of 7.8-13 ft/sec (12, 21). Experimental data on the effectiveness of electrochemical technology (cathodic protection) in mitigating corrosion and dealloying of copper alloys have been very limited (22, 23).

The corrosion resistance of copper and some copper alloys has been reported as markedly affected by changes in seawater velocity (24, 25). Some alloys were resistant to corrosion at low velocity (26), but experienced accelerated corrosion when the velocity was increased. In contrast, other copper alloys were resistant at the higher velocities but showed accelerated corrosion at lower velocities. Corrosion data obtained under one velocity condition cannot be used at the present time to predict the corrosion characteristics at another velocity or in quiescent seawater.

Because of the continuing use of copper alloys in applications involving relatively quiescent seawater, a broad spectrum of copper alloys were studied at one location in the same exposure condition. The alloys* studied and their chemical composition are listed in Table 1. Data on the corrosion characteristics, susceptibility to dealloying, marine fouling characteristics, electrochemical potentials, and the response to cathodic protection of copper and seventeen copper alloys after 735 days immersion in quiescent seawater at Key West, Florida, have been included in this report.

*CDA (Copper Development Association) identifying numbers (27) have been used throughout this report.

PROCEDURES

Duplicate specimens were prepared for each material. Twenty-eight specimens measured 8 x 12 in. and eight measured 6 x 12 in.; all specimens were approximately 1/16-in. thick.

The specimens were attached to painted aluminum exposure racks with nylon bolts, nuts, and washers. All specimens were electrically isolated from the racks with polyethylene strips which also served to introduce an intentional crevice. An insulated electrical test lead was attached to each specimen so the electrochemical potential could be measured periodically relative to a Ag/AgCl reference electrode. One specimen of each material was exposed unprotected, and the second specimen was provided with cathodic protection from a 1/2 x 1-1/4 x 6-in. zinc anode bolted directly to the specimen.

All electrical connections that were submerged in seawater were sealed with epoxy resin. The faying surface between the anode and the specimen was not sealed. Less than 0.001 ohm resistance between each anode and specimen was measured before exposure and again at the conclusion of the experiment. Prior to assembly, all specimens and anodes were solvent cleaned and weighed to the nearest gram. Each specimen was given a final solvent wipe immediately before exposure.

All specimens were suspended beneath a pier in quiescent, but not stagnant, seawater at the Naval Research Laboratory's Marine Corrosion Research Laboratory at Key West, Florida. The seawater characteristics during the experiment were as follows:

Temperature - 16.5 to 32.5 °C (62 to 90 °F)

Resistivity - 16 to 21 ohm-cm

pH - 8.1 to 8.4

After 399 days, the specimens were removed from the seawater, and the unprotected specimens were photographed and inspected for marine fouling. They were returned to the water within a few minutes of their removal.

At the conclusion of the experiment, the unprotected specimens were again photographed and inspected for marine fouling. The gross marine fouling was removed from the specimens with a high-pressure water jet (2 gpm at 500 psi). The specimens

were chemically cleaned in HCl (1:1), rinsed in tap water, and dried in air. The final weight of each specimen was measured to the nearest gram, and the depth of attack was measured to the nearest mil with a dial gage micrometer.

The parameters used to characterize the corrosion attack on the materials in this study were:

1. The deepest attack associated with the intentional crevice formed by the plastic mounting attachments.
2. The average value of the ten deepest points of attack associated with the intentional crevice.
3. The deepest attack on the surface not associated with the intentional crevice.
4. The average value of the ten deepest points of attack on the surface not associated with the intentional crevice.
5. The average corrosion rate in mils per year (mpy).
6. Metallographic examination - to determine the resistance of each material to dealloying, e.g., dezincification, and to determine the effectiveness of cathodic protection to prevent localized corrosion and dealloying.

DATA AND DISCUSSION

Depth of Attack and Corrosion Rates

The depth of attack and corrosion rate data for copper and the copper alloys have been shown in Table 2. All the unprotected materials had low corrosion rates; the maximum average rate observed was 0.74 mpy. The depth of attack data, however, showed that some materials had relatively severe localized corrosion.

The copper-nickel alloys which contained either 10 or 30 percent nickel and relatively low iron (CDA alloys 706 and 715) were most inherently resistant to pitting and crevice corrosion. In contrast, the copper-nickel alloy which contained 30 percent nickel and 5 percent iron (CDA alloy 716) was corroded locally to a depth of 43 mils around the crevice.

Under the quiescent seawater exposure conditions of this experiment, the aluminum bronzes (CDA alloys 608, 612, and 614) were comparable to the copper-nickel alloys 706 and 715 with regard to resistance to pitting and crevice corrosion.

The depth of attack observed for the other copper alloys varied, as shown in Table 2. As a group the alloys containing only zinc showed the most severe localized corrosion, this being especially true when the alloy contained more than 15 percent zinc. There was no direct correlation between zinc content of the alloy and the depth of localized corrosion, although there appeared to be a trend showing that the higher the zinc content the greater the corrosion rate.

The copper-cobalt-beryllium alloy (CDA alloy 175) showed somewhat less depth of attack in crevices compared to the copper-beryllium alloy (CDA alloy 172), and the corrosion rate of CDA alloy 175 was approximately one-fifth of that observed for CDA alloy 172.

The corrosion rate was highest for the high silicon bronze A (CDA alloy 655), but the depth of localized corrosion was considerably less for this alloy than for alloys such as CDA alloys 260 and 268 which showed corrosion rates of less than one-third the rate observed for alloy 655. This once again points out the fallacy in assessing the usefulness of an alloy solely on the basis of average corrosion rate.

The data in Table 2 also show that the most serious corrosion occurred within the crevice area indicating that under our experimental conditions metal ion concentration cells were not the controlling factor in crevice corrosion.

Dealloying (Metallographic Study)

The degree of dealloying and the effectiveness of cathodic protection from a zinc anode to prevent dealloying in quiescent seawater have been summarized in Figure 1. Photomicrographs at 75X and 500X magnifications (Figs. 2-21) show the extent of dealloying observed for each copper alloy and the effectiveness of cathodic protection for selected alloys.

The copper-beryllium (CDA alloy 172) and the copper-cobalt-beryllium (CDA alloy 175) were susceptible to dealloying (Figs. 2 & 3), but this dealloying was prevented by cathodic protection.

Commercial bronze, 90% (CDA alloy 220) and red brass, 85% (CDA alloy 230) were not completely immune to dealloying as shown in Figs. 4 and 5, respectively. Surprisingly, CDA alloy 220 showed slightly more dealloying than CDA alloy 230. These observations were not expected, because it has been reported that the lower the zinc content in a brass the less susceptible the alloy is to dezincification (9) and that alloys containing less than 15-20% zinc are believed to be immune to or rarely experience dezincification (28, 29). For the copper alloys containing only zinc as an alloying element (CDA alloys 220, 230, 260, 268, and 280) the present data indicated it was preferable to keep the zinc content below 15 percent (compare Figs. 4 and 5 with Figs. 6a, 7a, 8, 9a, and 10a), but this alone was not sufficient to completely prevent dealloying. In the CDA alloy 280, cathodic protection was also not sufficient to completely prevent dealloying (Fig. 10b). Admiralty brass inhibited with arsenic (CDA alloy 443) was not completely immune to dealloying (Fig. 11). Dealloying of this alloy was prevented, however, with cathodic protection by a zinc anode.

Naval brass (CDA alloy 464) showed considerable dealloying (Figs. 12a and 13a) when not protected, and cathodic protection from a zinc anode was not completely effective in preventing dealloying, as shown in Fig. 13b. It is interesting to note that other investigators had very disappointing results with cathodic protection of Naval brass by steel anodes or steel-sprayed water boxes (30).

Phosphor bronze, 10% D (CDA alloy 524) also showed some dealloying, Fig. 14, but this was prevented by cathodic protection. Each of the aluminum bronzes studied (CDA alloys 608, 612, and 614) showed only a small amount of dealloying (Figs. 15b, 16b, and 18a), and this dealloying was prevented by cathodic protection (Fig. 18b). High silicon bronze A (CDA alloy 655) also showed some dealloying (Fig. 19b), which was prevented by cathodic protection.

Copper nickel 30% Ni, 5% Fe (CDA 716) showed quite severe corrosion (Fig. 20a) and some dealloying (Fig. 20b), both of which were prevented by cathodic protection. Some copper of an amorphous appearance was evident on the surface of the unprotected copper specimen as shown in Fig. 21b.

A small amount of dealloying was observed on CDA alloys 230, 443, 608, 612, and 614. These alloys possibly could be used

unprotected for a two-year period in quiescent seawater, but this would depend on the quantity of dealloying tolerable in a specific application.

The two alloys (CDA alloys 280 and 464), in which cathodic protection from zinc anodes was not completely effective in preventing dealloying, dezincified at the faying surfaces of the alloy and the zinc anodes which were mounted directly on the copper alloys.

The selection of areas from which metallographic specimens were taken was based on visual observations indicative of dealloying, i.e., the specimens were sampled at locations that had a coppery appearance. The location at which dealloying was observed varied with the alloy. For CDA alloys 260, 268, 612, 614, and 716 the location varied from the crevice opening to inside the crevice. The remainder of the alloys which showed this type attack were dealloyed outside the crevice opening. The observations that several alloys dealloyed within the crevice did not support the often-quoted statement that "copper alloys corrode outside the crevices rather than within the crevices." These observations are significant, because in the past it had generally been conceded that metal ion concentration cells were principally involved in the corrosion of copper alloys in the presence of crevices and that areas outside the crevices would have a lower concentration of copper ions, thus be anodic and corroded.

Electrochemical Potentials

The electrochemical potential of each specimen was measured relative to a Ag/AgCl reference electrode with either a high impedance electronic voltmeter or potentiometer. The potential data obtained during the first 353 days of the study for specimens without cathodic protection have been plotted as a function of time in Figs. 22 through 25. The potentials of specimens cathodically protected with zinc anodes varied little during the same time interval. Within the limits of error of the experiment, all protected specimens were polarized to the same potential. Therefore, all potential data for protected specimens were pooled (486 measurements) for analysis. The mean potential was -1.007 volts with a standard deviation of 0.021 volts.

Although galvanic series based on electrochemical potentials are useful to the design engineer to appraise galvanic compatibility in the absence of other more direct data, there

was great practical difficulty in arranging alloys into such a series.

The criterion often used to prepare a galvanic series was the mean potential. This would be quite adequate for an alloy such as CDA alloy 268, yellow brass, which maintained the same potential within a very narrow range over the whole measuring period, but was hopelessly inadequate for an alloy such as CDA 716, copper-nickel, 30% Ni, 5% Fe. The authors have chosen to rank the alloys by preparing histograms of the number of observations versus the observed potential (Fig. 26) and ranking the alloys subjectively. The galvanic series determined in this manner is shown in Table 3. The mean, median, and standard deviations of the potential measurements have also been shown to facilitate direct comparison with data reported by other observers.

As indicated above, it was extremely difficult to establish a direct ranking because of the marked spread in the potential data for some alloys. Our data indicated that one would be unable to predict the more active alloy within a galvanic couple, and that this might reverse from time to time.

In general, the potentials reported in this paper were somewhat more electropositive than the potentials reported by others in seawater flowing at 8-13 ft/sec. (12). The more positive potentials observed under quiescent exposure conditions were not unexpected. In flowing seawater the corrosion products, which would generally be more electropositive to the base alloy, would be much more readily removed than under quiescent conditions. There was no correlation between the electrochemical potentials of the alloys studied and the type or severity of corrosion observed.

Marine Fouling Characteristics

The inherent ability of copper to resist marine fouling has been recognized for many years. As early as 1761 the British Admiralty took advantage of this characteristic and used copper as an antifouling sheathing for wooden ships; the characteristic is still of interest to the materials engineer for the design of modern marine apparatus. It has been reported that copper and copper alloys to remain free of fouling must corrode to liberate copper at a minimum rate of 5 mg/sq dm/day (mdd) (26, 31) (about 0.8 mpy). The corrosion rates of the materials in this study were less than the rate required to prevent

fouling. As would be expected, therefore, none of the alloys was completely free of marine fouling. The amount of marine fouling on the specimens was visually estimated after 399 and 735 days exposure. An arbitrary rating for fouling resistance was used to assess each specimen at each of the inspection times. These data are summarized in Table 4. The relative ease of removing the fouling has also been indicated.

Marine fouling was attached to all unprotected specimens to varying degrees. Unprotected yellow brass and Naval brass were the most resistant to fouling. Specimens which were cathodically protected did not corrode and therefore did not resist fouling. Some alloys resisted fouling for 399 days but were relatively heavily fouled after 735 days exposure. This behavior was probably the result of lower corrosion rates with time as discussed earlier (26).

SUMMARY AND CONCLUSIONS

1. Seventeen copper alloys and unalloyed copper which served as a control were exposed for 735 days in quiescent seawater at Key West, Florida. Two specimens of each material were studied. One specimen was unprotected, and the other was cathodically protected with a zinc anode.
2. All unprotected specimens had a low average corrosion rate; the maximum observed was 0.74 mpy. Some specimens had relatively severe localized corrosion. The maximum depth of localized attack was 43 mils, and it occurred near the crevice of the copper-nickel alloy which contained 30 percent nickel and 5 percent iron (CDA alloy 716).
3. Contrary to expectations several alloys showed localized corrosion and dealloyed within the crevices.
4. Low iron copper-nickels (CDA alloys 706 and 715) were essentially immune to dealloying in quiescent seawater even without cathodic protection.
5. Although a small amount of dealloying was observed on CDA alloys 230, 443, 608, 612, and 614, the present data indicated that these alloys could possibly be used unprotected for a two-year period in quiescent seawater. Their practical usefulness in the unprotected conditions, however, would depend on the quantity of dealloying tolerable in a specific application.

6. The other copper alloys studied varied considerably as to the amount of dealloying observed. CDA alloys 260, 268, 280, and 464 showed very severe dealloying.

7. Cathodic protection from a zinc anode was not sufficient to completely prevent dealloying of CDA alloys 280 and 464, but was effective in preventing dealloying and other corrosion observed on all other alloys studied.

8. A galvanic series for the copper alloys has been included in this report. Because of the spread in the electrochemical potentials observed it is difficult to predict for many of the alloys when they would be anodic or cathodic to some of the other copper alloys. The potentials observed in quiescent seawater were more positive, however, than the potentials of similar materials in flowing seawater reported by other investigators.

9. Marine fouling was attached to all unprotected specimens to varying degrees. Unprotected yellow brass and Naval brass were the most resistant to fouling. All cathodically protected specimens were heavily fouled.

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Table 1
Chemical Composition
Copper Alloys

| ALLOY | CDA No. (2) | PERCENT (1) | | | | | | | | | | | | | Other C ^r |
|----------------------------------|-------------|-------------|----------------------|--------|------|------|-------|-------|--------------------|----------------------|------|------|------|------|-------------------------|
| | | Cu | Zn | Pb | Fe | Sn | As | P | Al | Mn | Si | Be | Co | | |
| Copper-Beryllium | 172 | Rem. | 0.04 | 0.005 | 0.13 | 0.05 | - | - | 0.05 | 0.01 | - | 0.09 | 1.98 | 0.26 | <0.005 |
| Copper-Cobalt-Beryllium | 175 | Rem. | 0.01 | <0.005 | 0.06 | 0.03 | - | - | 0.02 | 0.01 | - | 0.03 | 0.50 | 2.60 | <0.005 |
| Commercial Bronze, 90% | 220 | 90.05 | 9.94 ⁽³⁾ | <0.01 | 0.01 | - | - | - | - | - | - | - | - | - | - |
| Red Bronze, 85% | 230 | 85.67 | 14.31 ⁽³⁾ | 0.01 | 0.01 | - | - | - | - | - | - | - | - | - | - |
| Cartridge Brass, 70% | 280 | 69.94 | 30.04 ⁽³⁾ | <0.01 | 0.02 | - | - | - | - | - | - | - | - | - | - |
| Yellow Brass, 66% | 288 | 66.73 | 33.24 ⁽³⁾ | 0.024 | 0.01 | - | - | - | - | - | - | - | - | - | - |
| Naval Metal, 80% | 280 | 60.97 | 39.00 ⁽³⁾ | <0.01 | 0.03 | - | - | - | - | - | - | - | - | - | - |
| Admiralty, Arsenical | 443 | 71.38 | 27.43 ⁽³⁾ | 0.02 | 0.02 | 1.09 | 0.085 | - | - | - | - | - | - | - | - |
| Naval Brass, Unalloyed (Grade A) | 464 | 60.44 | 38.82 ⁽³⁾ | 0.017 | 0.01 | 0.71 | - | - | - | - | - | - | - | - | - |
| Phosphor Bronze, 10% D | 524 | 89.86 | 0.20 | - | - | 9.71 | - | 0.23 | - | - | - | - | - | - | - |
| Aluminum Bronze, 5% Al | 606 | 94.52 | <0.10 | - | 0.02 | - | - | - | 5.4 ⁽³⁾ | <0.02 | - | - | - | - | - |
| Aluminum Bronze, 5% Al | 612 | 91.84 | - | - | 0.06 | - | - | - | 8.1 ⁽³⁾ | - | - | - | - | - | - |
| Aluminum Bronze D, 7% Al, 2% Fe | 614 | 90.01 | <0.10 | - | 3.68 | - | - | - | 6.3 ⁽³⁾ | 0.01 | - | - | - | - | - |
| High Silicon Bronze A | 655 | 95.64 | 0.15 | - | 0.04 | - | - | - | - | - | 1.08 | 3.19 | - | - | - |
| Copper-Nickel, 10% | 706 | 87.96 | <0.10 | <0.02 | 1.24 | - | - | 0.002 | - | 10.4 ⁽³⁾ | 0.33 | - | - | - | 0.009 |
| Copper-Nickel, 30% | 715 | 66.68 | 0.25 | 0.005 | 0.52 | - | - | 0.003 | - | 30.12 ⁽³⁾ | 0.40 | - | - | - | 0.017 |
| Copper-Nickel, 30% Ni, 5% Fe | 716 | 62.89 | 0.11 | <0.02 | 5.66 | - | - | 0.008 | - | 30.67 | 0.64 | - | - | - | Ti-0.06 C-0.025 |

(1) Source Analysis (2) CDA - Copper Development Association (3) By Difference MSC318

Table 2

Depth of Attack and Corrosion Rates of Copper and Copper Alloys
After 735 Days in Quiescent Seawater at Key West, Florida, Without Cathodic Protection⁽¹⁾

| Alloy Name | CMA No. | Depth of Attack (mils) | | | Average Corrosion Rate (mpy)(4) | |
|------------------------------------|---------|------------------------|------------|---------|---------------------------------|-----------|
| | | Crevice(2) | Surface(3) | Average | | |
| Copper | --- | 4 | 3 | 1 | <1 | 0.37 |
| Copper-Beryllium | 172 | 9 | 6 | <1 | <1 | 0.46 (d) |
| Copper-Cobalt-Beryllium | 175 | 3 | 2 | 2 | 1 | 0.096 (d) |
| Commercial Bronze, 90% | 220 | 6 | 2 | 4 | 3 | 0.085 (d) |
| Red Brass, 85% | 230 | 2 | 2 | 0(5) | 0(5) | 0.070 (d) |
| Cartridge Brass, 70% | 260 | 1(6) | 7(6) | 13(6) | 12(6) | 0.31 (d) |
| Yellow Brass, 66% | 288 | 2(6) | 11(6) | 15(6) | 12(6) | 0.31 (d) |
| Muntz Metal, 60% | 280 | --(6) | --(6) | --(6) | --(6) | 0.63 (d) |
| Admiralty, Arsenical | 443 | 4 | 2 | 2 | 1 | 0.34 (d) |
| Naval Brass, Uninhibited (Grade A) | 464 | 2(6) | 2(6) | --(6) | --(6) | 0.26 (d) |
| Phosphor Bronze, 10% D | 524 | 7 | 5 | 6 | 4 | 0.24 (d) |
| Aluminum Bronze, 5% Al | 608 | 0 | 0 | 0 | 0 | 0.13 (d) |
| Aluminum Bronze, 9% Al | 612 | <1 | <1 | 0 | 0 | 0.070 (d) |
| Aluminum Bronze D, 7% Al, 2% Fe | 614 | <1 | <1 | <1 | <1 | 0.048 (d) |
| High Silicon Bronze A | 655 | 12 | 6 | 3 | 2 | 0.74 (d) |
| Copper-Nickel, 10% | 706 | 0 | 0 | 0 | 0 | 0.065 |
| Copper-Nickel, 30% | 715 | 0 | 0 | 0 | 0 | 0.070 |
| Copper-Nickel, 30% Ni, 5% Fe | 716 | 43 | 26 | 4 | 1 | 0.14 (d) |

Notes:

MC319

- (1) There were no measurable pits and no detectable weight loss on specimens which were cathodically protected with zinc anodes.
- (2) The deepest and average of the ten deepest points of attack associated with a crevice.
- (3) The deepest and average of the ten deepest points of attack on the surface not associated with any known crevice.
- (4) The average corrosion rate is given for comparison only. Since uniform attack is assumed in its calculation, the average corrosion rate is applicable only to those alloys which did not experience localized attack or dealloying. (d) - dealloyed.
- (5) Alloy pitted on surfaces, but pits were too narrow for accurate measurement of depth of attack.
- (6) Copper deposits from dealloying made accurate measurement of depth of attack impractical.

Table 3

Galvanic Series - Copper Alloys (1)
353 Days Quiescent Seawater
Key West, Florida

| | Alloy Name | CDA No. | Electrochemical Potential to Ag/AgCl (Volts - Negative) | | |
|-----------------------------------|--------------------------------------|---------|--|---------------------|----------|
| | | | Median | Mean ⁽²⁾ | Std.Dev. |
| <u>Noble</u> (Cathodic End) | Copper-Nickel, 30% Ni, 5% Fe | 716 | 0.111 | 0.115 | 0.075 |
| | Phosphor Bronze, 10% D | 524 | 0.144 | 0.148 | 0.038 |
| | Copper-Beryllium | 172 | 0.196 | 0.181 | 0.042 |
| | Copper-Nickel, 30% | 715 | 0.200 | 0.199 | 0.013 |
| | Copper | -- | 0.200 | 0.199 | 0.043 |
| | High Silicon Bronze A | 655 | 0.204 | 0.204 | 0.015 |
| | Aluminum Bronze, D, 7% Al, 2% Fe | 614 | 0.209 | 0.180 | 0.056 |
| | Copper-Cobalt-Beryllium | 175 | 0.215 | 0.211 | 0.021 |
| | Yellow Brass, 66% | 268 | 0.220 | 0.217 | 0.012 |
| | Cartridge Brass, 70% | 260 | 0.222 | 0.222 | 0.010 |
| | Admiralty, Arsenical | 443 | 0.223 | 0.217 | 0.018 |
| | Aluminum Bronze, 5% Al | 608 | 0.226 | 0.228 | 0.018 |
| | Aluminum Bronze, 9% Al | 612 | 0.232 | 0.230 | 0.014 |
| | Copper-Nickel, 10% | 706 | 0.233 | 0.236 | 0.036 |
| | Naval Brass, Uninhibited, Grade A | 464 | 0.235 | 0.235 | 0.015 |
| | Commercial Bronze, 90% | 220 | 0.235 | 0.235 | 0.023 |
| | Red Brass, 85% | 230 | 0.273 | 0.270 | 0.058 |
| <u>Ignoble</u> (Anodic End) | Muntz Metal, 60% | 280 | 0.331 | 0.321 | 0.030 |

MC320

Notes:

- (1) Data were pooled (486 measurements) for specimens cathodically protected with zinc anodes. The mean potential was -1.007 volts to the Ag/AgCl reference electrode with a standard deviation of 0.021 volts.
- (2) The mean of twenty-seven measurements for each specimen.

Table 4

The Fouling Resistance of Copper and Copper
Alloys After 399 Days and 735 Days in
Quiescent Seawater at Key West, Florida,
Without Cathodic Protection

| Name | Alloy | CDA No. | Fouling Resistance ⁽¹⁾ | |
|-------------------------------------|-------|---------|-----------------------------------|-----------------------------|
| | | | 399 Days | 735 Days |
| Copper | | -- | Best | Intermediate ⁽²⁾ |
| Copper-Beryllium | | 172 | Best | Intermediate ⁽²⁾ |
| Copper-Cobalt-Beryllium | | 175 | Least | Least ⁽⁴⁾ |
| Commercial Bronze, 90% | | 220 | Least | Least ⁽⁴⁾ |
| Red Brass, 85% | | 230 | Least | Intermediate ⁽⁴⁾ |
| Cartridge Brass, 70% | | 260 | Best | Intermediate ⁽²⁾ |
| Yellow Brass, 66% | | 268 | Best | Best ⁽²⁾ |
| Muntz Metal, 60% | | 280 | Intermediate | Least ⁽⁵⁾ |
| Admiralty, Arsenical | | 443 | Best | Least ⁽²⁾ |
| Naval Brass, Uninhibited, (Grade A) | | 464 | Best | Best ⁽²⁾ |
| Phosphor Bronze, 10% D | | 524 | Intermediate | Intermediate ⁽²⁾ |
| Aluminum Bronze, 5% Al | | 608 | Least | Least ⁽⁴⁾ |
| Aluminum Bronze, 9% Al | | 612 | Intermediate | Intermediate ⁽³⁾ |
| Aluminum Bronze D, 7% Al, 2% Fe | | 614 | Intermediate | Intermediate ⁽⁴⁾ |
| High Silicon Bronze A | | 655 | Best | Least ⁽²⁾ |
| Copper-Nickel, 10% | | 706 | Intermediate | Intermediate ⁽³⁾ |
| Copper-Nickel, 30% | | 715 | Intermediate | Intermediate ⁽³⁾ |
| Copper-Nickel, 30% Ni, 5% Fe | | 716 | Least | Least ⁽⁵⁾ |

Notes:

MC321

- (1) The Relative fouling resistance of the alloys at the length of exposure indicated. "Best" indicates slight fouling and "least" complete fouling.
- (2) Fouling was completely and easily removed from these alloys by pressure washing (2 gpm at 500 psi).
- (3) A slight amount of hard fouling remained on these alloys after pressure washing.
- (4) A moderate amount of hard fouling including some barnacles remained on these alloys after pressure washing.
- (5) These alloys were almost completely covered with hard fouling and some barnacles after pressure washing.

COPPER DEVELOPMENT
ASSOCIATION
IDENTIFICATION

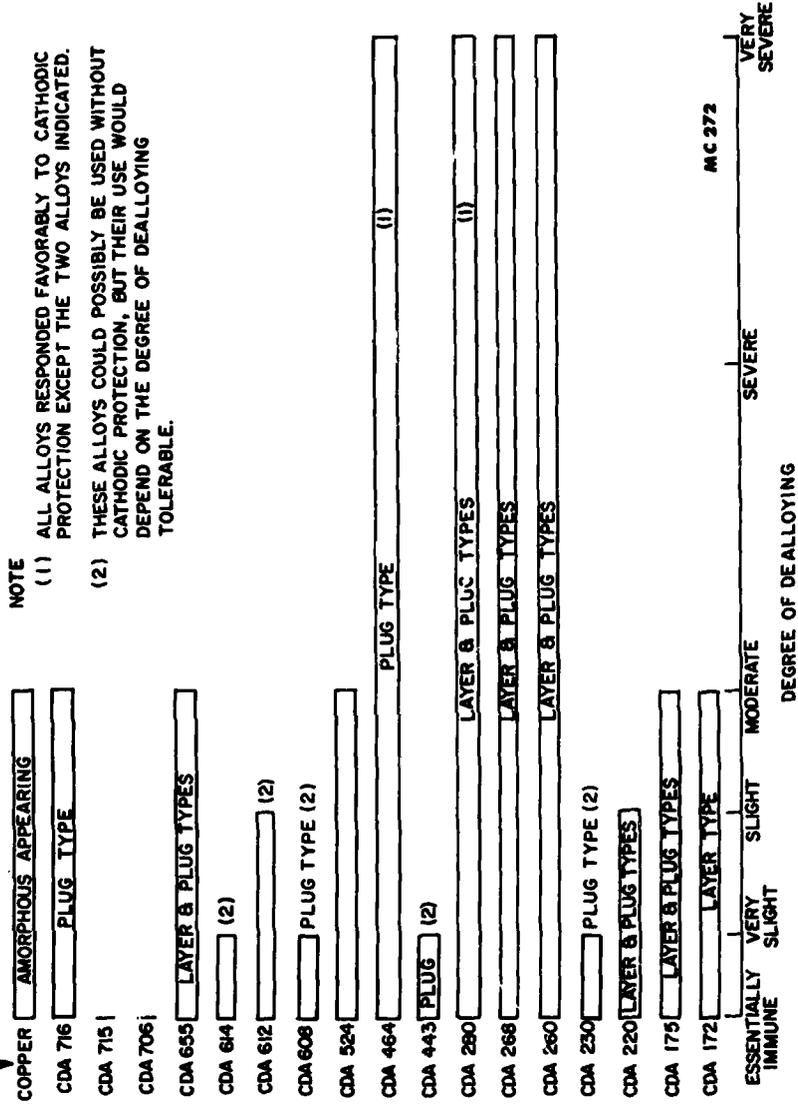
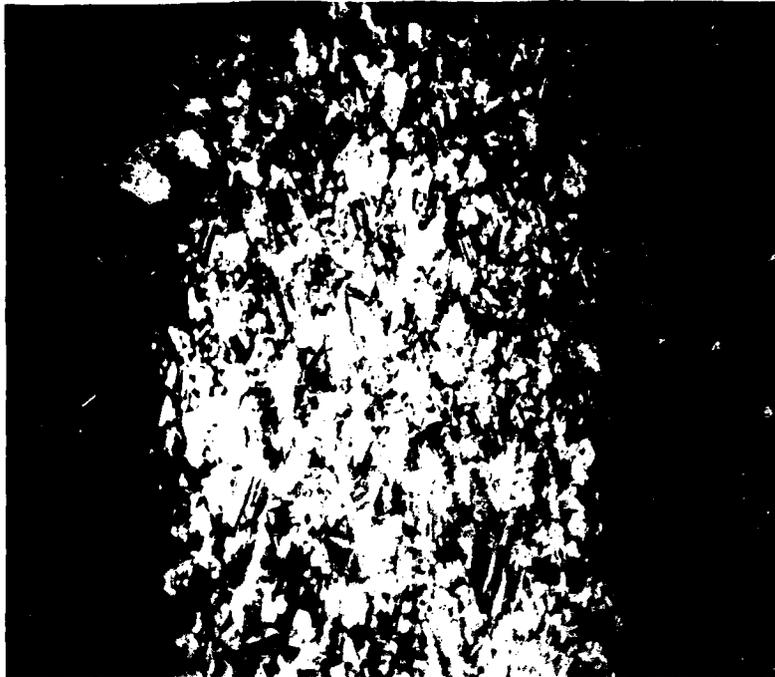


Fig. 1 - Qualitative summary of dealloying of copper alloys and the effectiveness of cathodic protection; 735 days in quiescent seawater at Key West, Florida.



(a)

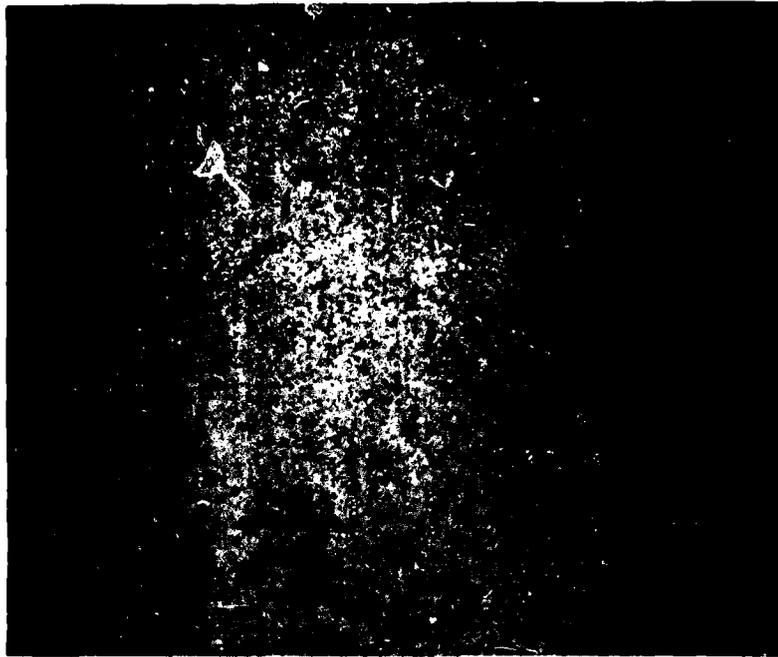
MC-273



(b)

MC-274

Fig. 2 - CDA alloy 172 (copper-beryllium). Sampled near crevice; 735 days in quiescent seawater at Key West Florida. Etched (0.5%CrO₃, 1 volt, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

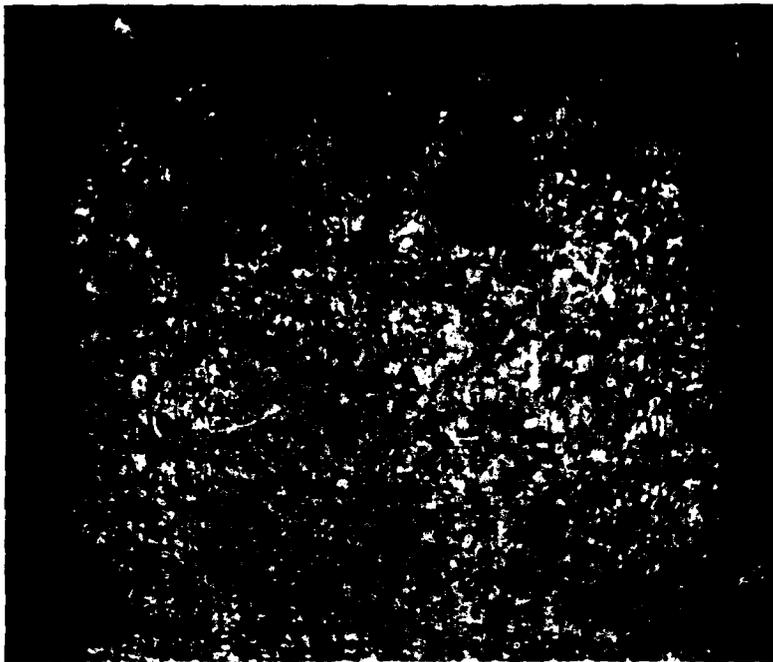
MC-275



(b)

MC-276

Fig. 3 - CDA alloy 175 (copper-cobalt-beryllium). Sampled just outside crevice; 735 days in quiescent seawater at Key West, Florida. Etched ($0.5\%CrO_3$, 1 volt, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

MC-277



(b)

MC-278

Fig. 4 - CDA alloy 220 (commercial bronze, 90%). Sampled near crevice; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

MC-279



(b)

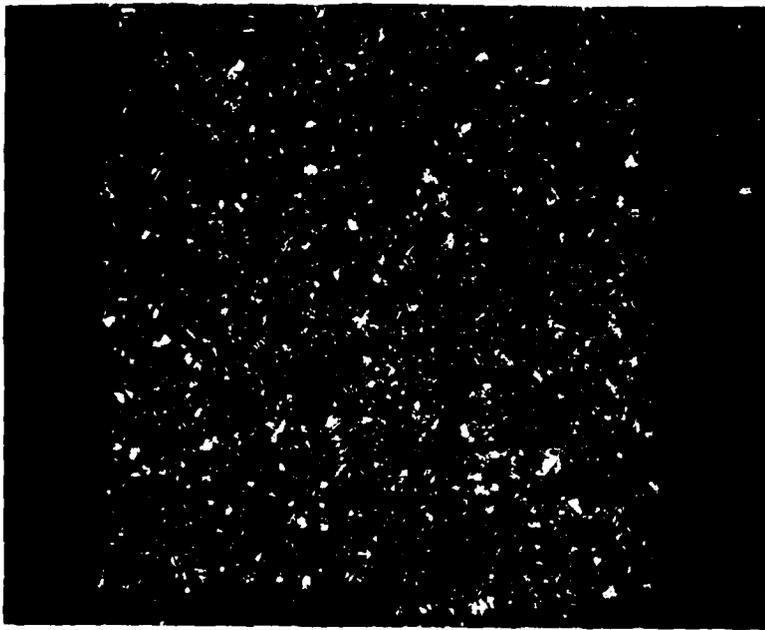
MC-280

Fig. 5 - CDA alloy 230 (red brass, 85%). Sampled at specimen center, i.e., remote from the crevice; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

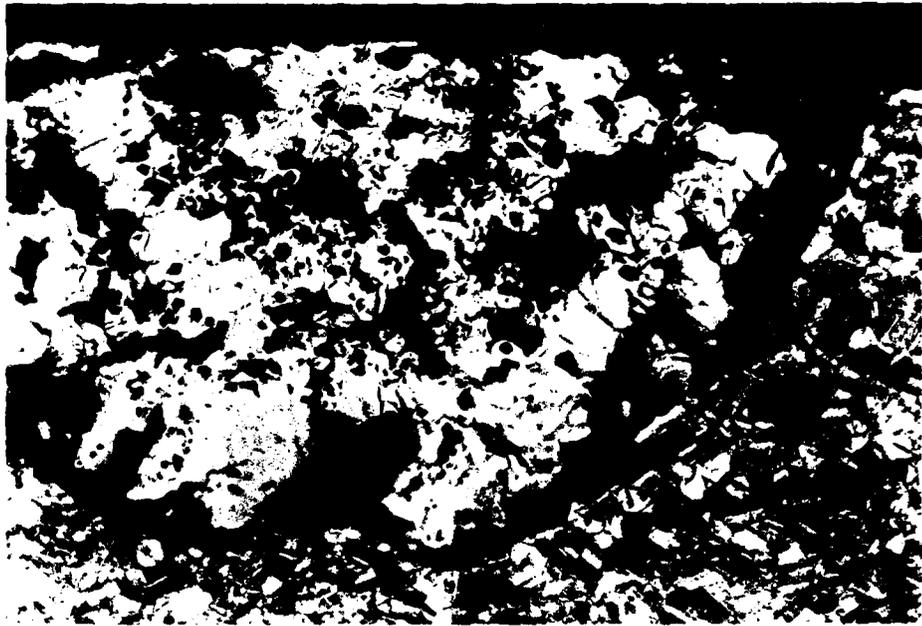
MC-281



(b)

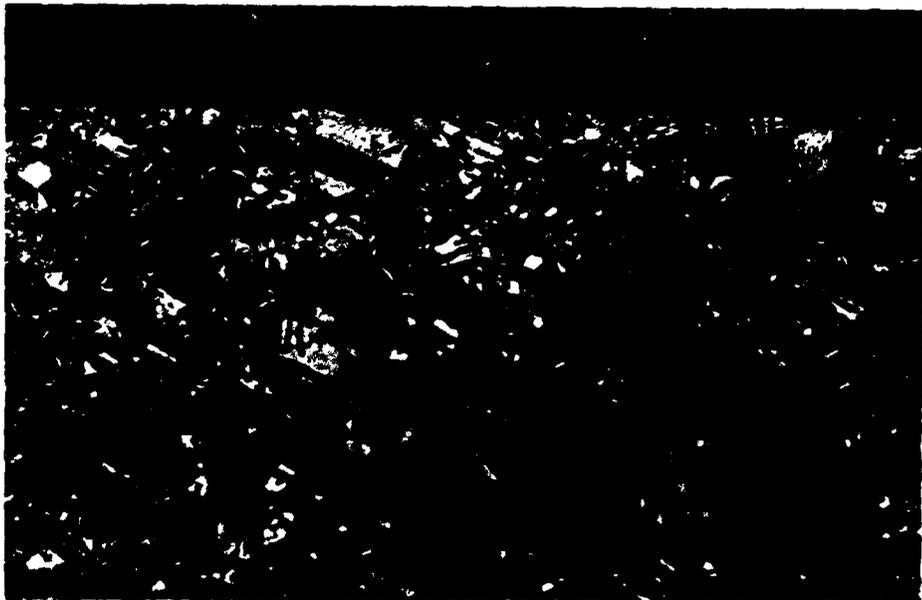
MC-282

Fig. 6 - CDA alloy 260 (cartridge brass, 70%). a) No cathodic protection, sampled at crevice opening; b) cathodic protection-zinc anode, sampled under zinc anode; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). 75X magnification.



(a)

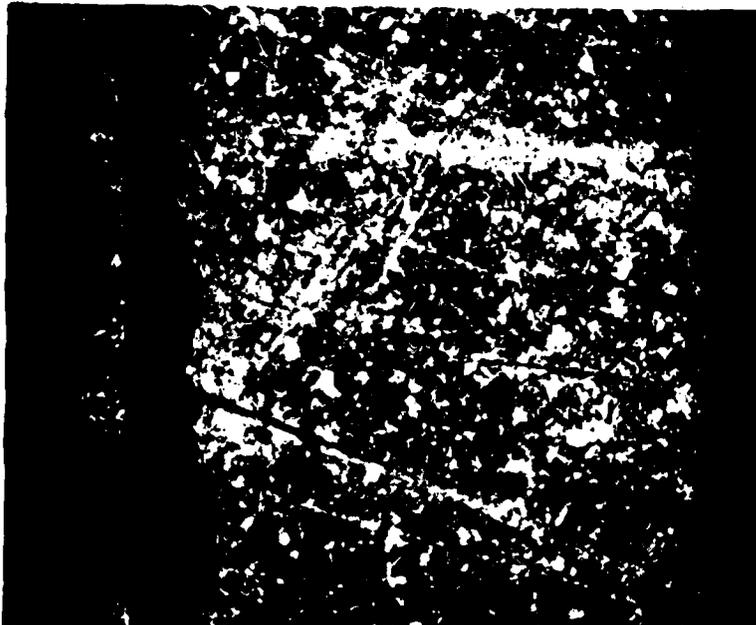
MC-283



(b)

MC-284

Fig. 7 - CDA alloy 260 (cartridge brass, 70%). a) No cathodic protection, sampled at crevice opening; b) cathodic protection-zinc anode, sampled under zinc anode; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). 500X magnification.



(a)

MC-285



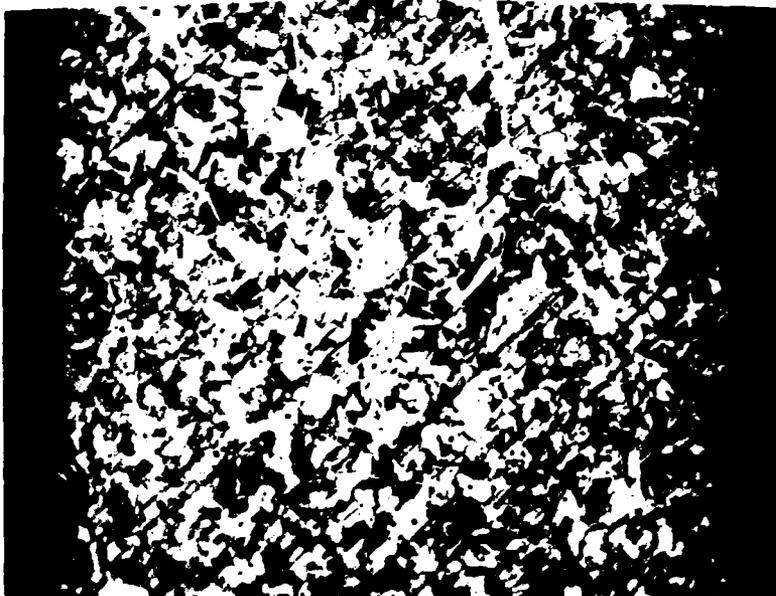
(b)

MC-286

Fig. 8 - CDA alloy 268 (yellow brass, 66%). Sampled in crevice; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)



(b)

Fig. 9 - CDA alloy 280 (Muntz metal, 60%). a) No cathodic protection, sampled near crevice (30-second etch); b) cathodic protection-zinc anode, sampled under zinc anode (5-second etch); 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts). 75 X magnification.



(a)

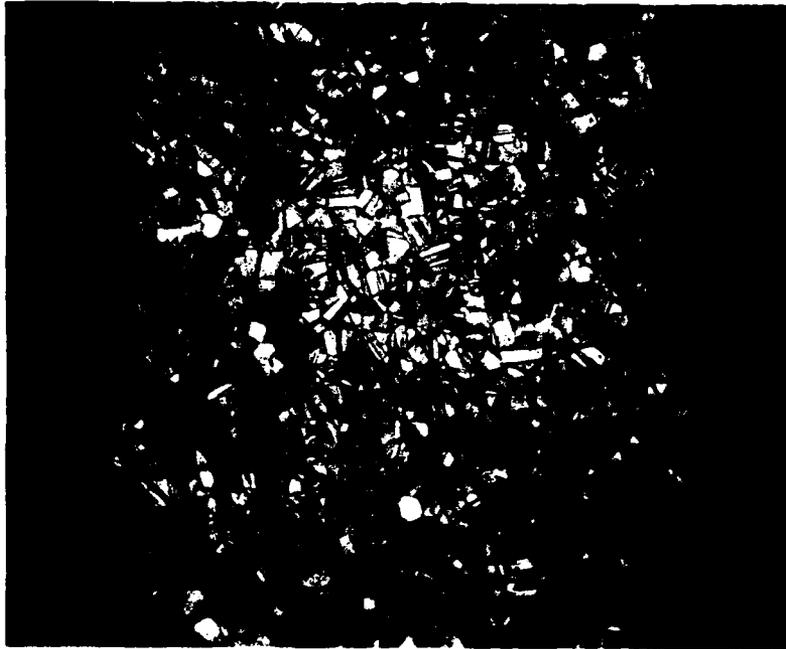
MC-289



(b)

MC-290

Fig. 10 - CDA alloy 280 (Muntz metal, 60%). a) No cathodic protection, sampled near crevice (30-second etch); b) cathodic protection-zinc anode, sampled under zinc anode (5-second etch); 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts). 500X magnification.

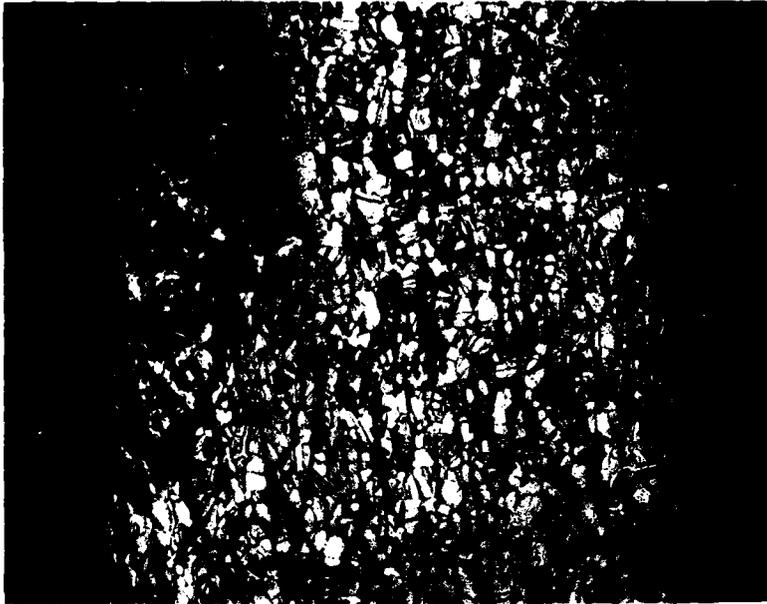


(a)



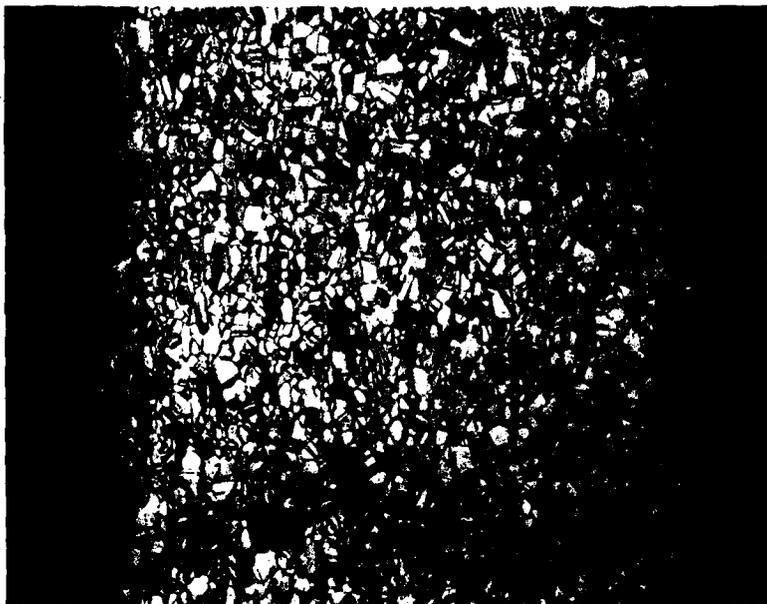
(b)

Fig. 11 - CDA alloy 443 (Admiralty, arsenical). Sampled just outside crevice; 735 days in quiescent seawater at Key West, Florida. Etched NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

MC-293



(b)

MC-294

Fig. 12 - CDA alloy 464 (Naval brass, uninhibited, Grade A). a) No cathodic protection, sampled near crevice; b) cathodic protection - zinc anode, sampled under zinc anode; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). 75X magnification.



(a)

MC-295



(b)

MC-296

Fig. 13 - CDA alloy 464 (Naval brass, uninhibited, Grade A). a) No cathodic protection, sampled near crevice; b) cathodic protection - zinc anode, sampled under zinc anode; 735 days in quiescent sea - water at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, $3\%\text{H}_2\text{O}_2$ -2 parts, 30 seconds). 500X magnification.



(a)

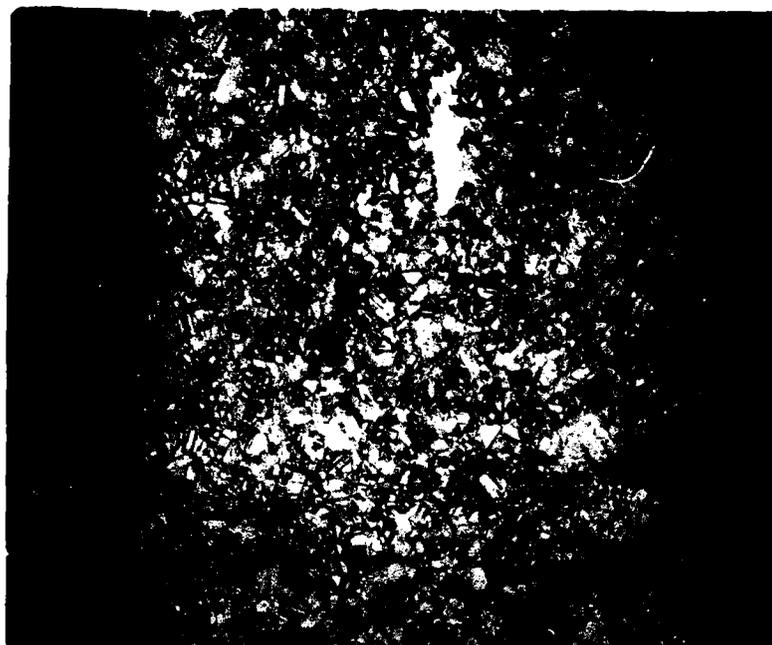
MC-297



(b)

MC-298

Fig. 14 - CDA alloy 524 (phosphor bronze, 10% D). Sampled just outside crevice; 735 days in quiescent seawater at Key West, Florida. Etched ($K_2Cr_2O_7$ -2 g, H_2SO_4 -8 ml, NaCl saturated solution-4 ml, H_2O -100 ml; all diluted with 2 vol H_2O , 15 seconds). a) 75X magnification; b) 500X magnification.



(a)

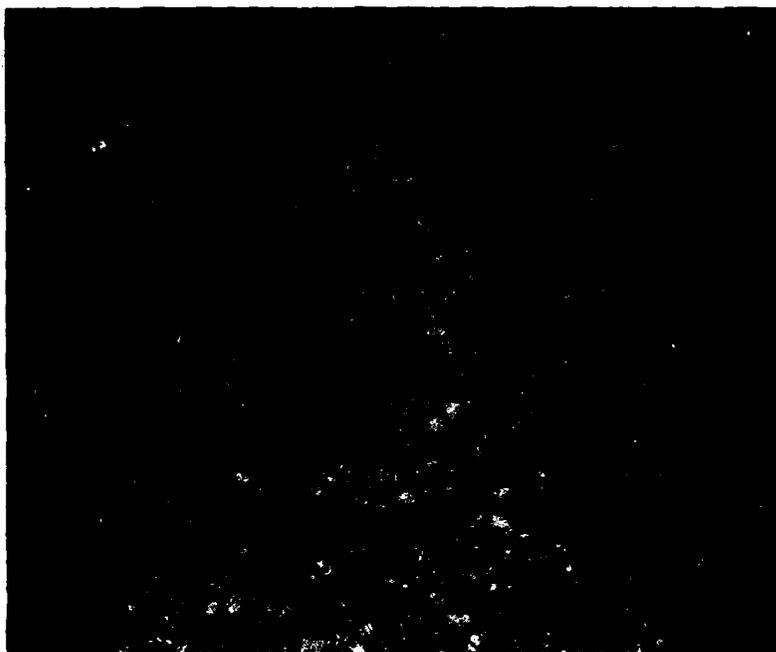
MC-299



(b)

MC-300

Fig. 15 - CDA alloy 608 (aluminum bronze, 5% Al). Sampled outside crevice; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.



(a)

MC-301

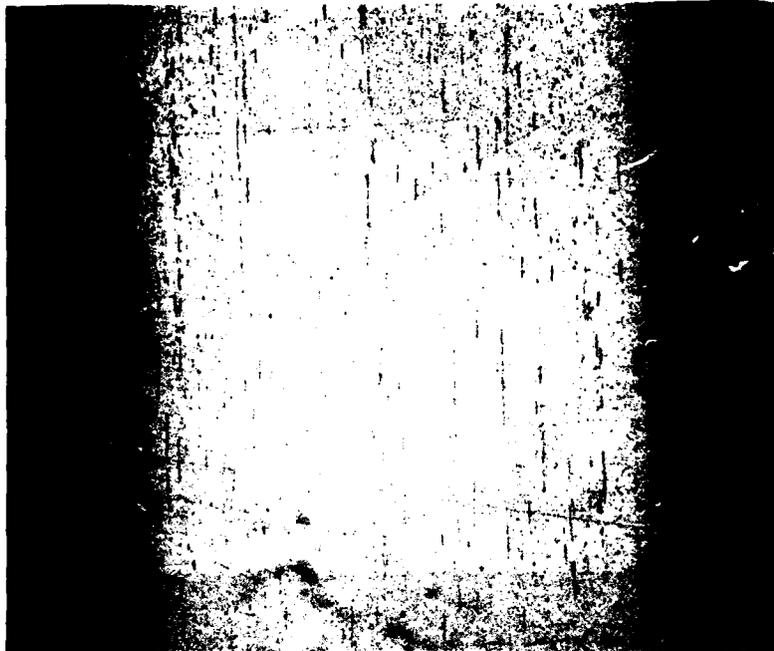


(b)

MC-302

Fig. 16 - CDA alloy 612 (aluminum bronze, 9%A1). Sampled at crevice opening; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.

NOT REPRODUCIBLE



(a)

MC-303



(b)

MC-304

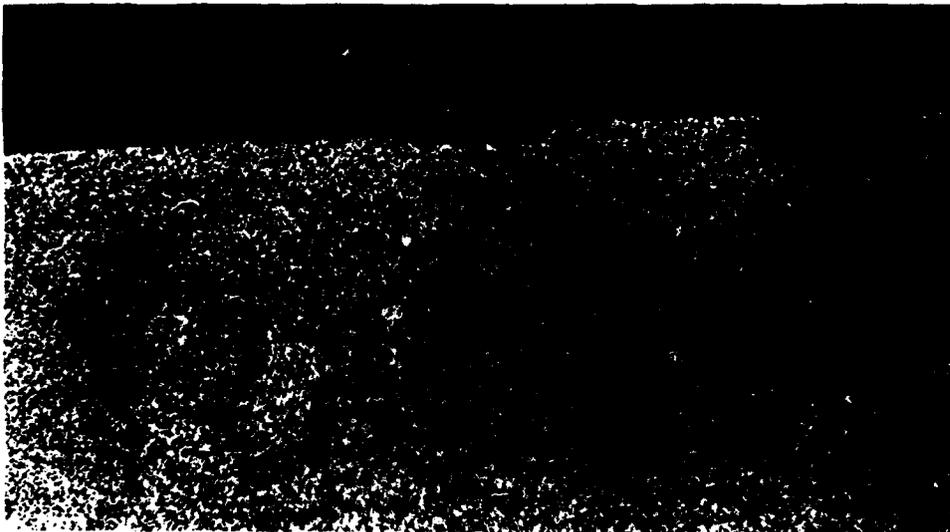
Fig. 17 - CDA alloy 614 (aluminum bronze, D, 7% Al, 2% Fe). a) No cathodic protection, sampled at crevice opening; b) cathodic protection-zinc anode, sampled in crevice; 735 days in quiescent seawater at Key West, Florida. Etched (0.5%CrO₃, 1 volt, 1 minute). 75X magnification.

NOT REPRODUCIBLE



(a)

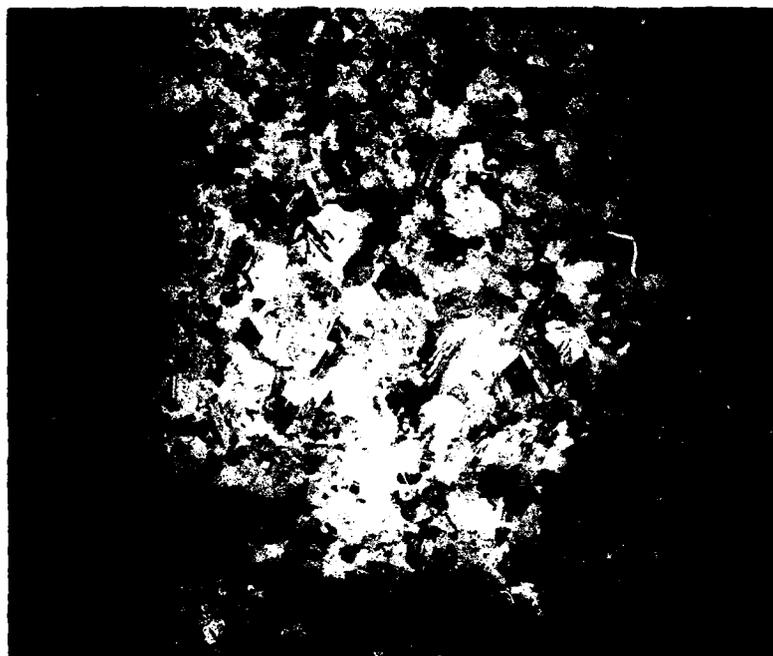
MC-305



(b)

MC-306

Fig. 18 - CDA alloy 614 (aluminum bronze, D, 7% Al, 2% Fe). a) No cathodic protection, sampled at crevice opening; b) cathodic protection-zinc anode, sampled in crevice; 735 days in quiescent seawater at Key West, Florida. Etched (0.5%CrO₃, 1 volt, 1 minute). 500X magnification.



(a)

MC-307

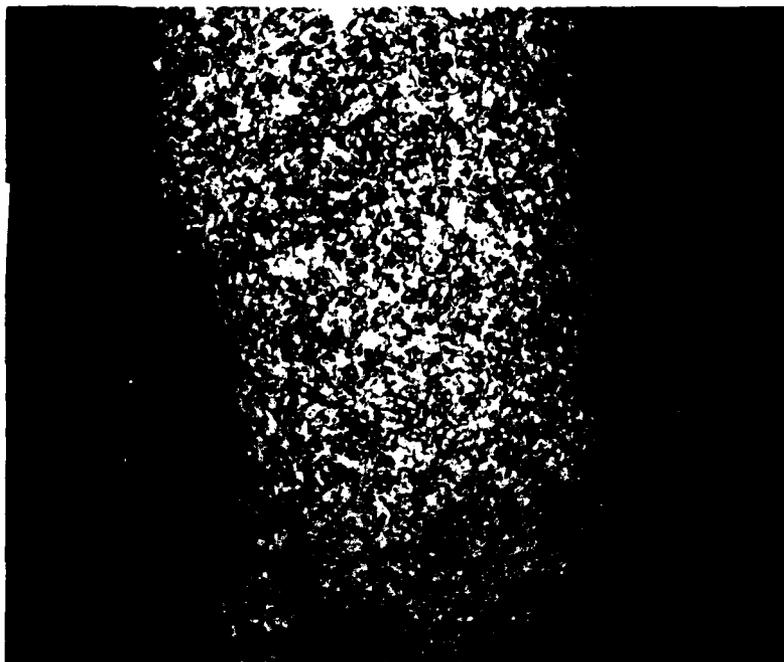


(b)

MC-308

Fig. 19 - CDA alloy 655 (high silicon bronze A). Sampled outside crevice; 735 days in quiescent seawater at Key West, Florida. Etched ($K_2Cr_2O_7$ -2 g, H_2SO_4 -8 ml, NaCl saturated solution-4 ml, H_2O -100 ml; all diluted with 2 vol H_2O , 10 seconds). a) 75X magnification; b) 500X magnification.

NOT REPRODUCIBLE



(a)

MC-309

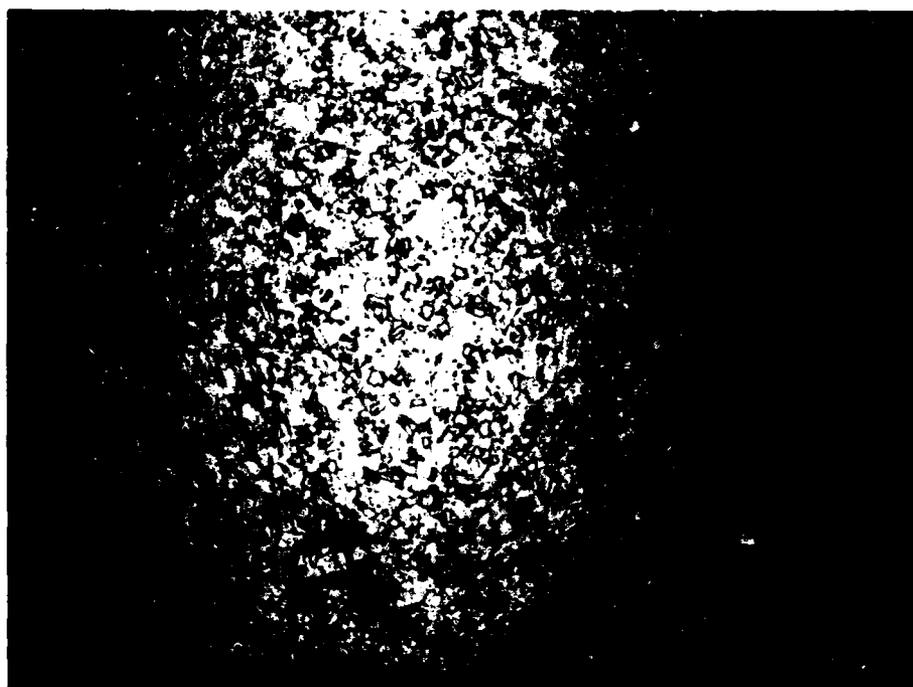


(b)

MC-310

Fig. 20 - CDA alloy 716 (copper nickel, 30% Ni, 5% Fe). Sampled at crevice opening; 735 days in quiescent seawater at Key West, Florida. Etched ($K_2Cr_2O_7$ -2 g, H_2SO_4 -8 ml, NaCl saturated solution - 4 ml, H_2O -100 ml; all diluted with 2 vol H_2O , 15 seconds). a) 75X magnification; b) 500X magnification.

NOT REPRODUCIBLE



(a)

MC-311



(b)

MC-312

Fig. 21 - Copper. Sampled in crevice; 735 days in quiescent seawater at Key West, Florida. Etched (NH_4OH -5 parts, H_2O -5 parts, 3% H_2O_2 -2 parts, 30 seconds). a) 75X magnification; b) 500X magnification.

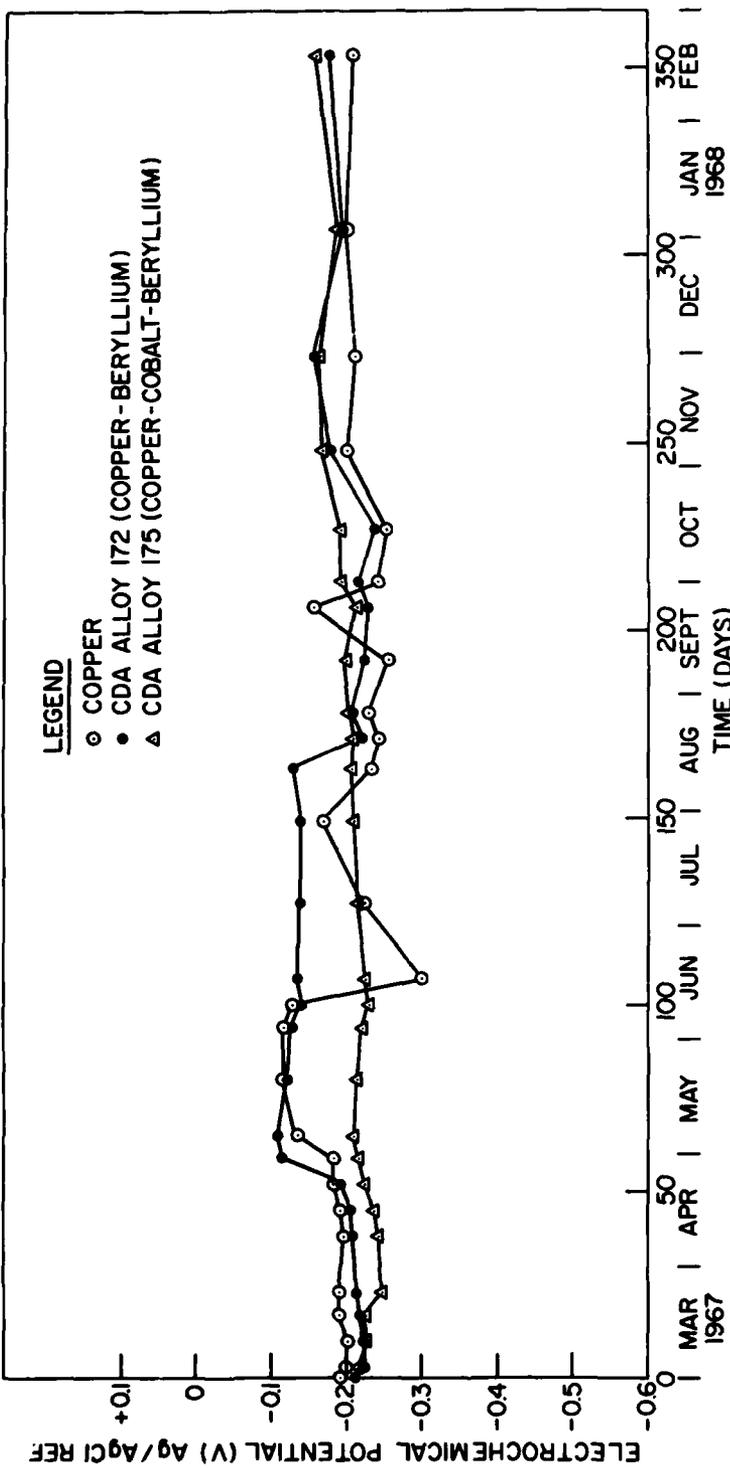


Fig. 22 - Electrochemical potentials as a function of time for copper and copper-beryllium and copper-cobalt-beryllium alloys exposed without cathodic protection in quiescent seawater at Key West, Florida.

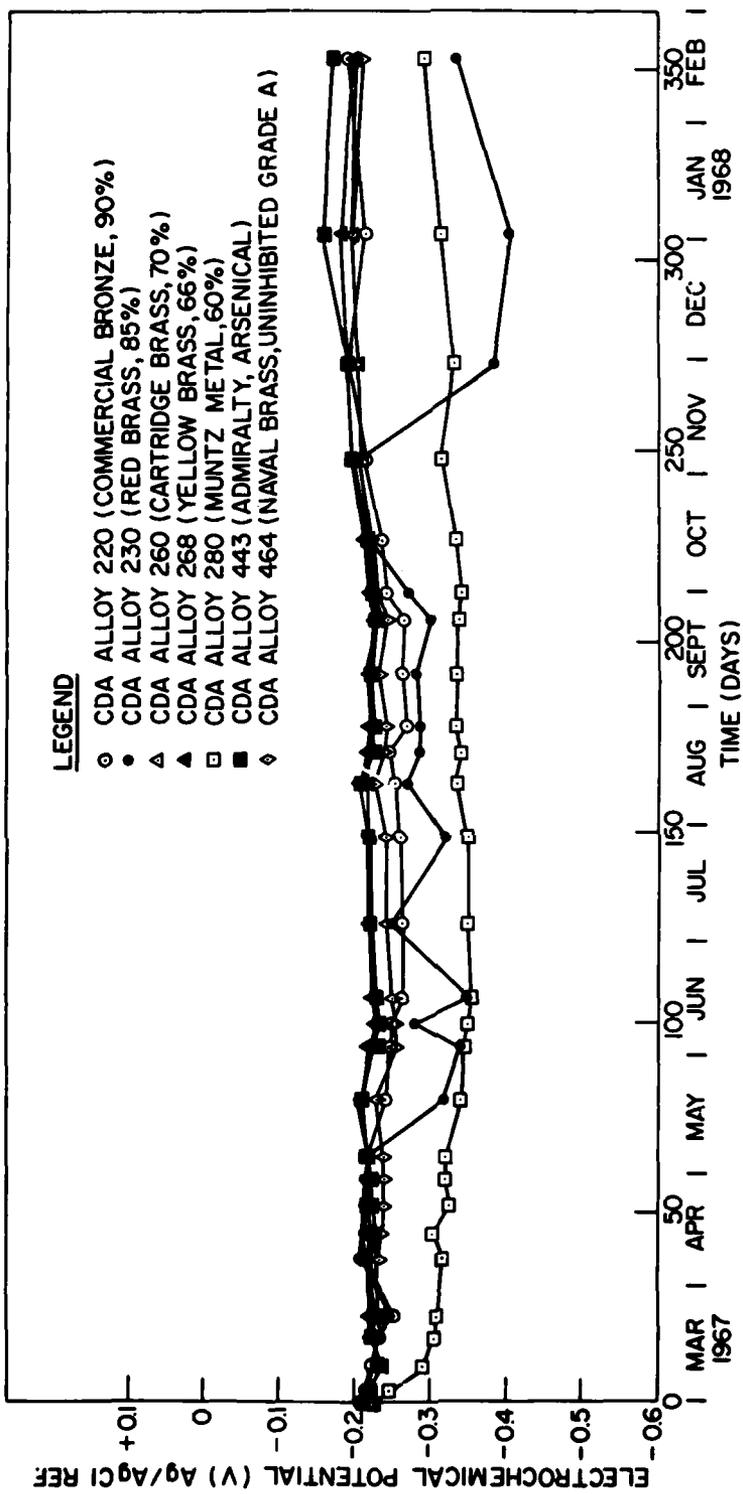


Fig. 23 - Electrochemical potentials as a function of time for copper-zinc alloys and copper-zinc-tin alloys exposed without cathodic protection in quiescent sea-water at Key West, Florida.

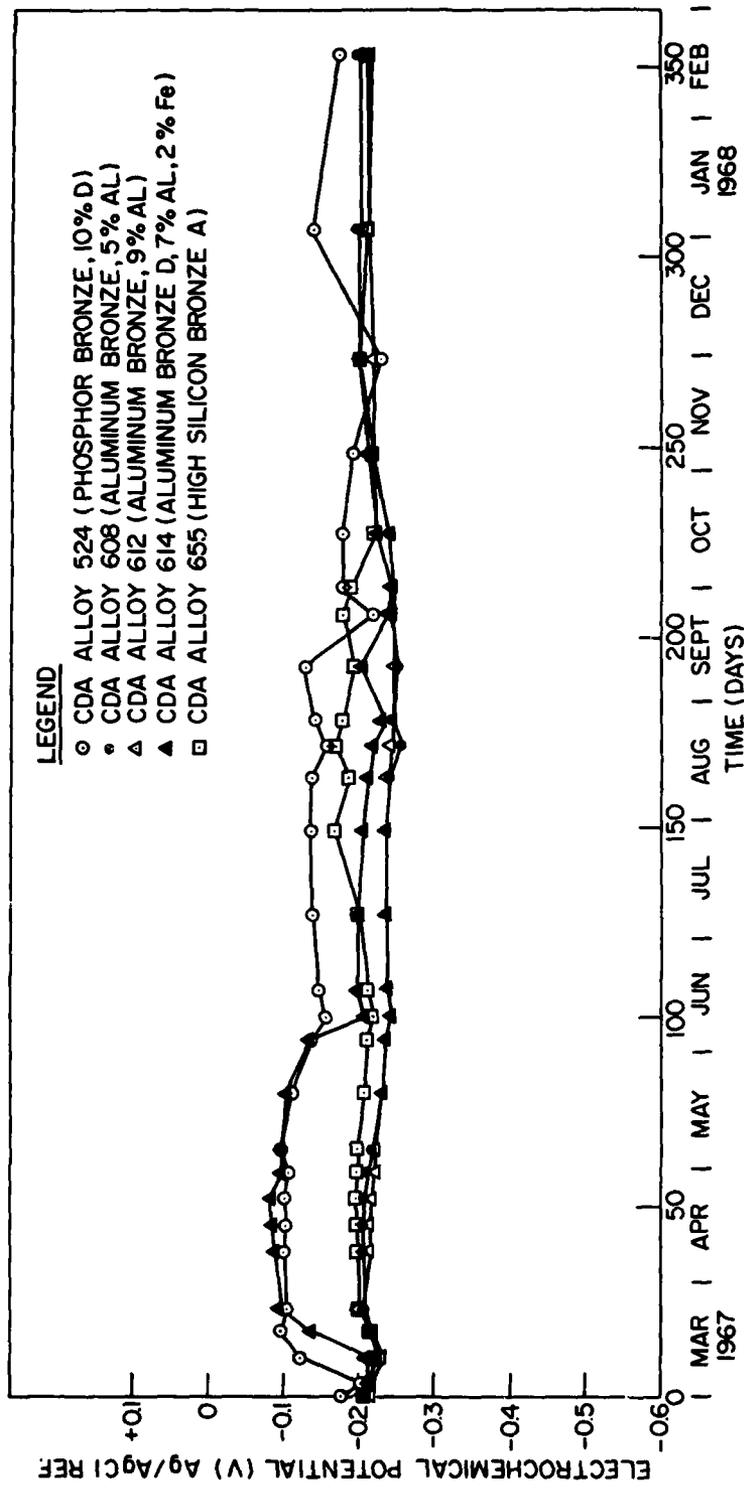


Fig. 24 - Electrochemical potentials as a function of time for copper-tin alloy, copper-aluminum alloys, and copper-silicon alloy exposed without cathodic protection in quiescent seawater at Key West, Florida.

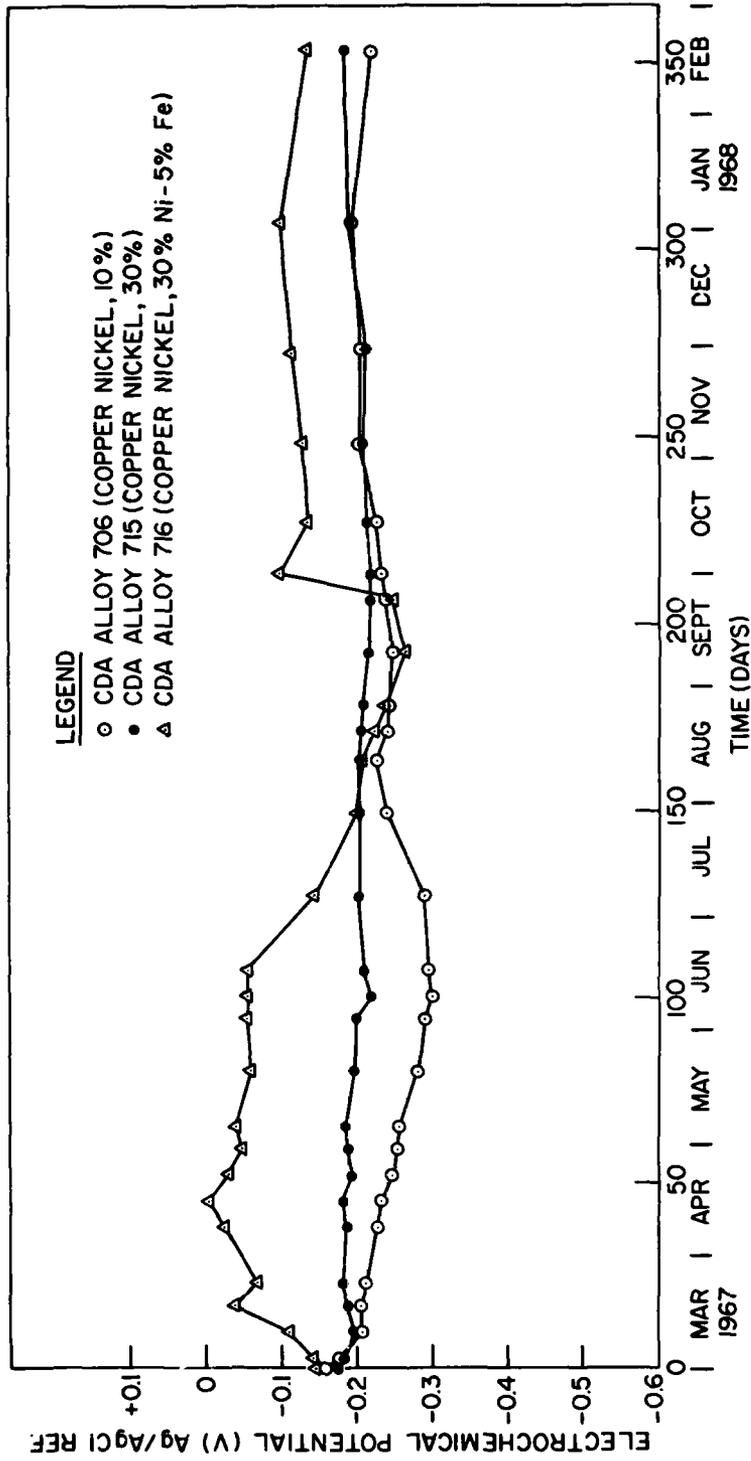
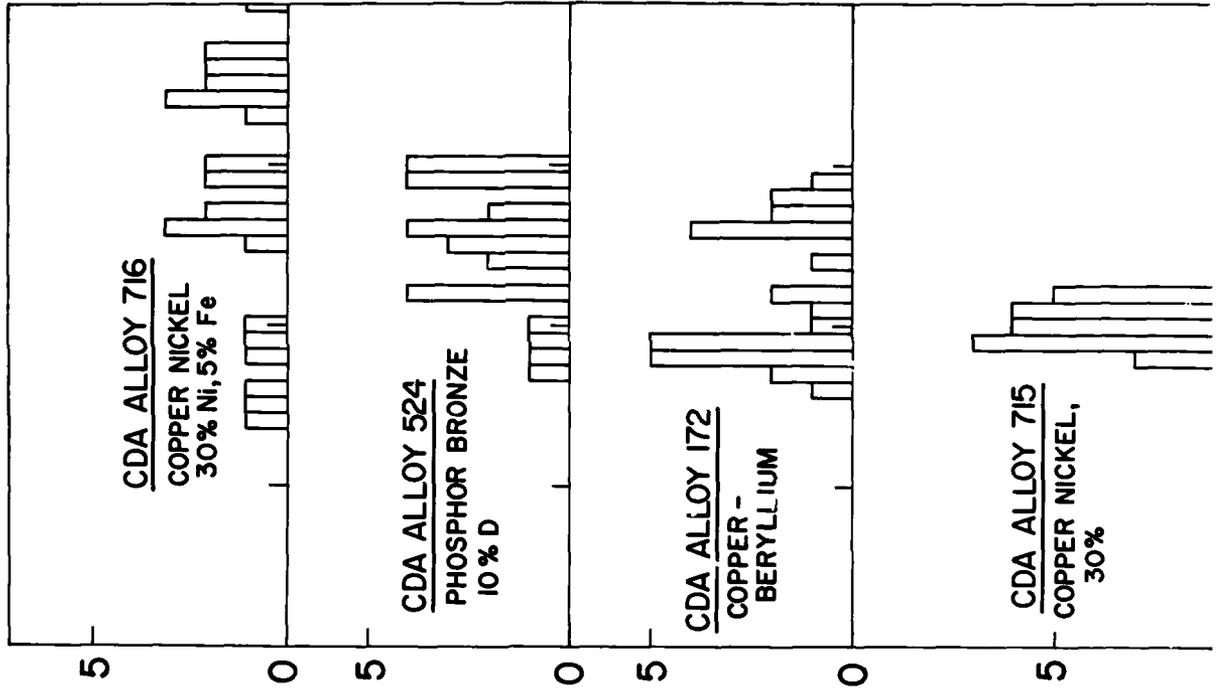
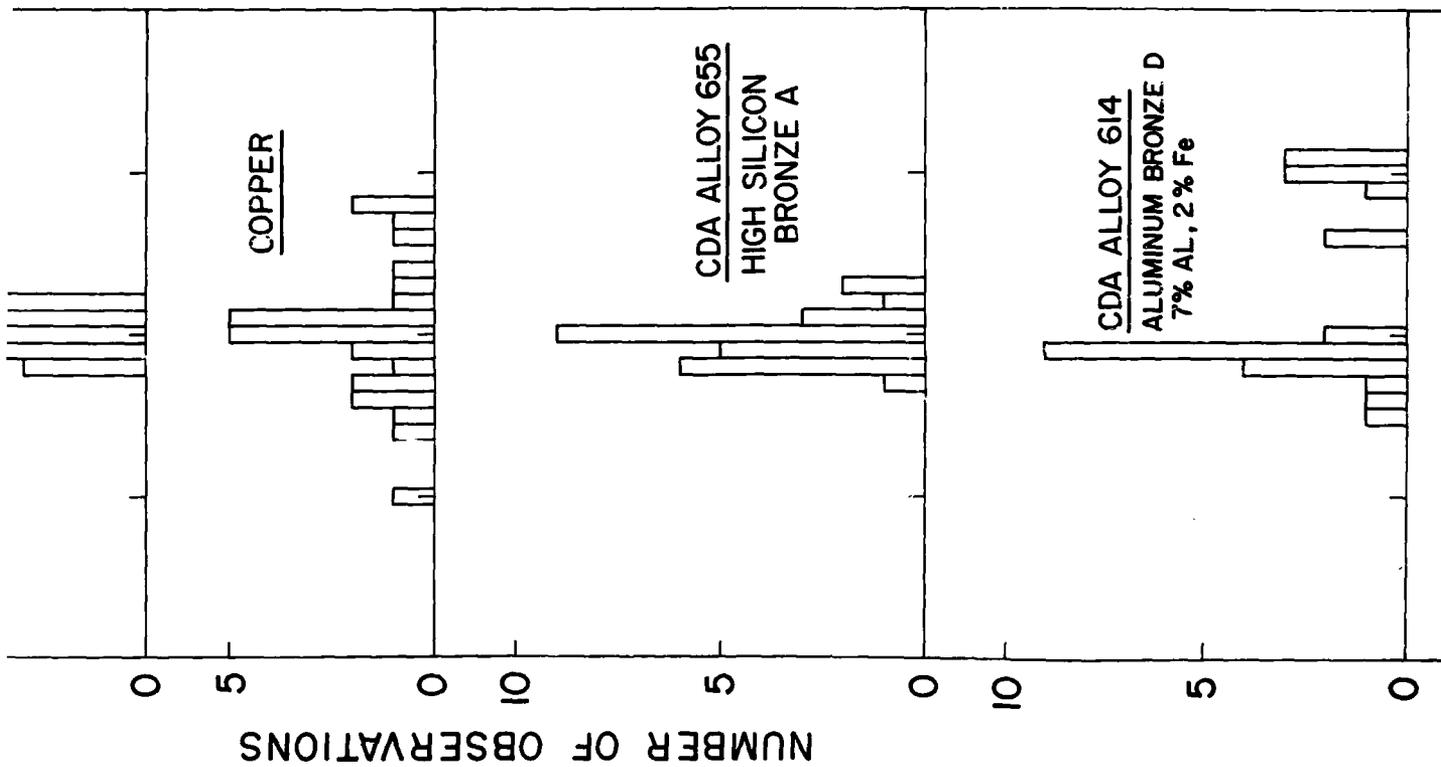


Fig. 25 - Electrochemical potentials as a function of time for copper-nickel alloys exposed without cathodic protection in quiescent seawater at Key West, Florida.

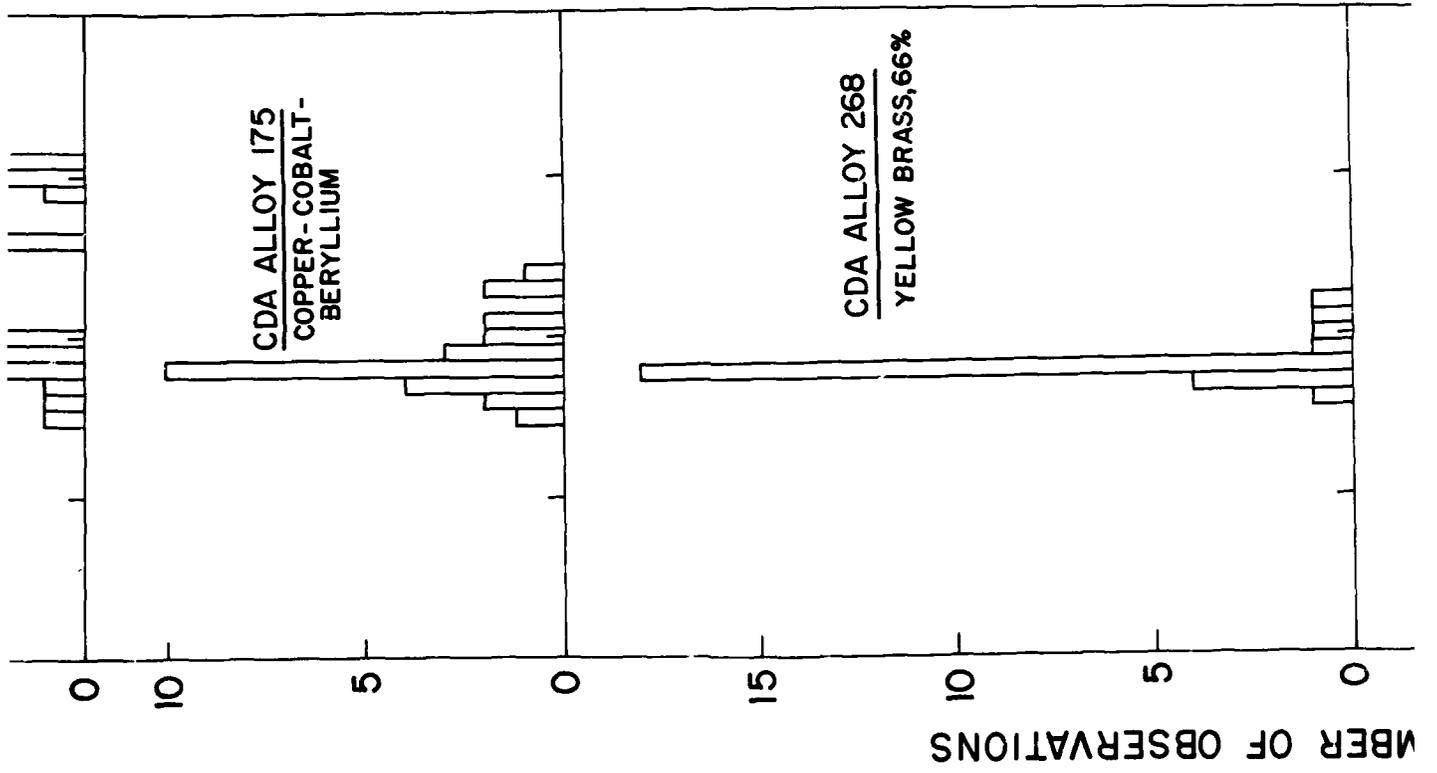


A

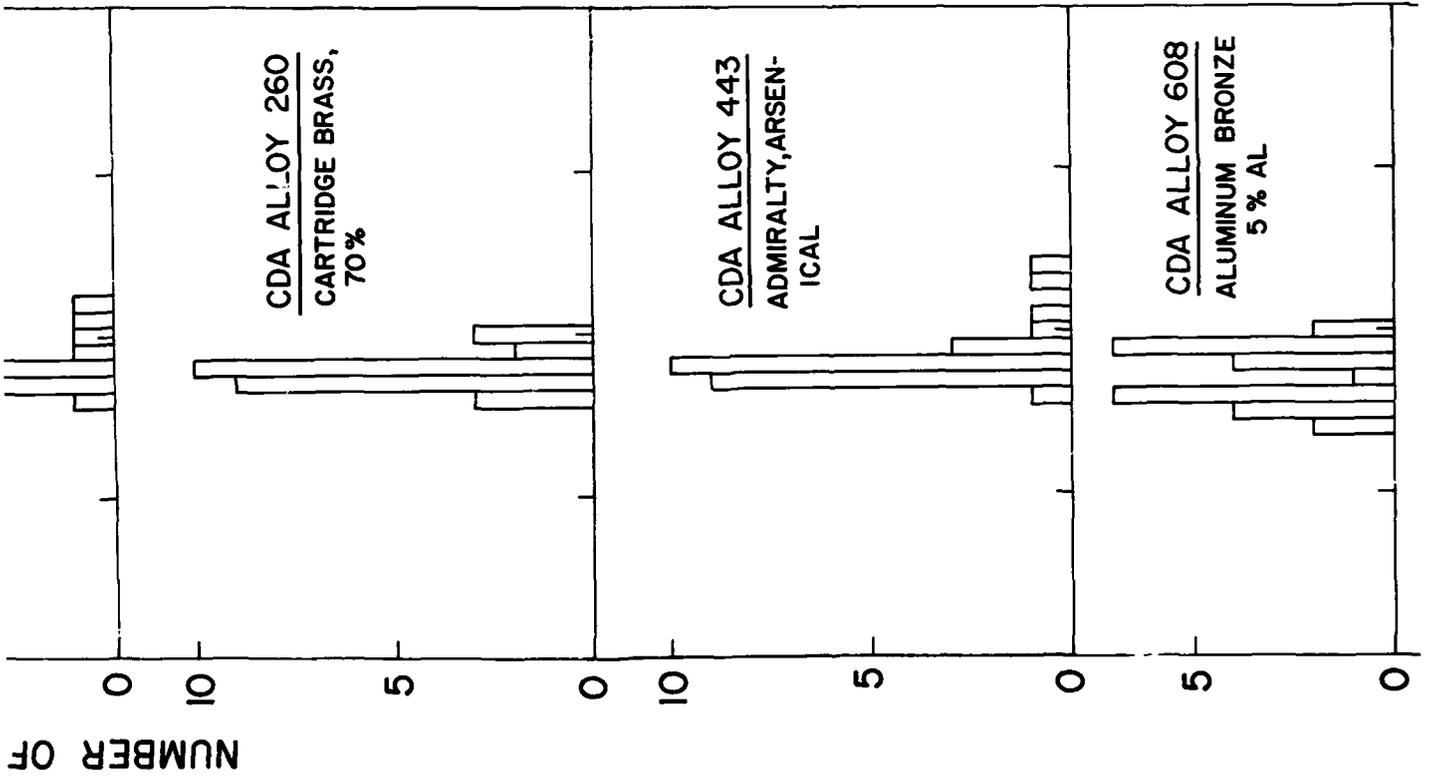
B



C



D



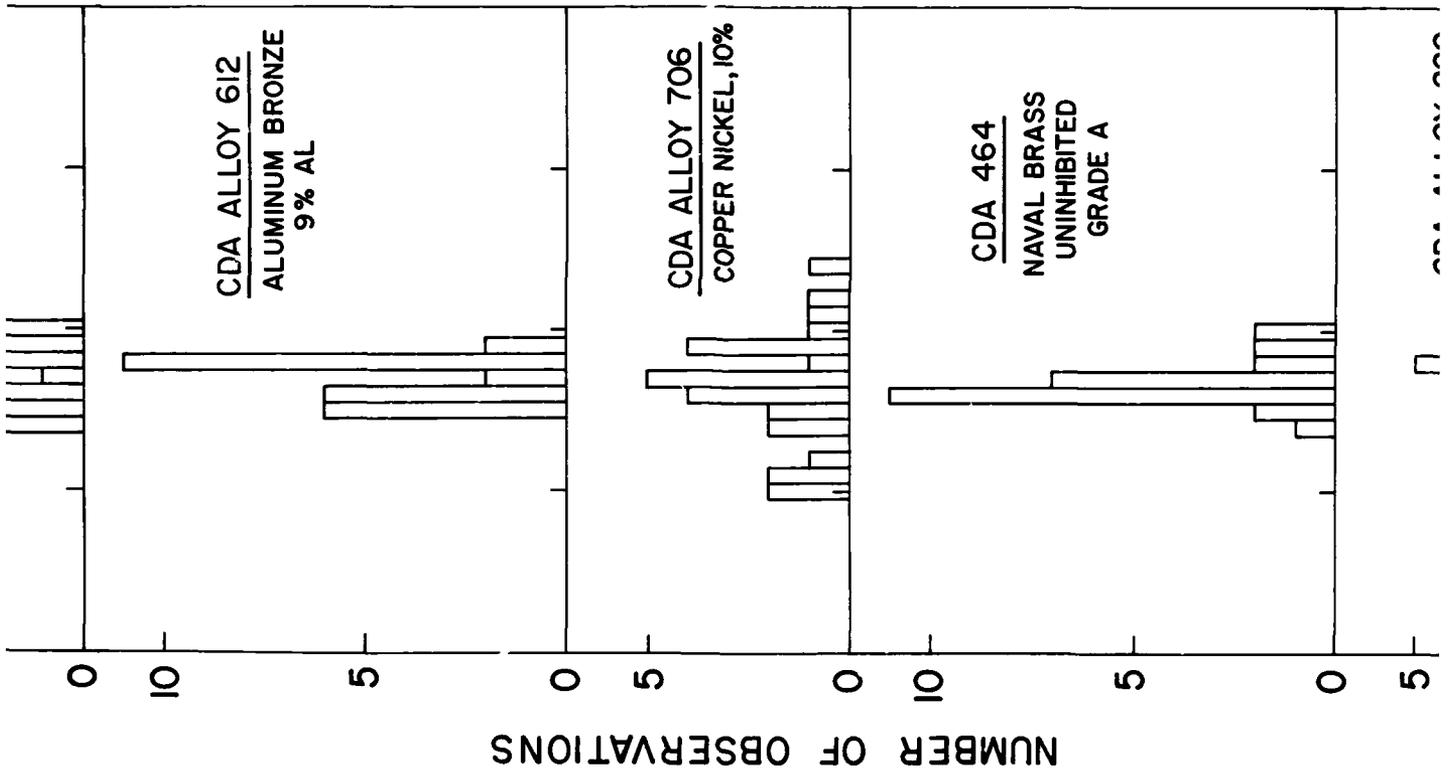


Fig. 26
observe
Florida.

E

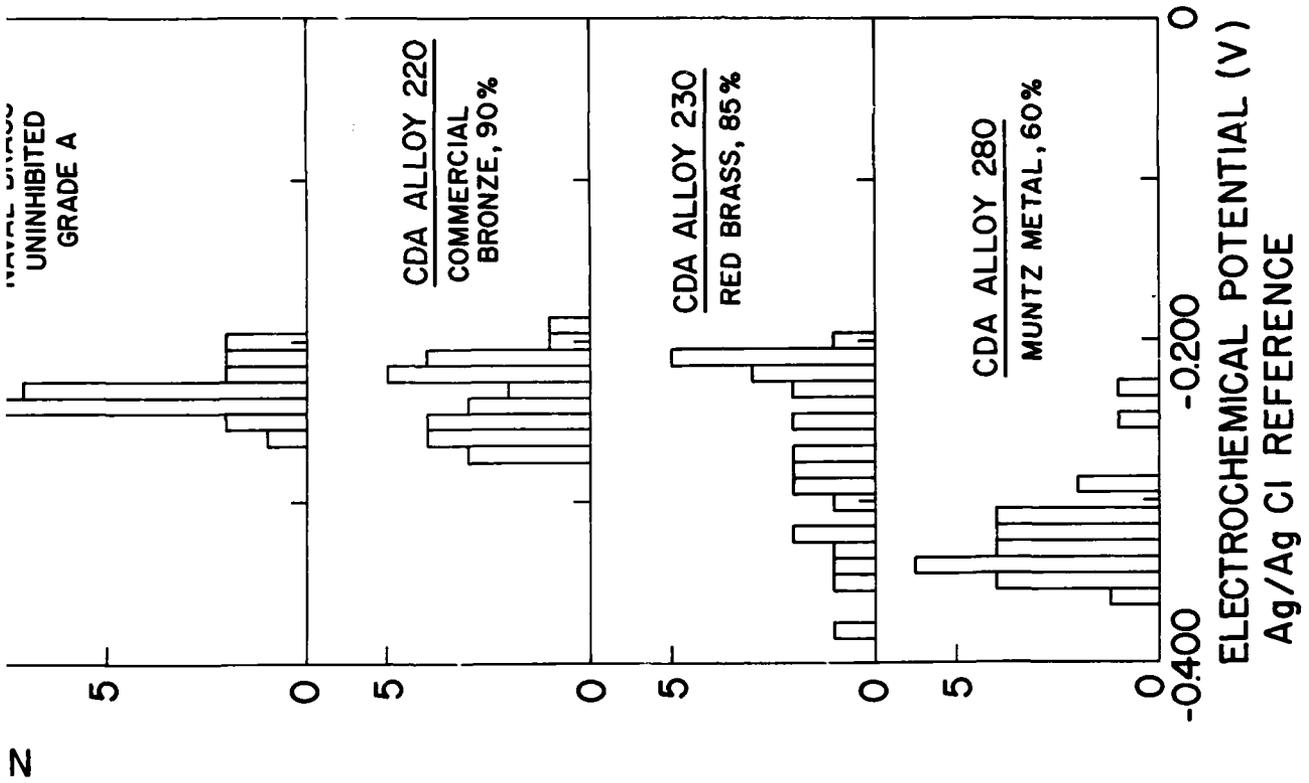


Fig. 26 - Histograms of the number of observations versus the potentials observed during immersion; 353 days in quiescent seawater at Key West, Florida.

F

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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| 13. ABSTRACT The corrosion characteristics, dealloying susceptibility, marine fouling characteristics, and the response to cathodic protection of seventeen copper alloys and unalloyed copper, which served as a control, were studied in quiescent seawater. Detailed examination after 735 days showed that several alloys in the unprotected condition had severely corroded either by deep localized attack or by dealloying. The corrosion rates were determined; on the unprotected specimens a maximum rate of 0.74 mils per year was observed. Cathodic protection from zinc anodes reduced the corrosion rate to essentially zero and prevented localized corrosion except in Naval brass and Muntz metal where metallurgical studies indicated that dealloying was not completely prevented. Histograms have been presented for the electrochemical potentials of each specimen, and a galvanic series for the copper alloys has been included. There was no correlation between the electrochemical potentials and the type or severity of corrosion. The resistance of the copper alloys to marine fouling varied widely. All unprotected specimens fouled to some extent, whereas the cathodically protected specimens were heavily fouled. | | | |

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|--|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Copper alloys Dealloying Cathodic protection Electrochemical potential Fouling Corrosion Seawater Galvanic series Zinc anodes Metallography | | | | | | |