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Marine Corrosion Studies

The Effects of Dissimilar Metal Couples and Toxicants from Antifouling Paints on the Corrosion of 5086 and 6061 Aluminum Alloys and Their Response to Cathodic Protection

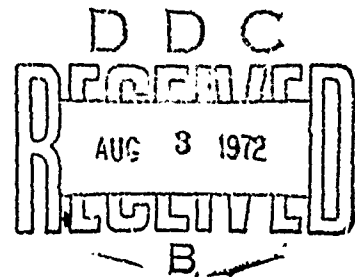
(Fourteenth Interim Report of Progress)

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Aluminum alloy 6061-T6 was severely corroded when continuously immersed in quiescent seawater or in the Potomac River. In seawater corrosion caused by the cuprous oxide toxicant was not as severe as that observed on uncoated and unprotected 6061-T6 aluminum, but in the Potomac River the depth of corrosion was significantly increased by the cuprous oxide antifouling coating. The depth of corrosion was less on the unprotected specimens coated with the tributyltin oxide toxicant than on the specimens coated with the cuprous oxide toxicant. The most effective method of reducing the corrosion on 6061-T6 aluminum coated with antifouling toxicants was the combination of the vinyl anticorrosive barrier, the tributyltin oxide toxicant, and cathodic protection.

The uncoated aluminum alloys were heavily fouled with marine growth in seawater, but in the Potomac River only slime developed on their surfaces. After 1264 days in seawater moderate fouling was observed on the cuprous oxide coated specimens and moderate to heavy fouling with a few barnacles on the tributyltin oxide coated specimens. Cathodic protection had little or no effect on the degree of fouling observed on the specimens immersed for 1264 days in seawater.

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ABSTRACT

Aluminum alloy 5086-H32 when not coupled to dissimilar metals was observed to be corrosion resistant in seawater or in the Potomac River at Washington, D.C. Severe corrosion occurred in seawater however when coupled to any of the following dissimilar metals: copper nickel, 10%; yellow brass; 304 stainless steel; or mild steel. This galvanic corrosion could not be completely prevented by cathodic protection. A magnesium anode also caused severe corrosion of the aluminum in seawater.

In the Potomac River at Washington, D. C. the dissimilar metal corrosion of 5086-H32 aluminum was more severe than in seawater. Except for the mild steel couple, cathodic protection did not significantly reduce the depth of corrosion caused by the dissimilar metals in the Potomac River water, although the incidence of attack was reduced.

Cuprous oxide antifouling paint caused corrosion at bared areas of 5086-H32 aluminum even when a vinyl anticorrosive barrier paint was applied beneath the antifouling paint. The corrosion caused by the cuprous oxide toxicant was more severe in the Potomac River than in seawater. The depth of corrosion on the cuprous oxide coated specimen that was cathodically protected and exposed in the Potomac River was not significantly less than on the unprotected specimen which was coated with the tributyltin oxide toxicant. If an antifouling paint is required, the best overall corrosion mitigation system on coated 5086-H32 aluminum was obtained on a specimen coated with tributyltin oxide and cathodically protected.

Aluminum alloy 6061-T6 was severely corroded when continuously immersed in quiescent seawater or in the Potomac River. In seawater corrosion caused by the cuprous oxide toxicant was not as severe as that observed on uncoated and unprotected 6061-T6 aluminum, but in the Potomac River the depth of corrosion was significantly increased by the cuprous oxide antifouling coating. The depth of corrosion was less on the unprotected specimens coated with the tributyltin oxide toxicant than on the specimens coated with the cuprous oxide toxicant. The most effective method of reducing the corrosion on 6061-T6 aluminum coated with antifouling toxicants was the combination of the vinyl anticorrosive barrier, the tributyltin oxide toxicant, and cathodic protection.

The uncoated aluminum alloys were heavily fouled with marine growth in seawater, but in the Potomac River only slime developed on their surfaces. After 1264 days in

seawater moderate fouling was observed on the cuprous oxide coated specimens and moderate to heavy fouling with a few barnacles on the tributyltin oxide coated specimens. Cathodic protection had little or no effect on the degree of fouling observed on the specimens immersed for 1264 days in seawater.

Status

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

Authorization

NRL Problem No. 63M04-02
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INTRODUCTION

Aluminum alloys have been used over the past several years for some ship hulls, other naval structures and oceanographic instrument packages. Alloys 6061-T6 and 5086-H32 have been of particular interest for use in seawater. The former alloy is weldable and heat treatable. The latter alloy is also weldable, but its strength is realized through strain hardening.

Marine structures are usually designed with strength requirements as the primary parameter governing the choice of materials. It may also be necessary to use more than one metal in the structure to obtain the desired mechanical strength. Because alloys with less than optimum corrosion resistance maybe used, and because of the accelerated corrosion that will be caused by dissimilar metal couples, it is prudent to control the corrosion to acceptable limits through the use of protective coatings and cathodic protection.

Antifouling coatings are also often required to limit weight increases and to minimize the additional drag created by marine organisms growing on the structure. The standard Navy antifouling coating is Formula No. 121 of MIL-P-15931 which contains cuprous oxide as the toxicant. At one time this antifouling toxicant was considered tolerable on aluminum provided there was a 6 mil barrier-layer of pore-free vinyl anticorrosive paint between the cuprous oxide and the aluminum. This undoubtedly would be satisfactory if the barrier film remained intact during service, but almost invariably the paint coating is damaged in service and bare metal is exposed at some areas.

The present study was initiated to determine the corrosion characteristics of 5086-H32 and 6061-T6 aluminum alloys in seawater and fresh water. Another objective was to determine whether cathodic protection could prevent the corrosion of aluminum alloys caused by dissimilar metals or the toxicants in antifouling paints. A comparison of the corrosive effects of cuprous oxide (Cu_2O) and tributyltin oxide (TBTO) antifouling paint toxicants on the aluminum alloys and the response to cathodic protection was also included in this study.

Interim results have been previously reported (1,2,3, and 4). The present report includes data from specimens exposed for longer time periods and correlates data for several time periods and different exposure locations.

PROCEDURES

Most of the study was conducted in seawater at the NRL Marine Corrosion Research Laboratory, Key West, Florida, and in the Potomac River at the Naval Research Laboratory, Washington, D.C.

Each aluminum specimen measured 12 x 12 inches and was sheared from larger plates. The 5086-H32 specimens were 1/8-inch thick except for the welded specimens which were 3/16-in. thick. Welded specimens were fabricated using 5356 filler metal. The 6061-T6 specimens were all 1/16-in. thick.

The dissimilar metals or galvanic anodes that were coupled to the aluminum specimens measured 1/2-in. x 1 1/4-in. x 6-in. with an area ratio of the dissimilar metal or cathodic protection anodes to the aluminum specimen of approximately 1:18. The dissimilar metals included copper nickel, 10%; yellow brass; 304 stainless steel; and mild steel. The galvanic anodes used for the cathodic protection phase of this study included proprietary aluminum anodes, zinc anodes (MIL-A-18001H), and magnesium anodes (MIL-A-21412A). The dissimilar metals and anodes were drilled and tapped and fastened to the aluminum by stainless steel bolts through the specimens. No insulating barrier was used between the faying surfaces of the aluminum specimen and the dissimilar metal (or anode), but the bolt heads and the area around the through bolts were sealed with epoxy resin. The metallic resistance between the aluminum specimens and the coupled metals (or anodes) was less than 0.001 ohm before and after these immersion studies.

The aluminum specimens were solvent-wiped prior to coating and the following anticorrosive paint system was applied:

- (a) one coat (0.5 mil) Wash Primer-Formula No. 117 of MIL-P-15328
- (b) six coats (6 mils) zinc chromate primer, Vinyl-Formula No. 120 of MIL-P-15930.

The antifouling paint toxicants were applied over the anticorrosive paint system and included the following two types:

- (a) (Cu₂O) - Two coats (4 mils) Antifouling Vinyl (red) - Formula No. 121 of MIL-P-15931
- (b) (TBTO) - Two coats (4 mils) Antifouling (proprietary vinyl formulation, copper-free but pigmented to a dark red color).

A circular window (bare area) of approximately one square inch was left uncoated at the center of one surface of each painted specimen. This window simulated a damaged area on the coating, permitted the study of any effects on the aluminum caused by the toxicants leached from the antifouling coatings, and provided for the evaluation of the response to cathodic protection from the galvanic anodes.

Specimens were mounted on reinforced phenolic rods and spacers with the flat surfaces of the specimens parallel and were exposed in the totally immersed condition. Individual specimens were spaced approximately 4 inches apart. This mounting method provided an intentional crevice and reduced the number of support racks required for the experiment. A typical exposure rack is shown in Fig. 1.

The aluminum alloy specimens and coupled metals were individually weighed to within one gram prior to assembly and at the completion of the experiment. All of the bare specimens were cleaned of fouling after removal from exposure, rinsed with fresh water, dried, and sprayed with an inhibited spray before returning them to NRL for detailed evaluation.

Final chemical cleaning of the uncoated specimens consisted of immersion with alternate brushing in a solution of 2 wt. % chromic acid - 5 wt. % H_3PO_4 at 80-85° C (175-185° F). This was followed by a fresh water rinse and drying. The paint on the coated specimens was removed by repeated immersion in acetone and brushing. The stripped specimens were then cleaned as noted above for the uncoated specimens.

EXPERIMENTAL RESULTS

Uncoated 5086-H32 Aluminum - Seawater Performance - Effects of Weldments, Dissimilar Metal Couples and Cathodic Protection. Exposure Periods Up to 809 Days (26½ Months).

The depth of corrosion and the response to cathodic protection for various areas on the welded specimens of 5086-H32 aluminum are shown in Fig. 2. These data showed that the deepest corrosion on any of the welded specimens in seawater was 13 mils and that cathodic protection effectively reduced the depth of corrosion except at the area immediately adjacent to the weld on the circular welded specimen. There was evidence of cracks in the welds, notably on the circular welded specimen. The weld cracks were evident after exposure whether or not the specimen was cathodically protected by an aluminum anode, but it was not certain whether these cracks were present prior to the exposure. The weld area and areas adjacent to the weld on

the unprotected specimen are shown in Fig. 3. A similar area of the protected specimen is shown in Fig. 4.

The depth of corrosion at various locations on the 5086-H32 aluminum caused by the dissimilar metals and the response to cathodic protection in preventing this corrosion are summarized in Figs. 5 thru 8.

Each of the following dissimilar metals: copper nickel, 10%; yellow brass; 304 stainless steel; and mild steel caused accelerated corrosion at some location on the 5086-H32 aluminum. Of all the dissimilar metals studied the copper nickel caused the deepest corrosion beneath the dissimilar metal and on the general areas of the specimen. The 304 stainless steel accelerated the corrosion of the aluminum the most at the crevice formed by the phenolic mounting spacers. Edge corrosion of the aluminum was also caused by each of the dissimilar metals.

Cathodic protection from the aluminum anodes reduced the depth of corrosion on the 5086-H32 aluminum caused by the dissimilar metals, but only in the case of the 304 stainless steel couple (Fig. 7) was the depth of corrosion reduced to that observed on the bare, uncoupled and unprotected 5086-H32 aluminum. The depth of corrosion on bare 5086-H32 aluminum (with and without cathodic protection) and not coupled to a dissimilar metal has been shown on Fig. 9. The data for the maximum corrosion depth for bare and unprotected 5086-H32 aluminum have been shown on the appropriate graphs for comparative purposes.

The weight loss data have also been included in Figs. 5 thru 9 for comparative purposes although the weight loss data were not indicative of the severity of the corrosion on the aluminum caused by the dissimilar metals. However, weight loss data as well as depth of corrosion data did show the accelerated corrosion on 5086-H32 aluminum when cathodic protection was attempted from a magnesium anode (Fig. 9). There was also some indication that the depth of corrosion on the general areas of the specimen may have been slightly accelerated by cathodic protection from a zinc anode. Cathodic protection from aluminum anodes prevented the edge corrosion on the aluminum alloy specimens that were coupled to the dissimilar metals.

The photographs in Figs. 10 thru 18 depict the corrosion of the 5086-H32 aluminum caused by the dissimilar metals and the response to cathodic protection. In most instances the areas shown were under and immediately adjacent to the location of the dissimilar metals on the specimens. Figure 19 shows the excellent corrosion resistance of bare

unprotected 5086-H32 aluminum after 809 days in seawater when not coupled to a dissimilar metal.

Comparative data showing the depth of corrosion on 5086-H32 aluminum and the effectiveness of cathodic protection in counteracting the detrimental effects of the dissimilar metals are shown in Figs. 20 thru 23. These data were obtained for two time periods from exposures at Key West, and two time periods from exposures at Ft. Amador, Canal Zone. The depth of corrosion on unprotected specimens was generally greater at Key West than at Ft. Amador. This was evident except when copper nickel was the dissimilar metal and the exposure time at Key West was relatively short.

The Ft. Amador experiments did not indicate an increase of corrosion depth with time. The 540 days Ft. Amador data and the 319 days Key West data also indicated that cathodic protection from an aluminum anode was completely effective in preventing corrosion caused by the dissimilar metals. The longer term (809 days) Key West data indicated, however, that a prolonged incubation period existed before the detrimental effects of the dissimilar metals copper nickel, 10% and 304 stainless steel became evident (Figs. 20 and 22). The longer term Key West data also showed that cathodic protection was not completely effective in counteracting the detrimental effects on the aluminum caused by any of the dissimilar metals studied.

Uncoated 5086-H32 Aluminum - Lake and River Water Performance.
Effects of Weldments, Dissimilar Metal Couples and Cathodic Protection. Exposure Periods up to 675 days (22 Months).

The data for the depth of corrosion on the welded specimens of 5086-H32 aluminum exposed for 675 days in the Potomac River are summarized in Fig. 24. The 5086-H32 aluminum corroded to a depth of 56 mils adjacent to the weld and to 33 mils on general areas of the specimen. The deepest corrosion occurred on the circular welded specimen which also showed slight cracks in the weld, but it was not certain whether these cracks were present prior to exposure. The weld and adjacent areas on this specimen are shown in Fig. 25.

A comparison of the data in Figs. 2 and 24, and 3 and 25, indicates that the corrosion of the unprotected welded specimen was more severe in the Potomac River than in seawater at Key West. The response to cathodic protection in preventing the corrosion on the welded specimens in the Potomac River is not known because these specimens were lost when the dock from which the specimens were suspended was removed by a demolition crew unbeknownst to the authors.

The depth of corrosion produced on the 5086-H32 aluminum by the dissimilar metal couples in the Potomac River and the response to cathodic protection have been shown in Figs. 26 thru 29. Each of the dissimilar metals: copper nickel, 10%; yellow brass; 304 stainless steel; and mild steel caused severe corrosion of the 5086-H32 aluminum. On the general areas of the aluminum the corrosion in the Potomac River was $1\frac{1}{2}$ to 2 times deeper than on similar specimens exposed in seawater at Key West. (Compare Figs. 5,6,7,8 with Figs. 26,27,28, and 29, respectively).

Cathodic protection from the aluminum anodes did not significantly reduce the depth of corrosion caused by the dissimilar metals; copper nickel, 10%; yellow brass; or 304 stainless steel in the Potomac River exposures except in crevice areas formed by the mounting spacers. Only in the crevice areas was the depth of corrosion reduced to that observed on bare, unprotected 5086-H32 aluminum not coupled to dissimilar metals, Figs. 26,27,28, and 30.

In the case of the mild steel couple in the Potomac River cathodic protection was effective and significantly reduced the depth of corrosion at all locations on the 5086-H32 aluminum, Fig. 29.

Figures 31 to 40 show the appearance of the specimens with and without cathodic protection from the aluminum anodes. On the 5086-H32 aluminum specimens coupled to the dissimilar metals, copper nickel, 10%; yellow brass; and 304 stainless steel, Figs. 31 through 36, the incidence of corrosion was reduced by cathodic protection, but as indicated previously the depth of corrosion was not significantly reduced except at the crevice areas. There was sufficient weight loss on the unprotected specimens of 5086-H32 aluminum coupled to copper nickel, 10%; and yellow brass, (Figs. 26 and 27) to indicate that cathodic protection from the aluminum anodes also reduced the incidence of corrosion. A comparison of Figs. 37 and 38 shows that essentially complete protection was obtained by cathodic protection on the 5086-H32 aluminum coupled to mild steel. Figures 39 and 40 show the excellent corrosion resistance of bare 5086-H32 aluminum not coupled to a dissimilar metal after 675 days in the Potomac River.

Figure 41 shows the area on 5086-H32 aluminum beneath a magnesium anode used for cathodic protection in the Potomac River. This photograph and the data in Fig. 30 indicate that the magnesium anode caused some corrosion on the 5086-H32 aluminum, but it was much less severe than the accelerated corrosion observed in seawater (compare Figs. 9 and 30).

Figures 42 through 45 compare the depth of corrosion after 540 days in Gatun Lake, Canal Zone and after 675 days in the Potomac River. The depth of corrosion data from specimens at these two locations indicate the severe detrimental effects caused by the copper nickel, 10%; yellow brass; and 304 stainless steel at both sites, and the ineffectiveness of cathodic protection from an aluminum anode in counteracting this corrosion, Figs. 42 thru 44. The detrimental effect of the mild steel couple was not significantly reduced by cathodic protection in the Gatun Lake although cathodic protection was effective in the Potomac River, Fig. 45.

Coated 5086-H32 Aluminum (with and without weldments) Sea-water Performance - Effects of Cu_2O and TBTO antifouling coatings and cathodic protection. Exposure Periods up to 1264 days (41½ months).

The depth of corrosion and response to cathodic protection at the intentionally bared areas and under the paint on the welded 5086-H32 aluminum specimens exposed for 1264 days in quiescent seawater at Key West are shown in Fig. 46. These data and the photographs in Fig. 47 show that the Cu_2O antifouling coating caused accelerated corrosion of the aluminum even with the vinyl anticorrosive barrier coating between the metal and the antifouling coating. Figs. 46 and 47 also indicate that cathodic protection from the aluminum anode was effective in preventing the detrimental effects of the Cu_2O antifouling coating. The data (Fig. 46) also show that the TBTO antifouling coating was not detrimental to the 5086-H32 welded aluminum and that cathodic protection was completely effective in preventing any corrosion of the aluminum when TBTO was the toxicant in the antifouling paint. Figure 48 shows the welded specimens coated with TBTO, with and without cathodic protection, and the one area on the unprotected specimen which showed some corrosion.

The accelerated corrosion caused by the Cu_2O in the antifouling paint on unwelded 5086-H32 aluminum and the effectiveness of cathodic protection in preventing this corrosion are shown in Figs. 49 and 50. Cathodic protection reduced the corrosion on the specimen coated with the Cu_2O antifouling paint but the least corrosion was observed on the cathodically protected specimen with the TBTO as the toxicant. (Figs. 49 and 51.)

The depth of corrosion data after 809 days exposure in quiescent seawater at Key West have also been included in Fig. 49. The 809 day data would appear to indicate that cathodic protection was less effective in reducing the corrosion caused by the Cu_2O and that TBTO antifouling paint

plus cathodic protection was only slightly better to control corrosion on 5086-H32 aluminum than Cu_2O plus cathodic protection.

However, the 1264 day data confirmed an earlier suspicion that the procedure used to remove the coatings from the specimens after 809 days exposure caused an artifact in the data. Cleaning of the coated specimens after 809 days exposure was on a mass-production type basis in which the stripping solutions normally used by a commercial paint shop to remove old paint from aluminum prior to repainting were used. The anomalies in the data caused by this cleaning procedure confirm that extreme caution must be exercised in removing paint from corrosion specimens. Undue expedience in any phase of a corrosion study is generally unwise especially when considerable exposure time is involved.

Coated 5086-H32 Aluminum - Potomac River Water Performance. Effects of Cu_2O and TBTO antifouling coatings and cathodic protection. Exposure period of 675 days (22 months).

The depth of corrosion and response to cathodic protection data at the intentionally bared window areas and under the paint on the 5086-H32 aluminum exposed for 675 days in the Potomac River are shown in Fig. 52. Figure 53 is a photograph of the severe corrosion that occurred at the window area of the specimen coated with the Cu_2O antifouling paint. As noted with the dissimilar metal couples, the corrosion observed on the Cu_2O antifouling paint coated 5086-H32 aluminum was more severe in the Potomac River than in seawater. Cathodic protection of either the Cu_2O or TBTO coated specimens did not reduce the corrosion significantly below the corrosion depth observed on the unprotected TBTO coated specimen. Figure 54 is a photograph showing the condition at the window area of the cathodically protected Cu_2O coated specimen. Figure 55 shows the appearance at the window area of unprotected 5086-H32 aluminum coated with TBTO, and Fig. 56 shows a similar specimen that had been cathodically protected.

Coated 6061-T6 Aluminum - Seawater Performance. Effects of Cu_2O and TBTO antifouling coatings and cathodic protection. Exposure Periods up to 1264 days (41½ months).

The depth of corrosion and response to cathodic protection data at the bared window areas and under the paint on the 6061-T6 aluminum exposed for 1264 days in quiescent seawater at Key West are summarized in Fig. 57. The unprotected specimen coated with Cu_2O antifouling paint was severely corroded. The depth of corrosion was not as great as on the uncoated specimen, but was approximately twice as

deep as on the unprotected specimen coated with TBTO. Although cathodic protection reduced the depth of corrosion on the Cu_2O coated specimen, the most effective combination for reducing corrosion on the antifouling coated specimens of 6061-T6 aluminum was the TBTO antifouling paint and cathodic protection.

The 809 day data on the coated 6061-T6 aluminum alloy showed similar trends although the effectiveness of the TBTO antifouling paint system plus the cathodic protection from an aluminum anode was less evident. This is believed to be a result of the previously discussed artifact caused by the method used to remove the coating from these specimens. Figures 58 and 59 are photographs of 6061-T6 aluminum specimens coated with Cu_2O and TBTO antifouling coatings, respectively. Selected areas on the cathodically protected specimens are also shown.

Coated 6061-T6 Aluminum - Potomac River Water Performance. Effects of Cu_2O and TBTO antifouling coatings and cathodic protection. Exposure Period of 675 days (22 months).

The data for the depth of corrosion and response to cathodic protection at the bared window areas and under the paint on the 6061-T6 aluminum exposed for 675 days in the Potomac River are summarized in Fig. 60. Uncoated and unprotected 6061-T6 aluminum corroded to a depth of 20 mils. The data in Fig. 60 and the photograph in Fig. 61 show that the Cu_2O antifouling paint increased the depth of corrosion.

The data in Figure 60 and a comparison of Figs. 61 and 62 show that cathodic protection from an aluminum anode significantly reduced the depth of corrosion caused by the Cu_2O antifouling paint. As indicated in other phases of this study, the TBTO antifouling paint caused less severe corrosion on the aluminum alloy, and the combination of TBTO and cathodic protection from an aluminum anode resulted in the greatest corrosion protection. Photographs of the corrosion on the unprotected and protected specimens of 6061-T6 aluminum coated with TBTO are shown in Figs. 63 and 64, respectively.

Effectiveness of Antifouling Coatings and Response to Cathodic Protection.

A qualitative summary of the corrosion of 5086-H32 and 6061-T6 aluminum alloys, the corrosion caused by antifouling paint toxicants, the response to cathodic protection, and the order of ranking of each material in the specific environment are shown in Table 1. This should be a useful guide in appraising the relative performance of these alloys when bare or coated with Cu_2O or TBTO type antifouling paints.

Bare 5086-H32 aluminum was highly corrosion resistant when continuously immersed in either quiescent seawater or in the Potomac River even without cathodic protection. From a corrosion viewpoint TBTO is preferred over Cu_2O as an antifouling toxicant on 5086-H32 aluminum. When TBTO was used in conjunction with cathodic protection corrosion of the aluminum was at a minimum. In the Potomac River bare 5086-H32 aluminum either with or without cathodic protection was least corroded.

Table 1 also shows that bare 6061-T6 aluminum was severely corroded in both seawater and Potomac River water when not cathodically protected. In either environment the most satisfactory corrosion protection was obtained with the TBTO type antifouling paint and cathodic protection from an aluminum anode.

Marine Growth (Fouling) Characteristics

Uncoated (bare) 5086-H32 and 6061-T6 aluminum fouled severely in seawater. In the Potomac River the only fouling observed was slime.

The Cu_2O and TBTO antifouling paints resisted marine growth equally well for approximately 10 months in seawater. At $10\frac{1}{2}$ months the first growth of barnacles was noted on some of the TBTO coated specimens. The Cu_2O coated specimens were free of fouling during the same time period.

After 809 days ($26\frac{1}{2}$ months) in seawater a difference in the effectiveness of the antifouling coatings was more evident. The Cu_2O coated specimens were still essentially free of marine fouling, but the TBTO coated specimens were fouled over approximately 20 percent of the surface. There was also a slight discernible difference in the fouling characteristics attributable to the cathodic protection from the aluminum and zinc anodes. The slight reduction in antifouling properties attributable to cathodic protection was evident only on the specimens coated with the TBTO antifouling paint.

The characteristics of the antifouling paints on 5086-H32 and 6061-T6 aluminum after 1264 days in seawater are summarized in Table 2. These data show that moderate fouling was observed on the Cu_2O coated specimens and moderate to heavy fouling with a few barnacles on the TBTO coated specimens. Essentially no difference in the degree of fouling was observed on the protected and unprotected specimens after 1264 days in seawater.

There was a marked difference between the color retention on the Cu_2O and TBTO coated specimens. The Cu_2O anti-fouling paint changed from a deep red color to that of the usual green patina on copper, while the TBTO paint essentially retained its original reddish color.

In the Potomac River, specimens coated with TBTO initially seemed to have less slime on the bared window areas, but this was only a temporary effect, i.e., for a time period much less than the 675 days exposure period. Slime was the principle type of fouling observed on the specimens exposed in the Potomac River.

SUMMARY

1. Bare, uncoupled, and unprotected 5086-H32 aluminum was inherently corrosion resistant in quiescent seawater, in lake water, and in the Potomac River.
2. The following dissimilar metals: copper nickel, 10%; yellow brass; 304 stainless steel; and mild steel, accelerated the corrosion of 5086-H32 aluminum in seawater. Cathodic protection from aluminum anodes reduced the depth of corrosion caused by the dissimilar metals, but was not completely effective. There were indications that a prolonged incubation period existed before the accelerated corrosion, caused by the copper nickel, 10%; and 304 stainless steel, became evident on the aluminum. Cathodic protection from a magnesium anode also caused accelerated corrosion of the aluminum.
3. Cracks were noted on the circular welded uncoated specimens of 5086-H32 aluminum in seawater even when cathodically protected, but they may have been present prior to exposure.
4. The depth of corrosion on 5086-H32 aluminum caused by the dissimilar metals was greater in the Potomac River than in seawater. Each of the dissimilar metals, copper nickel, 10%; yellow brass; 304 stainless steel; and mild steel, caused accelerated corrosion of the aluminum exposed in the Potomac River. Cathodic protection did not significantly reduce the depth of corrosion caused by copper nickel, 10%; yellow brass; and 304 stainless steel except in crevices formed by the mounting spacers. Cathodic protection was effective, however, and did significantly reduce the depth of corrosion on 5086-H32 aluminum caused by the mild steel in the Potomac River exposure, but not in the fresh water lake exposure. The incidence of corrosion on the 5086-H32 aluminum caused by the dissimilar metals was reduced by cathodic protection.

5. Cracks were evident on the welded specimens of 5086-H32 aluminum exposed in the Potomac River but the response to cathodic protection could not be established because specimens were lost due to circumstances beyond our control. These cracks may have been present prior to exposure.

6. Cu_2O antifouling paint applied over a vinyl anti-corrosive barrier coating accelerated corrosion at bared areas on 5086-H32 aluminum in seawater. Cathodic protection reduced the corrosion caused by the Cu_2O toxicant in the antifouling coating, but did not eliminate it.

7. TBTO antifouling paint did not accelerate the corrosion of 5086-H32 aluminum in seawater even at bared areas in the vinyl anticorrosion barrier coating. The best corrosion mitigation on the coated aluminum specimens was obtained, however, when TBTO was the toxicant in the antifouling paint and the specimens were cathodically protected.

8. Severe corrosion was caused by the Cu_2O antifouling paint at bared areas on 5086-H32 aluminum exposed in the Potomac River despite the vinyl anticorrosive barrier coating. The corrosion caused by the Cu_2O was more severe in the river exposure than in seawater. TBTO antifouling paint did not cause as severe corrosion as the Cu_2O antifouling paint in the river exposure. Cathodic protection on either the Cu_2O or TBTO coated specimens did not reduce the depth of corrosion below that observed on the unprotected TBTO coated specimens.

9. Bare, uncoupled and unprotected 6061-T6 aluminum was severely corroded in quiescent seawater or in the Potomac River.

10. Unprotected specimens of 6061-T6 aluminum coated with Cu_2O were severely corroded in seawater, but the depth of corrosion was less than on the uncoated specimen. The depth of corrosion on the unprotected specimen coated with TBTO antifouling paint was approximately one-half that observed on the unprotected specimen coated with Cu_2O . Cathodic protection reduced the depth of corrosion on the Cu_2O coated specimen, but the most effective anticorrosive system for 6061-T6 aluminum in seawater was TBTO antifouling paint over a vinyl anticorrosive barrier and cathodic protection from an aluminum anode.

11. Cu_2O antifouling paint significantly accelerated the depth of corrosion on 6061-T6 aluminum in the Potomac River despite the vinyl anticorrosive barrier coating. Cathodic protection from an aluminum anode reduced the depth of corrosion caused by the Cu_2O toxicant but the

least corrosion occurred when the antifouling toxicant was TBTO and the specimen was cathodically protected.

12. Bare 5086-H32 and 6061-T6 aluminum alloys were heavily fouled by marine growth during exposure in quiescent seawater. In the Potomac River these aluminum alloys developed only slime on their surfaces.

13. After 1264 days in seawater moderate fouling was observed on the Cu_2O coated specimens and moderate to heavy fouling with a few barnacles was observed on the TBTO coated specimens. Cathodic protection had little or no effect on the degree of fouling observed after 1264 days in seawater.

14. There was a marked difference between the color retention on the Cu_2O and TBTO coated specimens with the TBTO coated specimens essentially retaining their original reddish color.

ACKNOWLEDGMENT

The assistance of Messrs. C.W. Billow and W. Lazier (retired) of the NRL Marine Corrosion Research Laboratory, Key West, Florida, in conducting the experimental phase of this study is acknowledged. The coated aluminum specimens were prepared by Mr. W.J. Francis of the Chemical Laboratory, Norfolk Naval Shipyard. This work was sponsored by the Naval Ship Systems Command.

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1. B.F. Brown et al., "Marine Corrosion Studies (Second Interim Report of Progress)," NRL Memorandum Report 1574, Nov 1964.

2. B.F. Brown et al., "Marine Corrosion Studies (Third Interim Report of Progress)," NRM Memorandum Report 1634, July 1965.

3. T.J. Lennox Jr., et al., "Marine Corrosion Studies (Fourth Interim Report of Progress)," NRL Memorandum Report 1711, May 1966.

4. T.J. Lennox, Jr., M.H. Peterson, and R.E. Groover, "Corrosion of Aluminum Alloys by Antifouling Paint Toxicants and Effects of Cathodic Protection," Proceedings NACE 24th Conference, Cleveland, Ohio, March 18-22, 1968. National Association Corrosion Engineers, Houston, Texas, 1969.

Table 1

Qualitative Summary of Corrosion of 5086-H32 and 6061-T6 Aluminum Alloys by Antifouling Paint Toxicants, Response to Cathodic Protection and Order of Ranking in Specific Environments

Exposure Condition	5086-H32 Aluminum		
	1264 Days in Seawater - Key West, Fla.	675 Days in Potomac River - Washington, D.C.	
	Bare	Cu ₂ O	TBTO
No cathodic protection	high corrosion resistance and weight loss accelerated	lower incidence and depth of local corrosion compared to unprotected Cu ₂ O coated specimens	essentially immune to corrosion
	I	6	2
Cathodic Protection - Al anode	incidence of local corrosion reduced	incidence and depth of local corrosion reduced	essentially immune to corrosion
	I	3	I
No cathodic protection	severe local corrosion	incidence of local corrosion less than for uncoated specimen	depth of local corrosion less than in seawater
	6	5	4
Cathodic protection - Al anode	cathodic protection effective	depth of local corrosion similar to unprotected specimen coated with TBTO	cathodic protection effective
	I	4	I

Exposure Condition	6061-T6 Aluminum		
	Bare	Cu ₂ O	TBTO
No cathodic protection	incidence and depth of local corrosion not reduced compared to unprotected TBTO specimen or coated specimen	incidence and depth of local corrosion reduced	essentially immune to corrosion
	I	2	I
Cathodic protection - Al anode	incidence and depth of local corrosion reduced	incidence and depth of local corrosion reduced	essentially immune to corrosion
	I	3	I
No cathodic protection	depth of local corrosion significantly reduced compared to unprotected specimen	depth of local corrosion less than in seawater	depth of local corrosion less than in seawater
	6	5	4
Cathodic protection - Al anode	depth of local corrosion essentially free	depth of local corrosion essentially free	depth of local corrosion essentially free
	I	4	I

Note: Order of ranking for each material in the specific environment.
 1. Best corrosion resistance. 6. Worst corrosion - so severe that usefulness questionable for long-term service.

Table 2

Characteristics of the Antifouling Paints
 on 5086-H32 and 6061-T6 Aluminum
 After 1264 Days in Seawater at Key West, Florida

Antifouling Type Coating System and Exposure Condition	Degree Fouling	Coating Condition
<u>5086-H32 Aluminum</u> Cu ₂ O - No CP	moderate	large blisters near crevice, edge, and window with corrosion products evident
Cu ₂ O - CP Al Anode	moderate	no apparent blisters or corrosion products
TBTO - No CP	moderate to heavy few barnacles	moderate blistering around crevice but corrosion products not visible
TBTO - CP Al anode	moderate to heavy few barnacles	no apparent blisters or corrosion products
<u>6061-T6 Aluminum</u>		
Cu ₂ O - No CP	moderate	large blisters in coating; heavy corrosion products in blisters and window
Cu ₂ O - CP Al anode	light to heavy; light - on flat areas; moderate - crevices and edges; heavy near epoxy seal over anode attachment screw	no apparent blisters or corrosion products
TBTO - No CP	moderate to heavy	no apparent blisters or corrosion products
TBTO - CP Al anode	moderate to heavy few barnacles	no apparent blisters or corrosion products

MC 468

Note: CP = cathodic protection

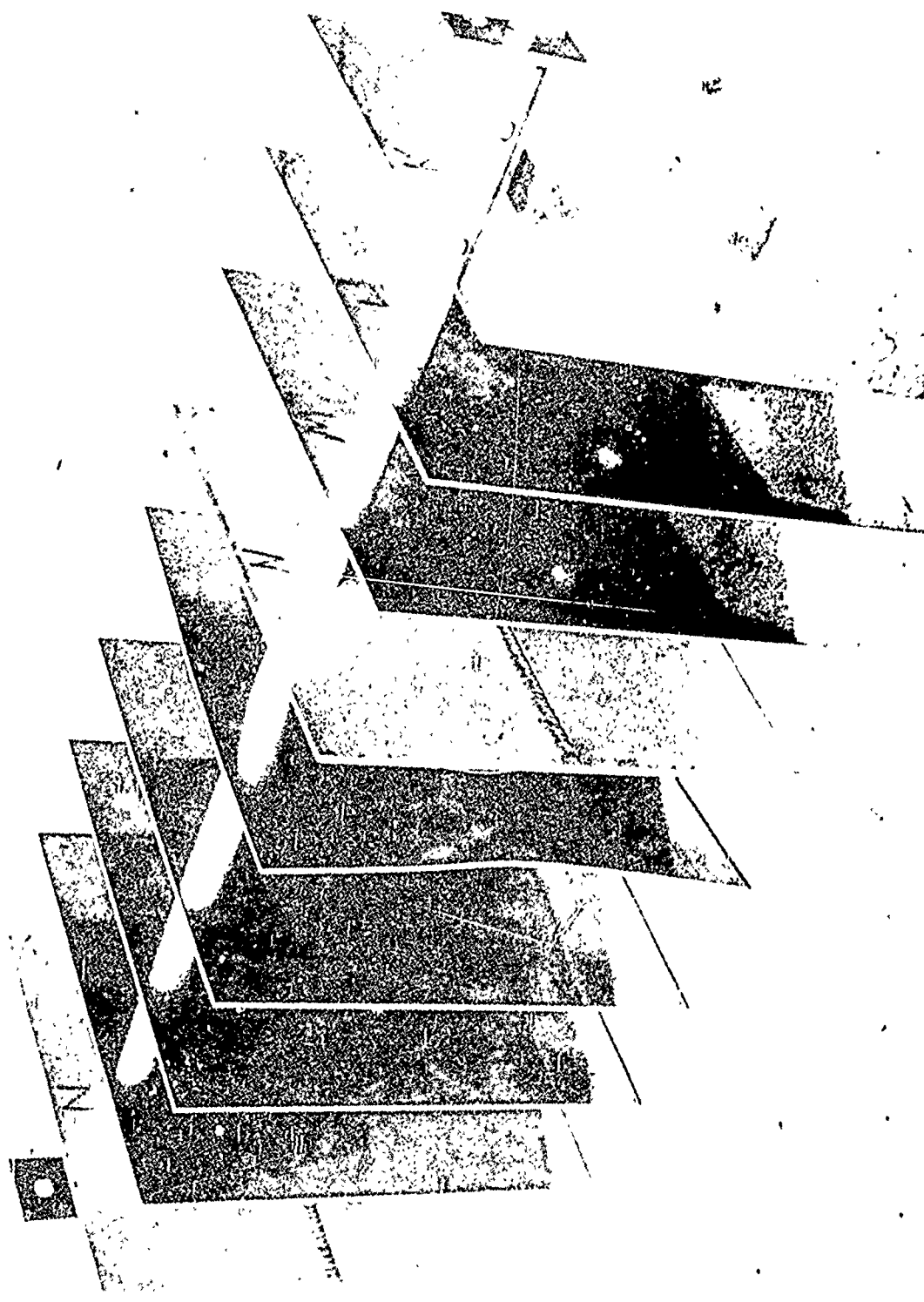


Fig. 1 - Typical exposure rack.

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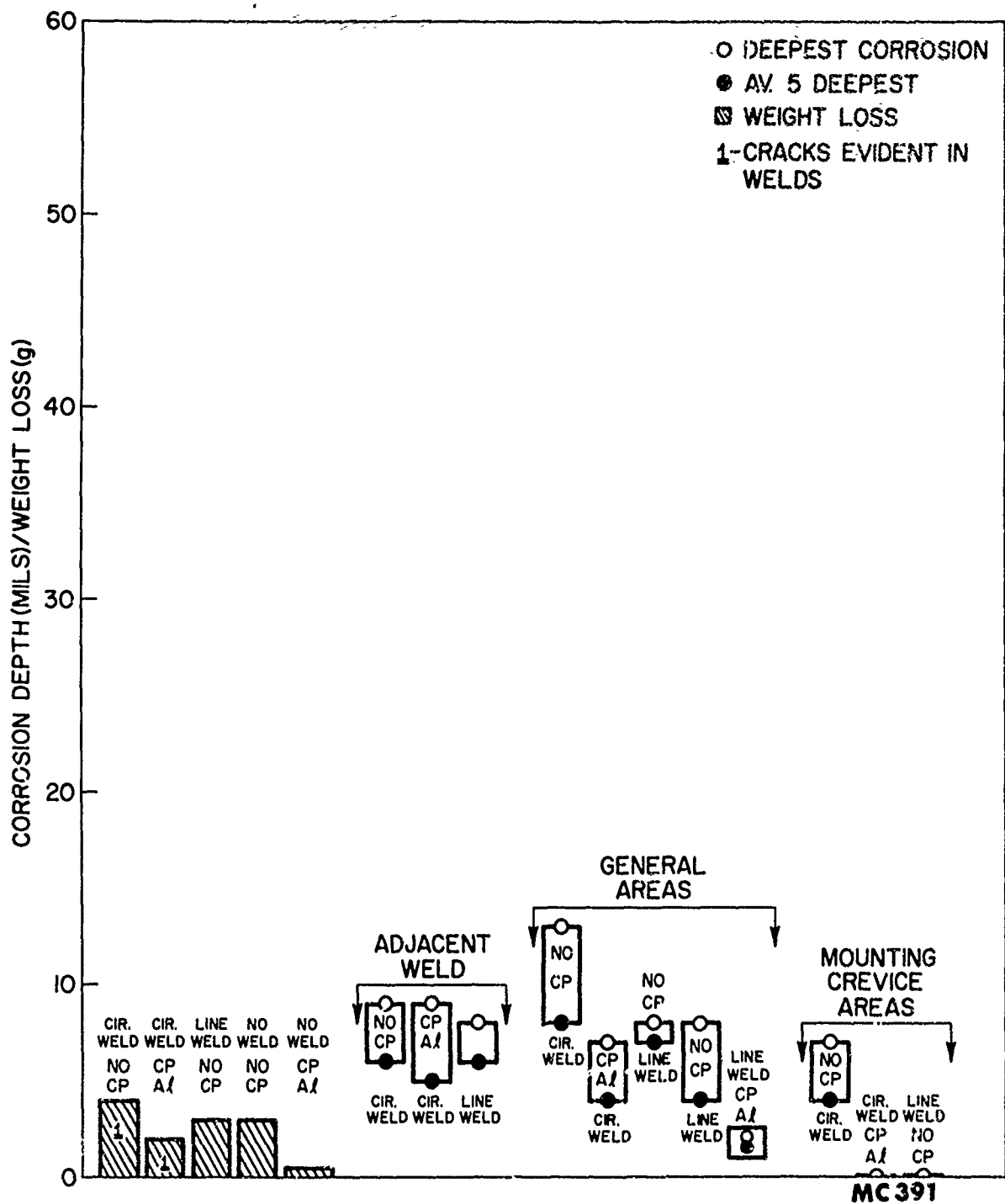
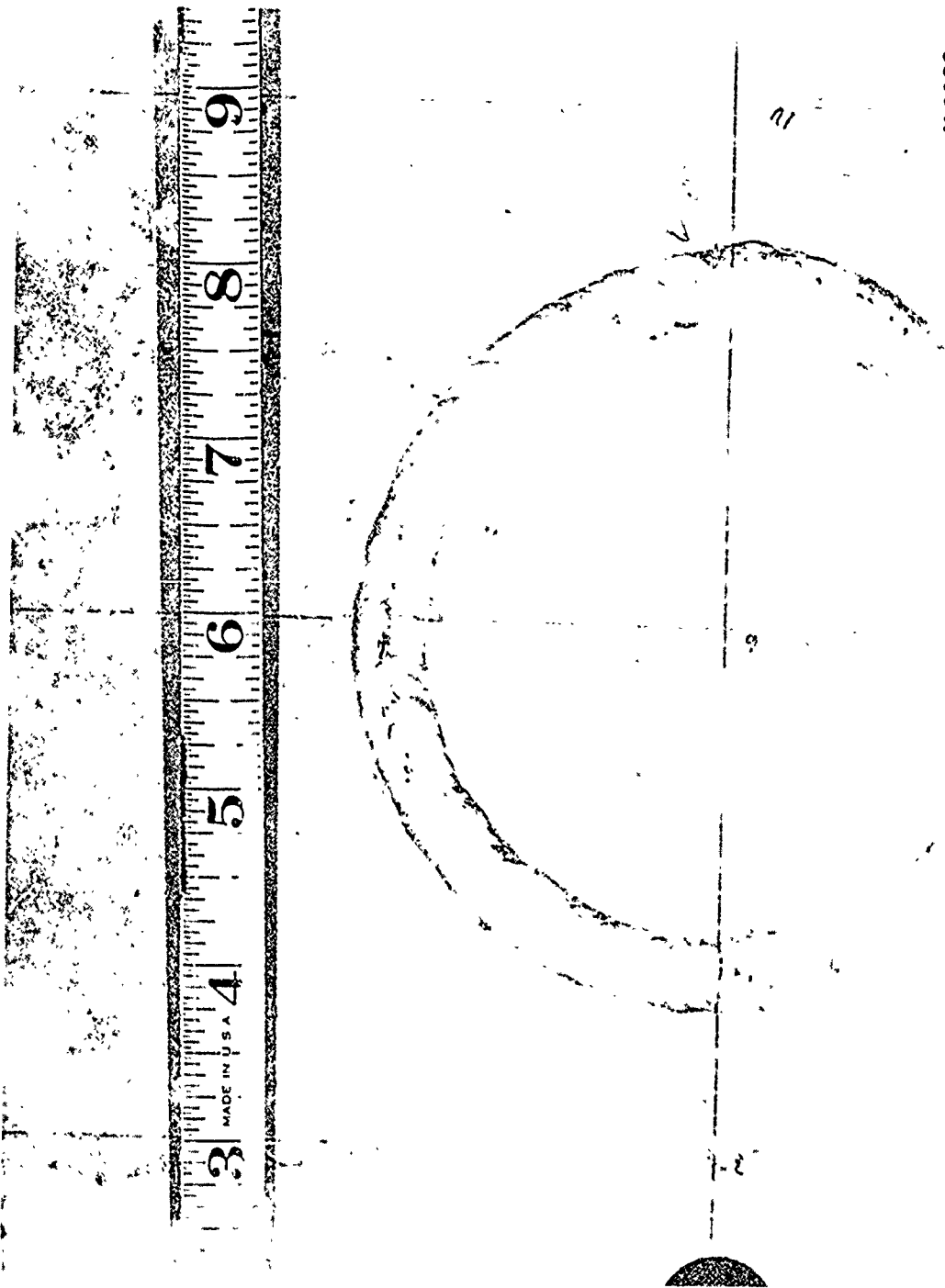


Fig. 2 - Welded 5086-H32 aluminum; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.



MC392

Fig. 3 - Circular weld in 5086-H32 aluminum; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.25 X

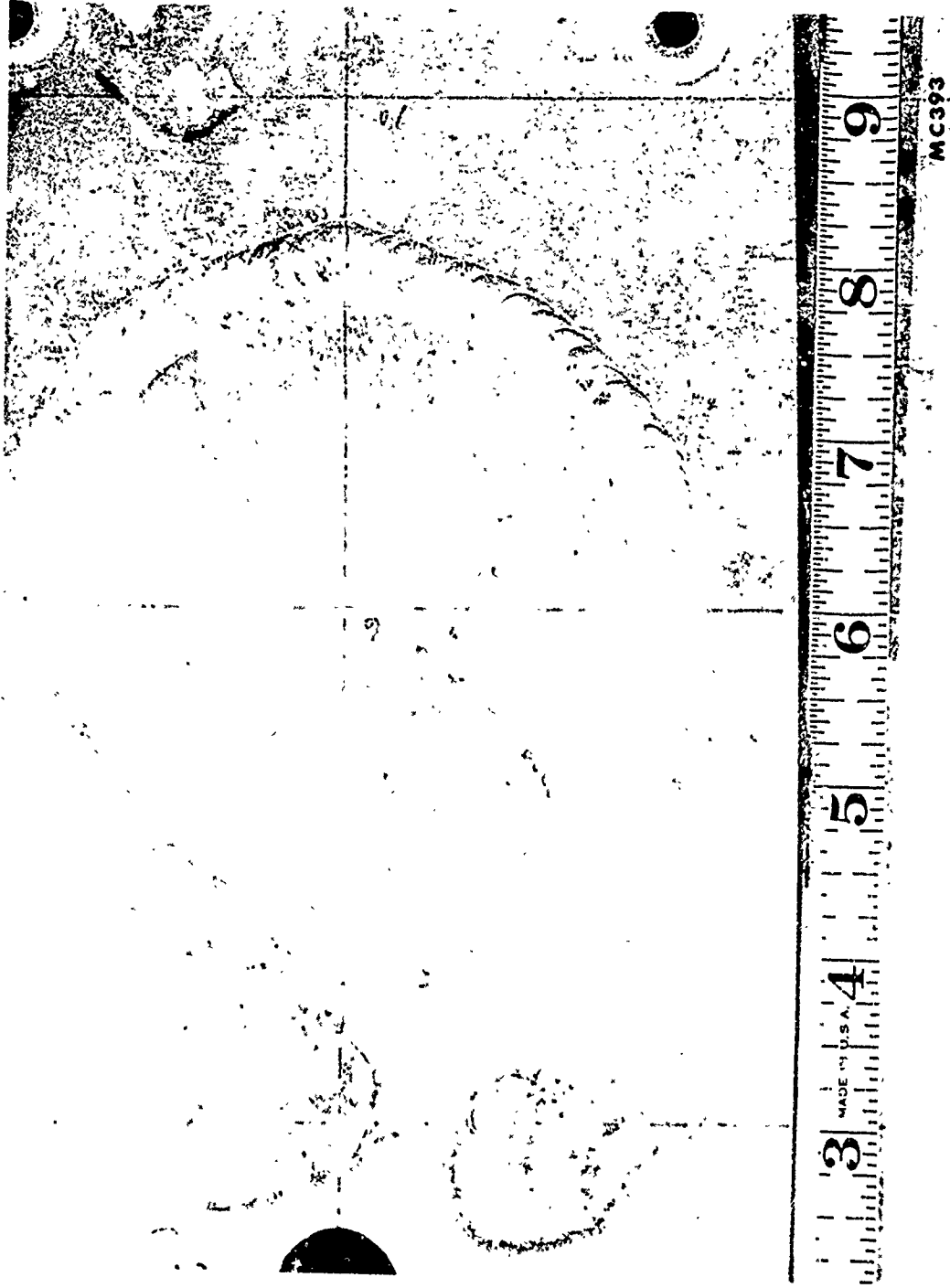


Fig. 4 - Circular weld in 5086-H32 aluminum; with cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.25 X

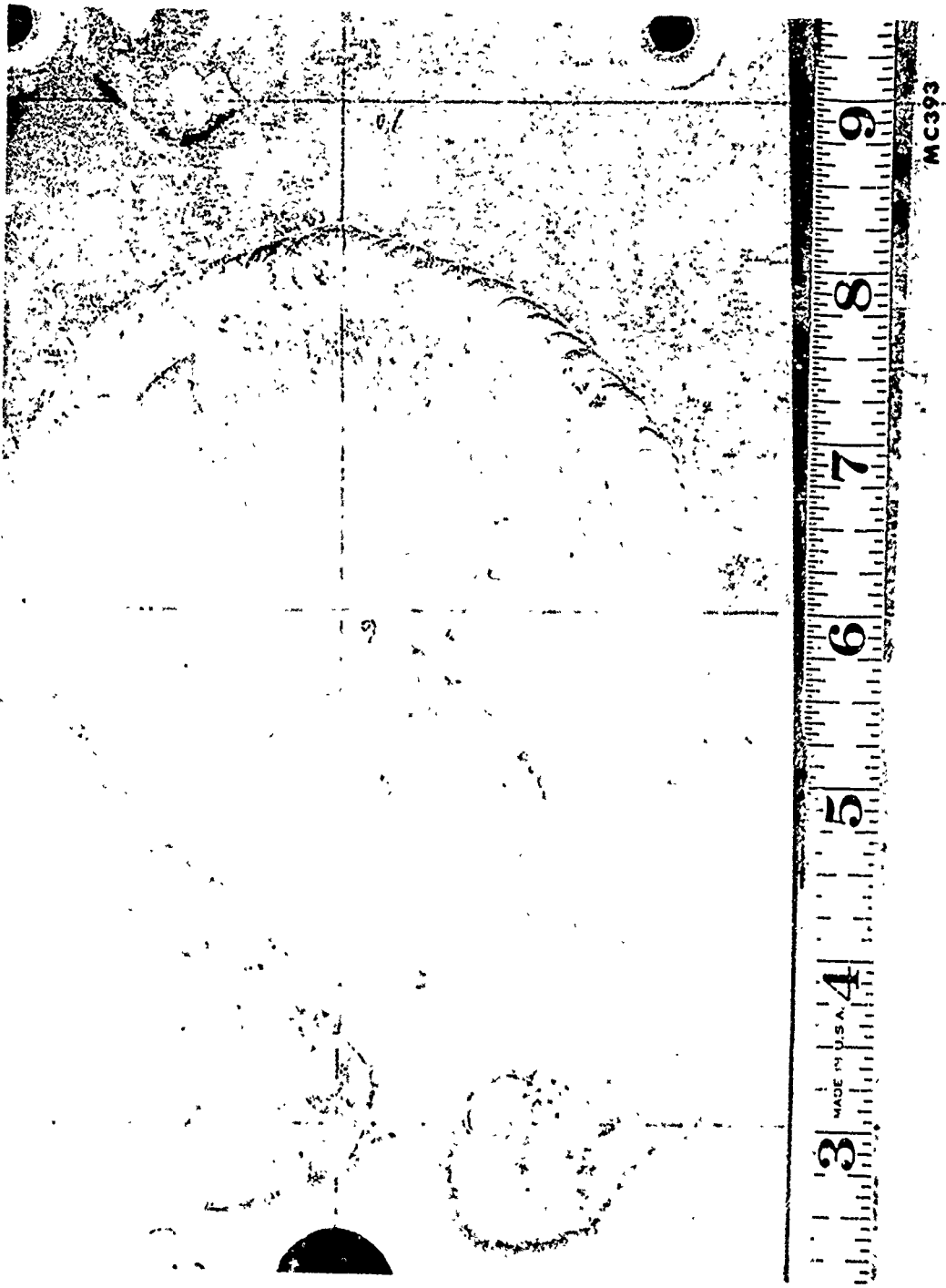


Fig. 4 - Circular weld in 5086-H32 aluminum; with cathodic protection, 809 days in sea water at Key West, Florida. Original magnification 1.25 X

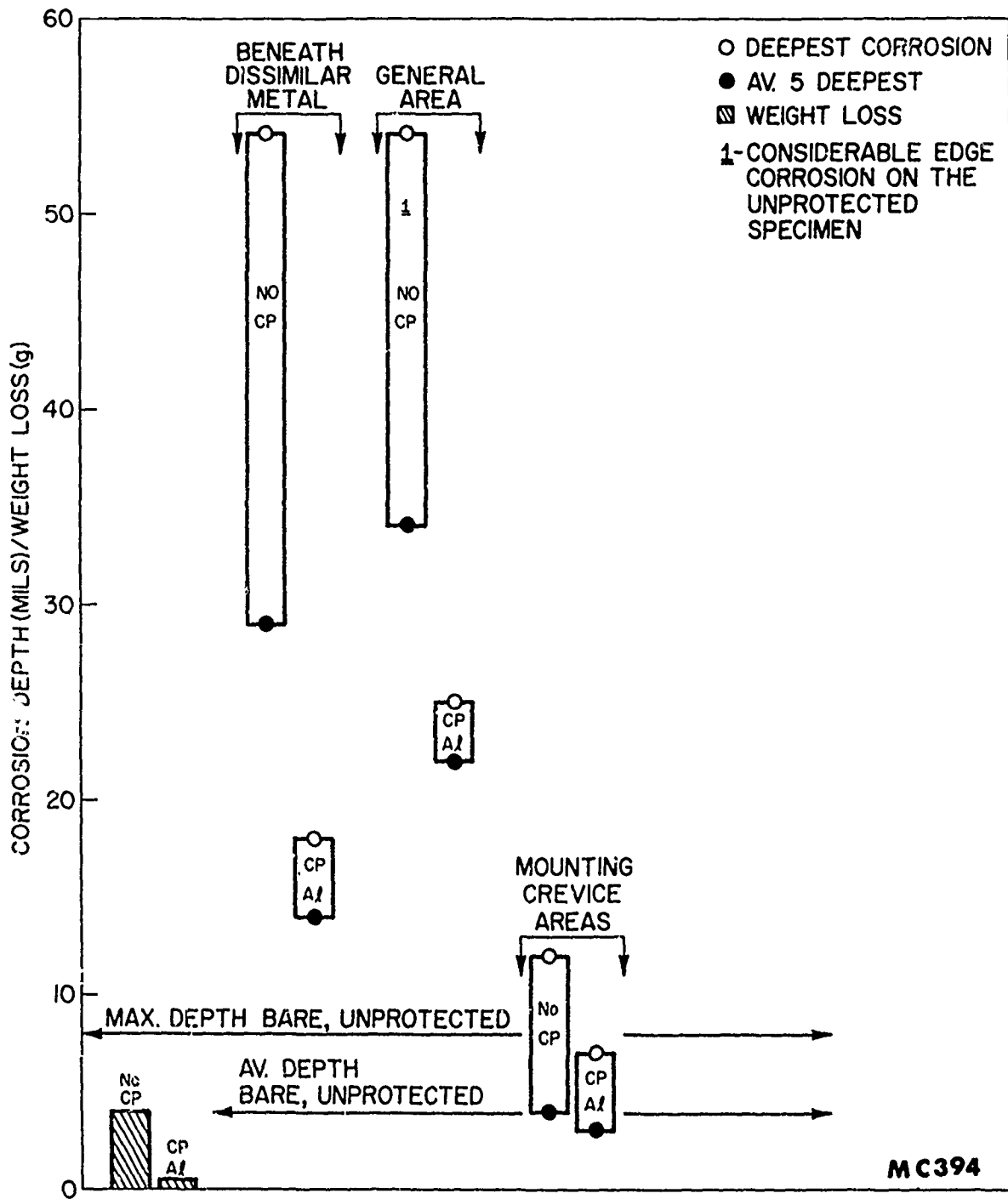


Fig. 5 - 5086-H32 aluminum coupled to copper nickel, 10%; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.

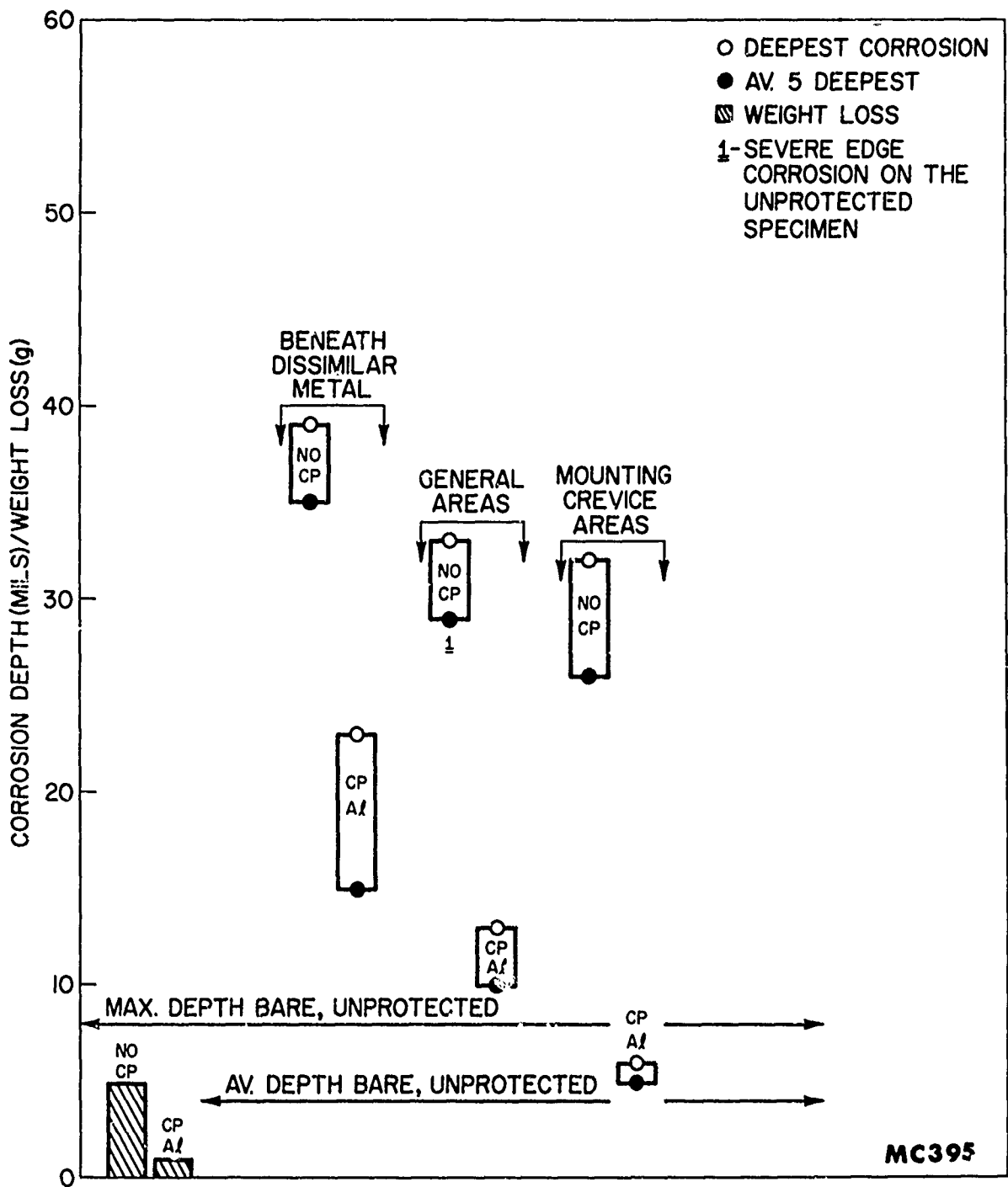


Fig. 6 - 5086-H32 aluminum coupled to yellow brass; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.

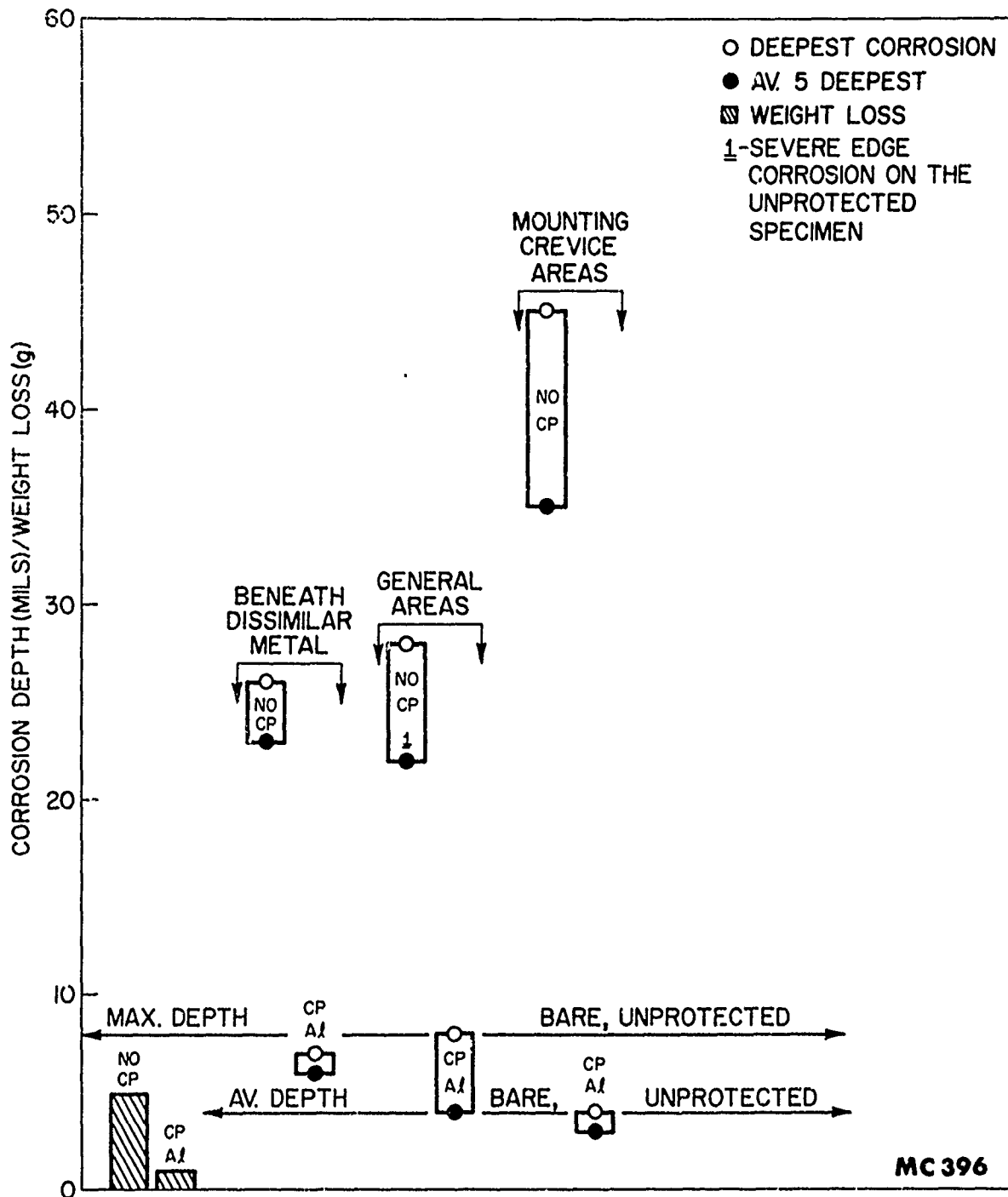


Fig. 7 - 5086-H32 aluminum coupled to 304 stainless steel; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.

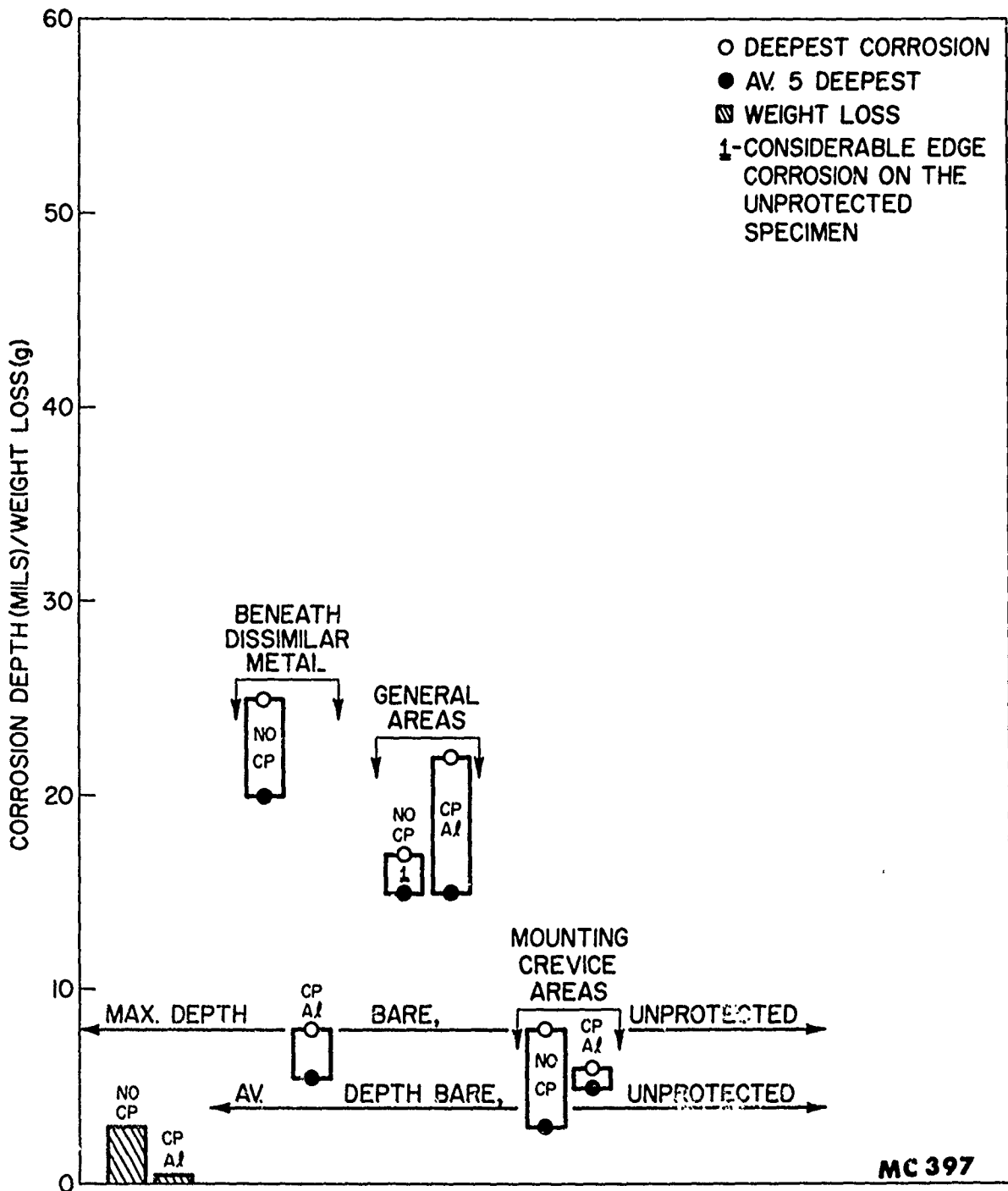


Fig. 8 - 5086-H32 aluminum coupled to mild steel; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.

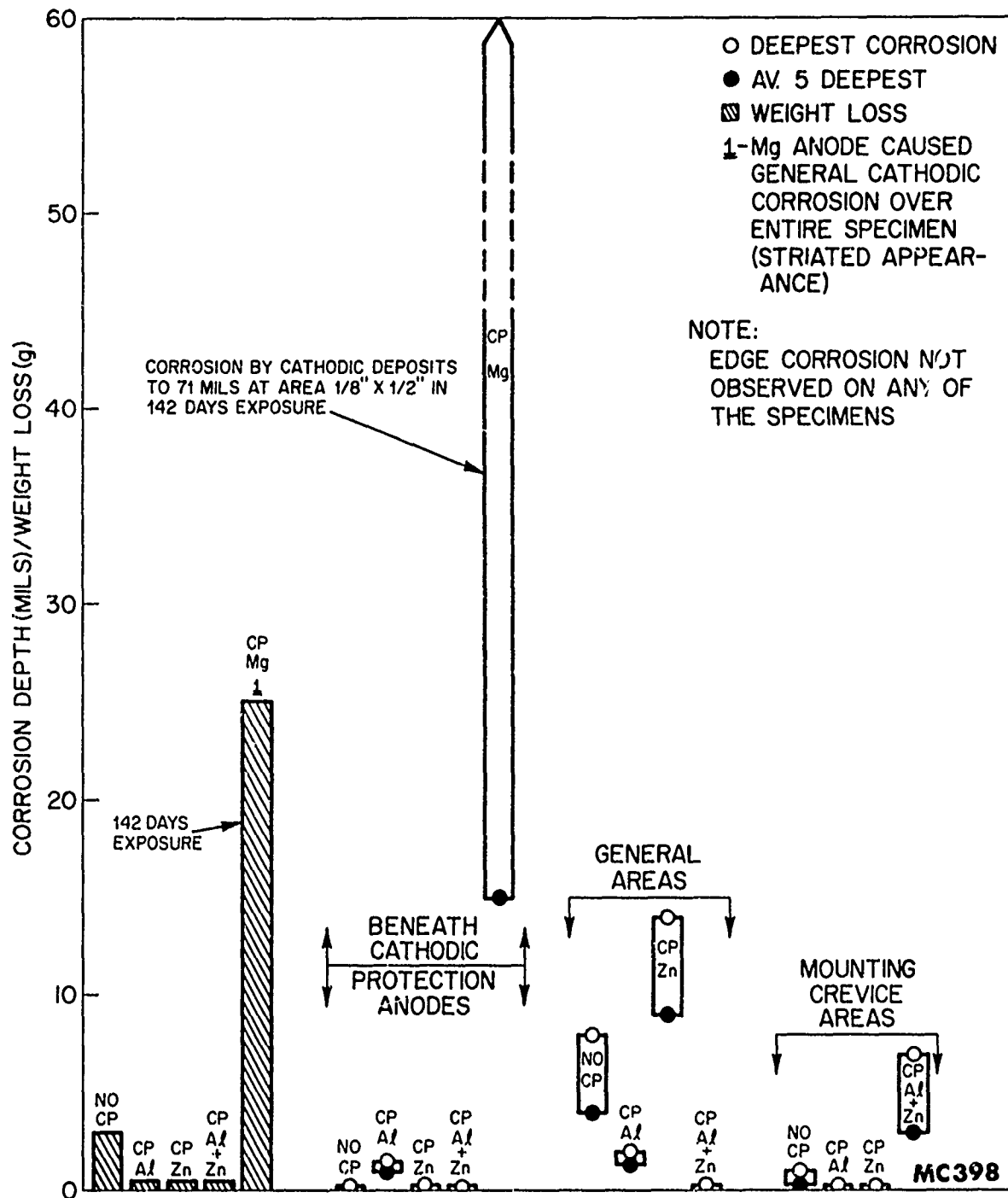
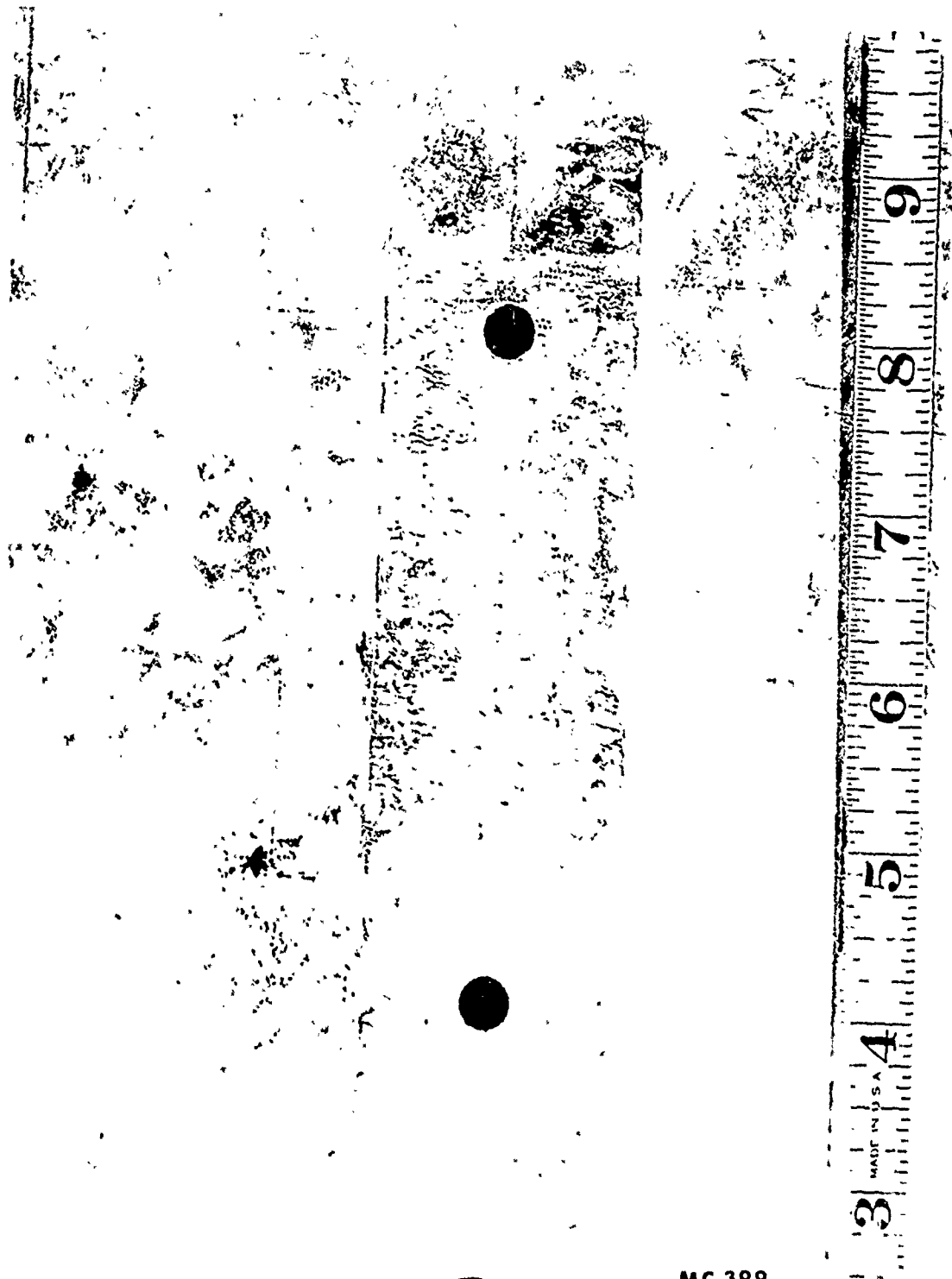
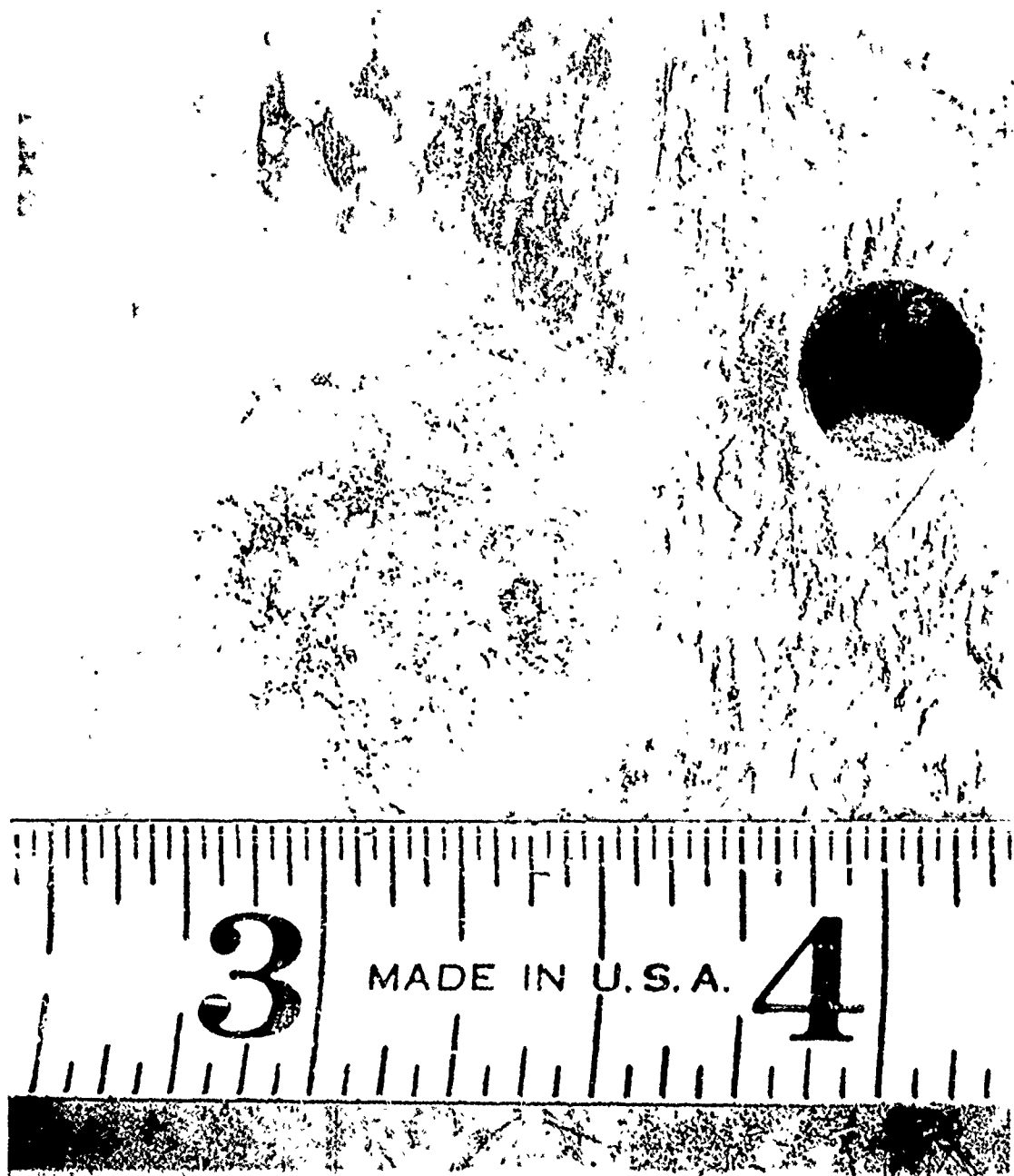


Fig. 9 - 5086-H32 aluminum; with and without cathodic protection (CP), 809 days in seawater at Key West, Florida.



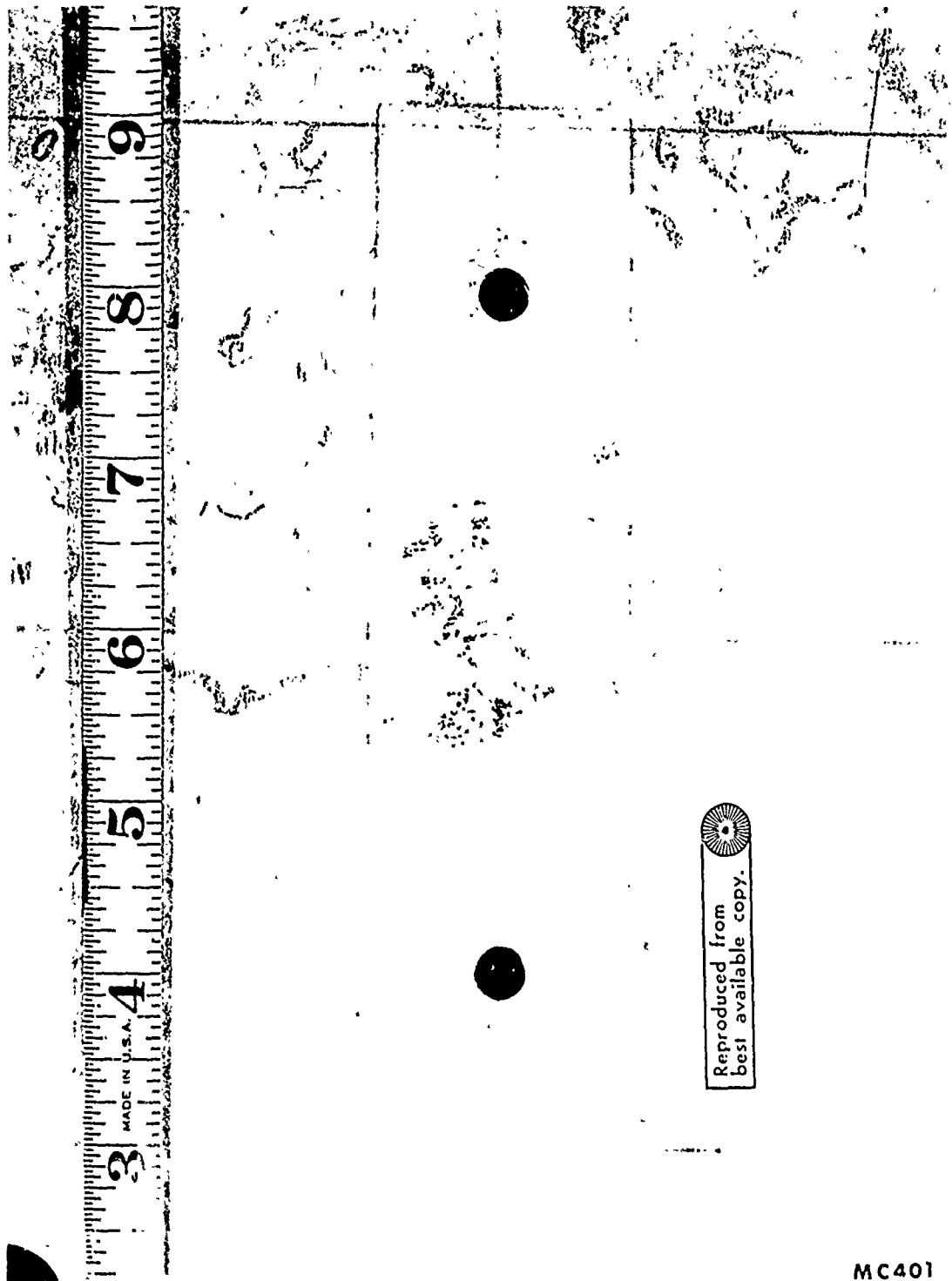
MC 399

Fig. 10 - 5086-H32 aluminum coupled to copper nickel, 10%; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X



MC 400

Fig. 11 - 5086-H32 aluminum coupled to copper nickel, 10%; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 4 X



MC401

Fig. 12 - 5086-H32 aluminum coupled to copper nickel, 10%; with cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

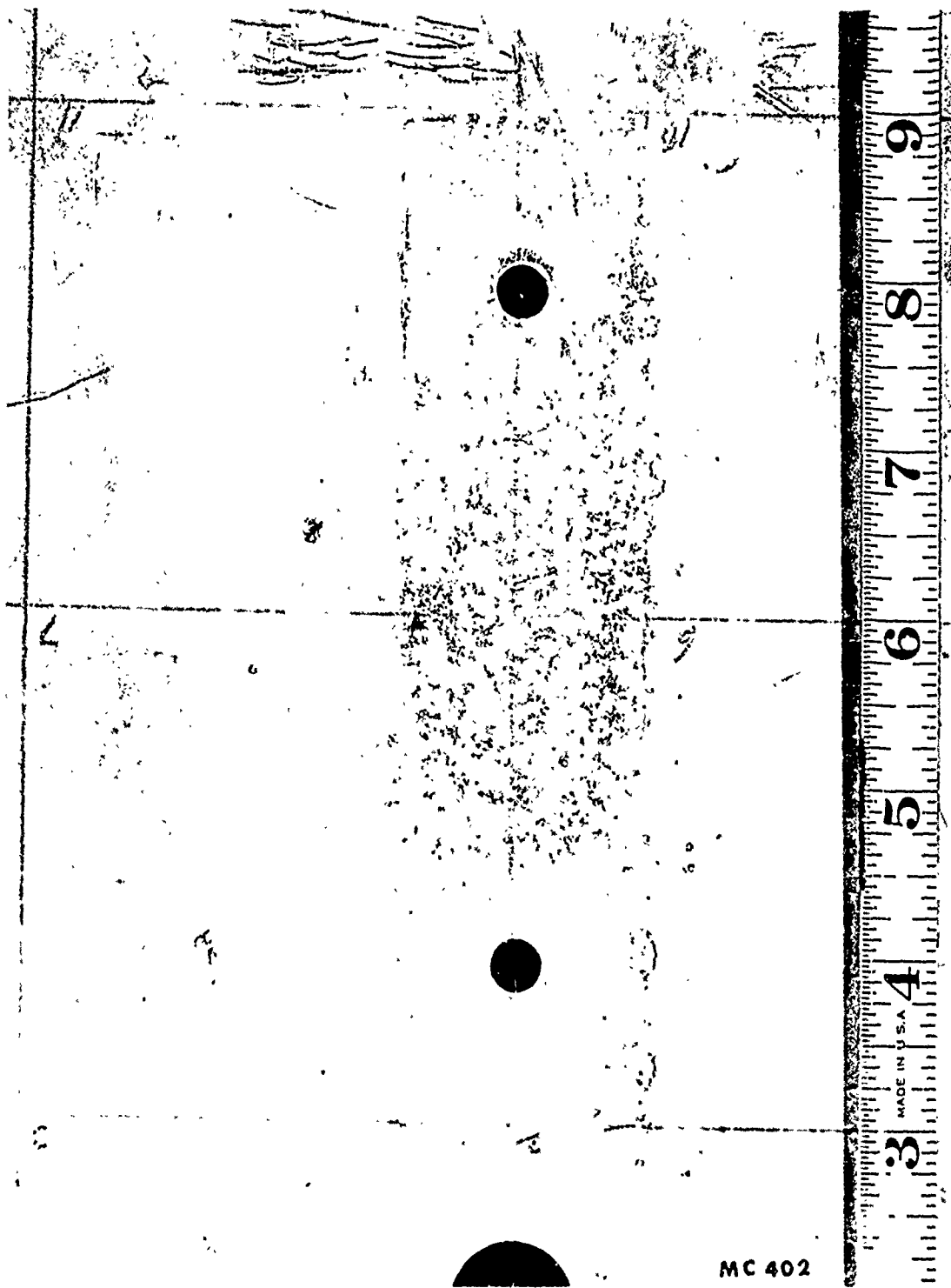


Fig. 13 - 5086-H132 aluminum coupled to yellow brass; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

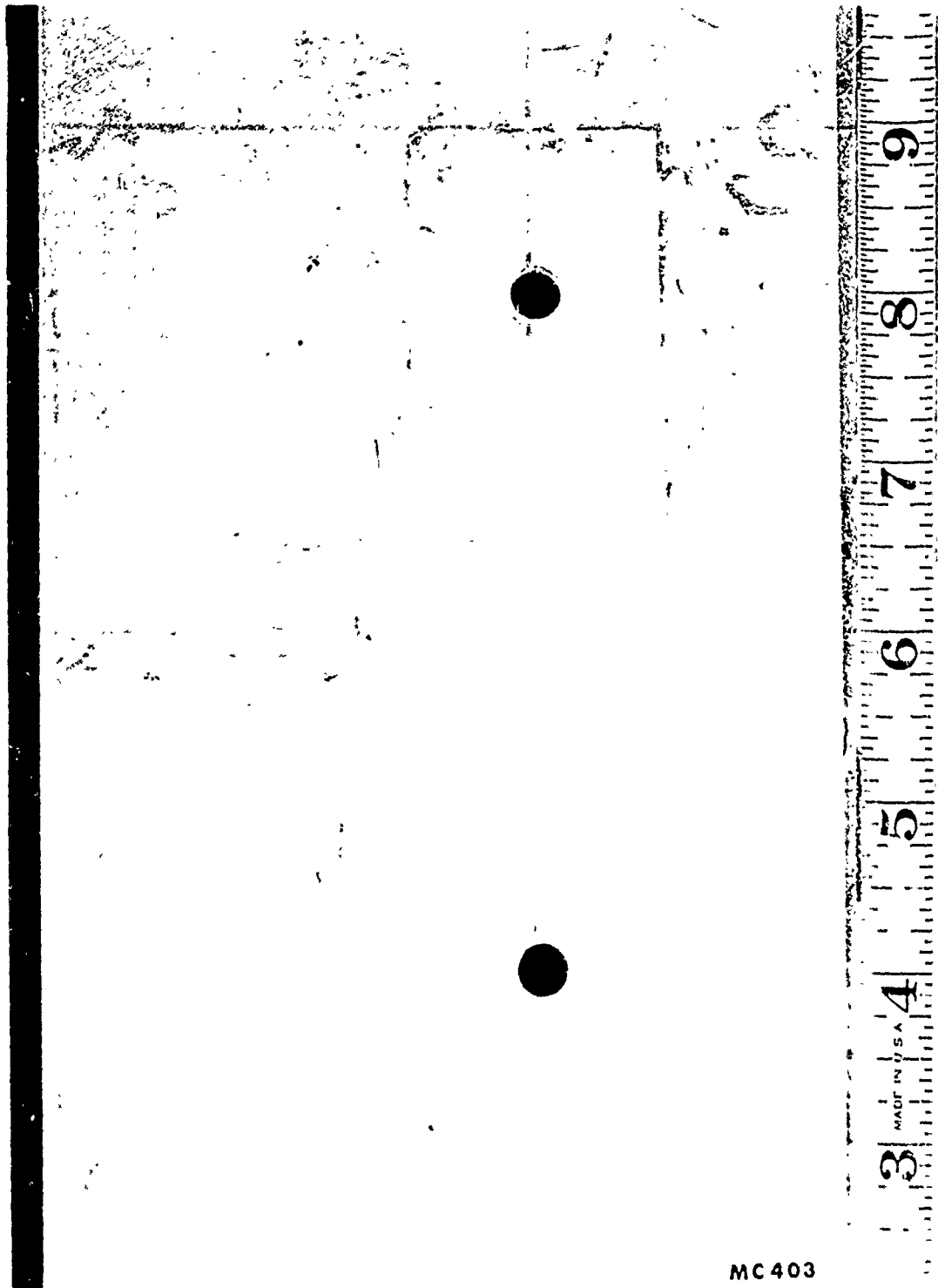


Fig. 14 - 5086-H32 aluminum coupled to yellow brass; with cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

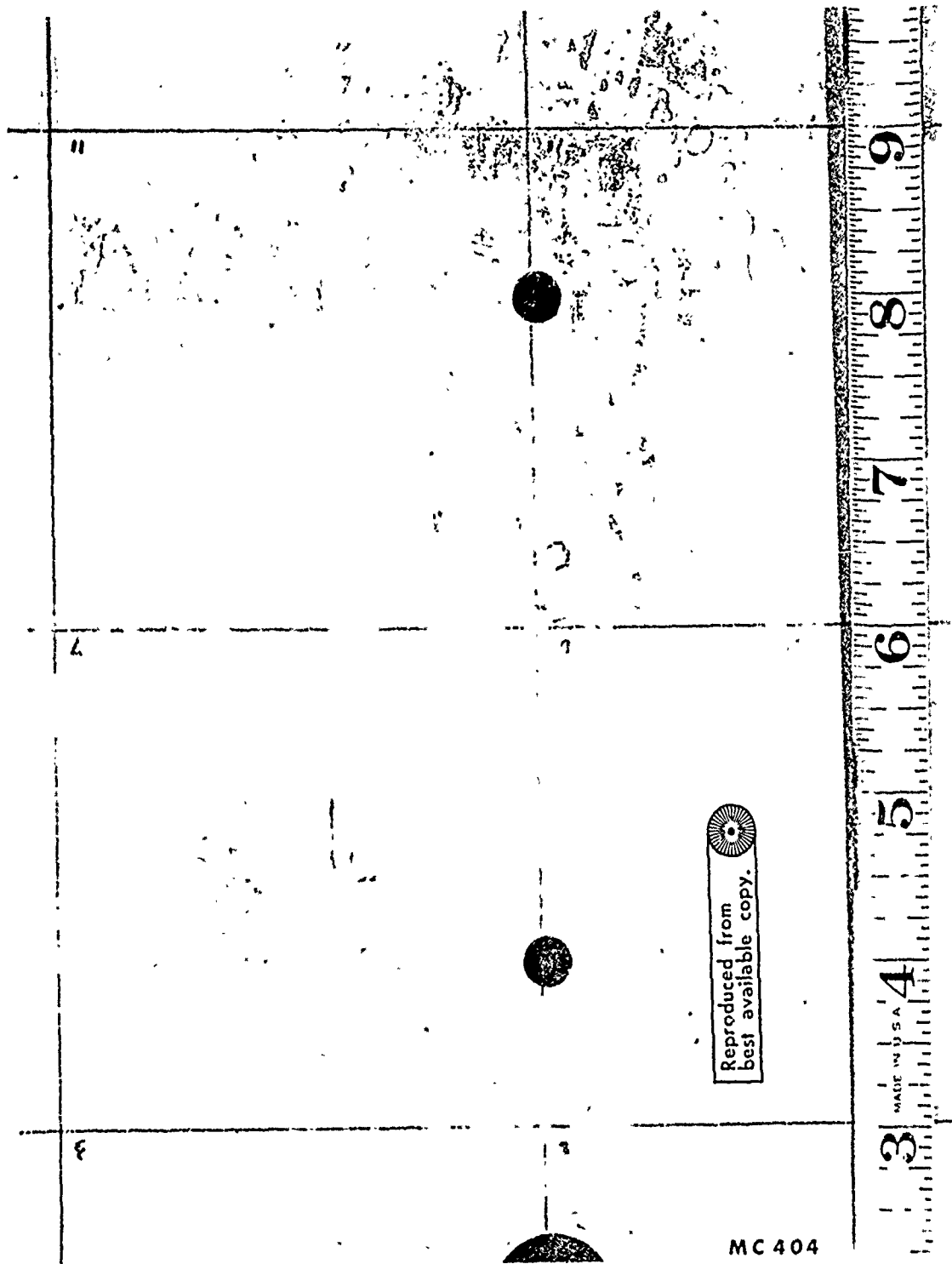


Fig. 15 - 5086-H32 aluminum coupled to 304 stainless steel; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

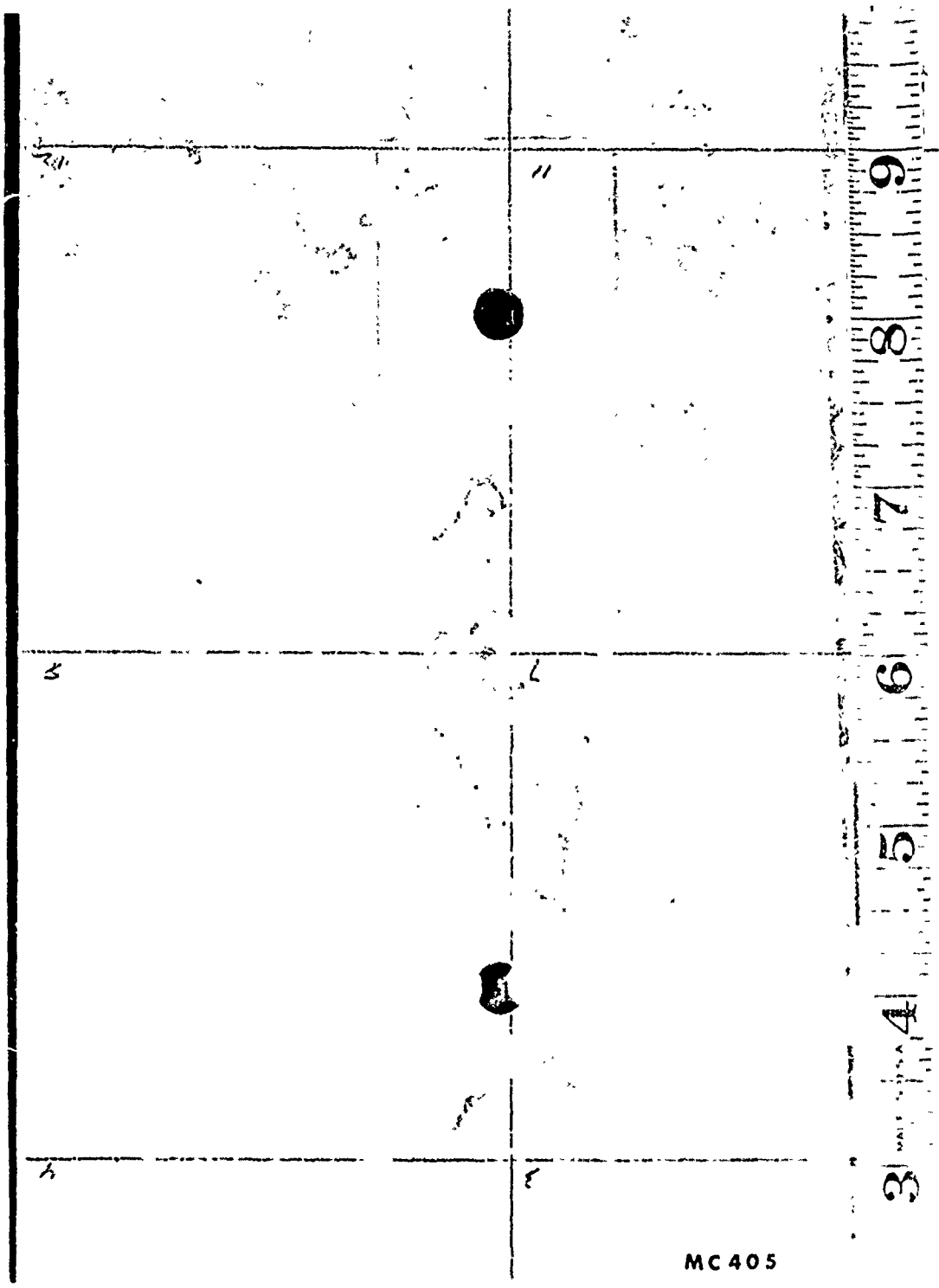
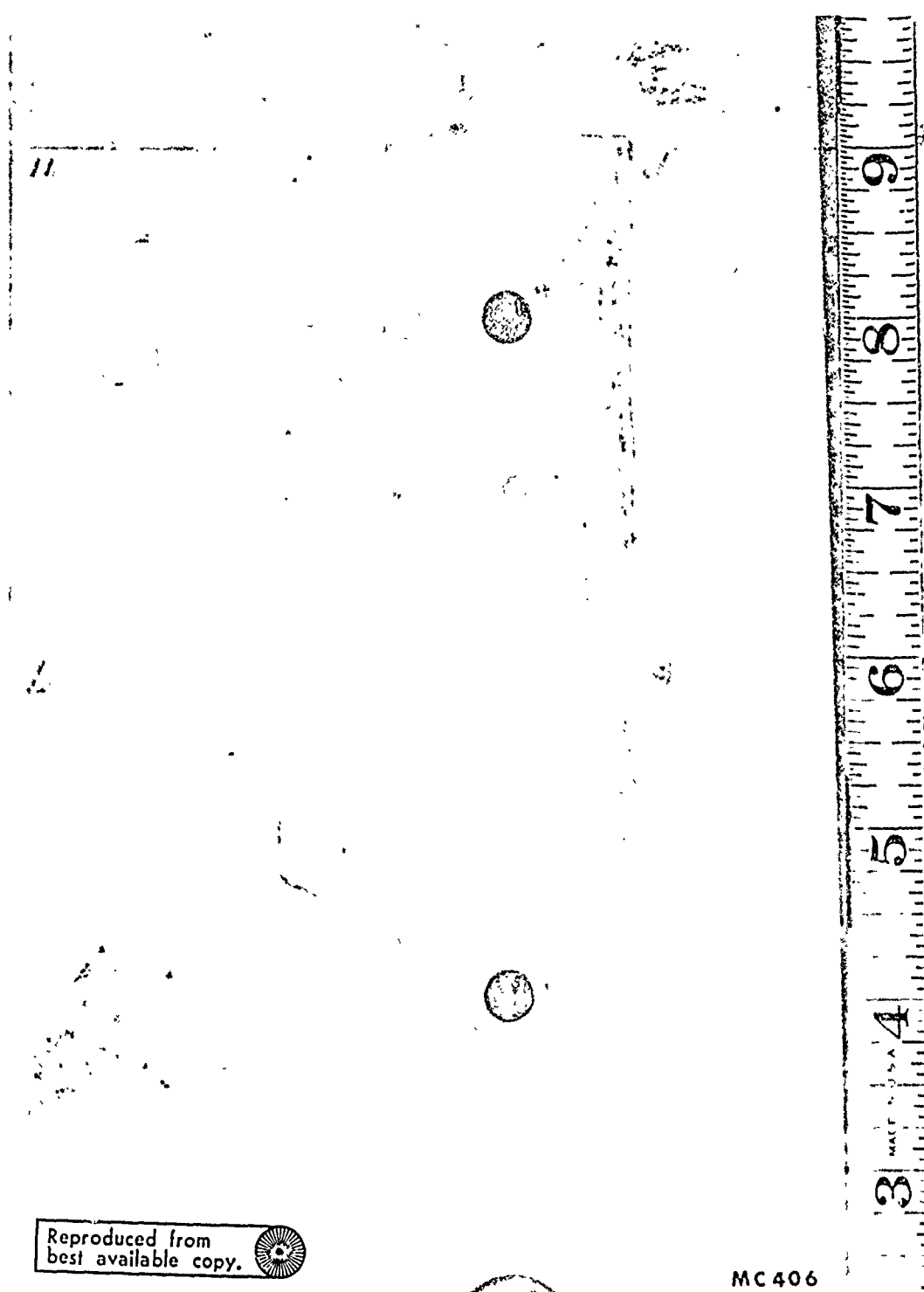



Fig. 16 - 5086-H32 aluminum coupled to 304 stainless steel; with cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X



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Fig. 17 - 5086-H32 aluminum coupled to mild steel; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

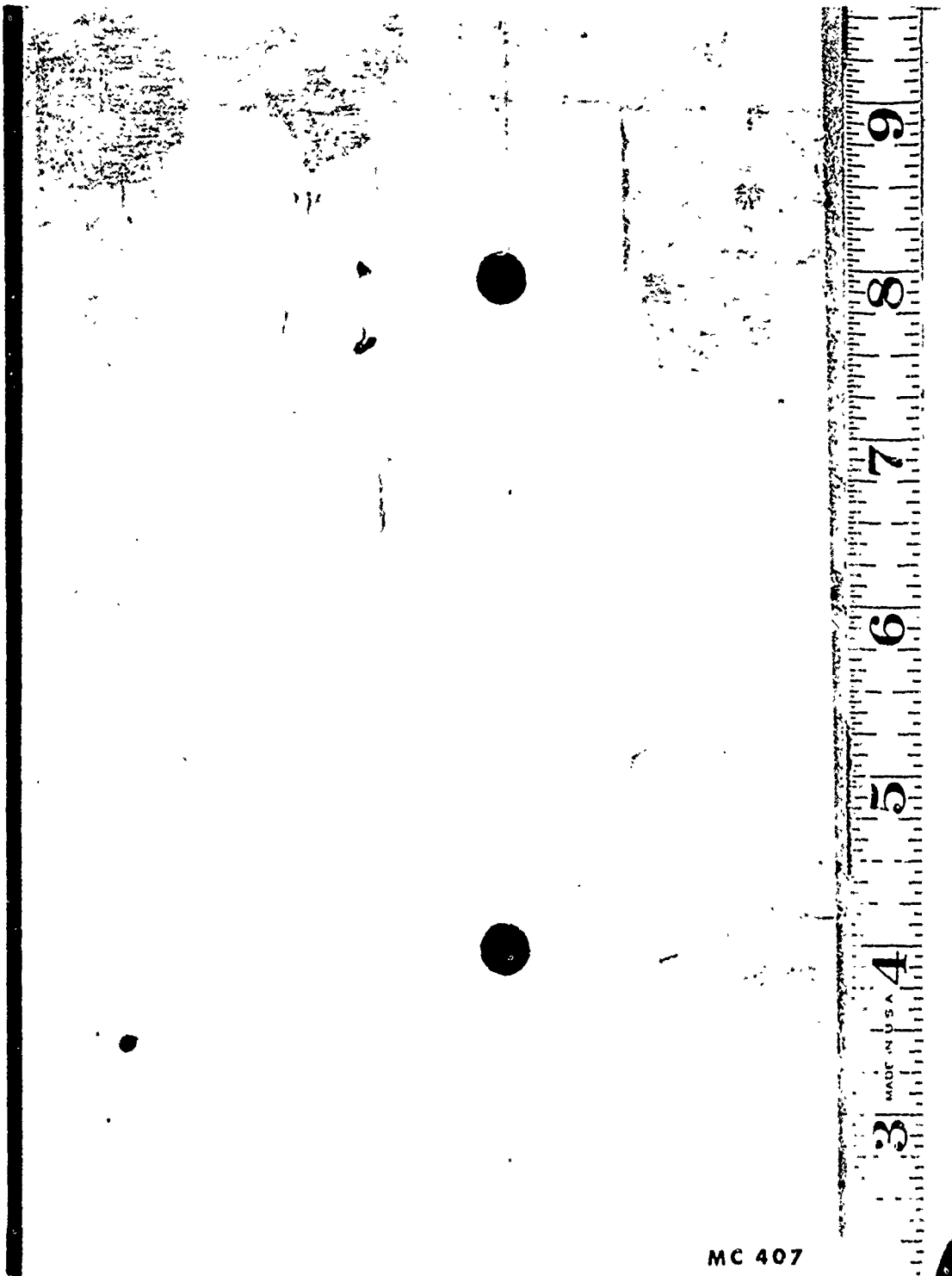


Fig. 18 - 5086-H32 aluminum coupled to mild steel; with cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X



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Fig. 19 - 5086-H32 aluminum; without cathodic protection, 809 days in seawater at Key West, Florida. Original magnification 1.2 X

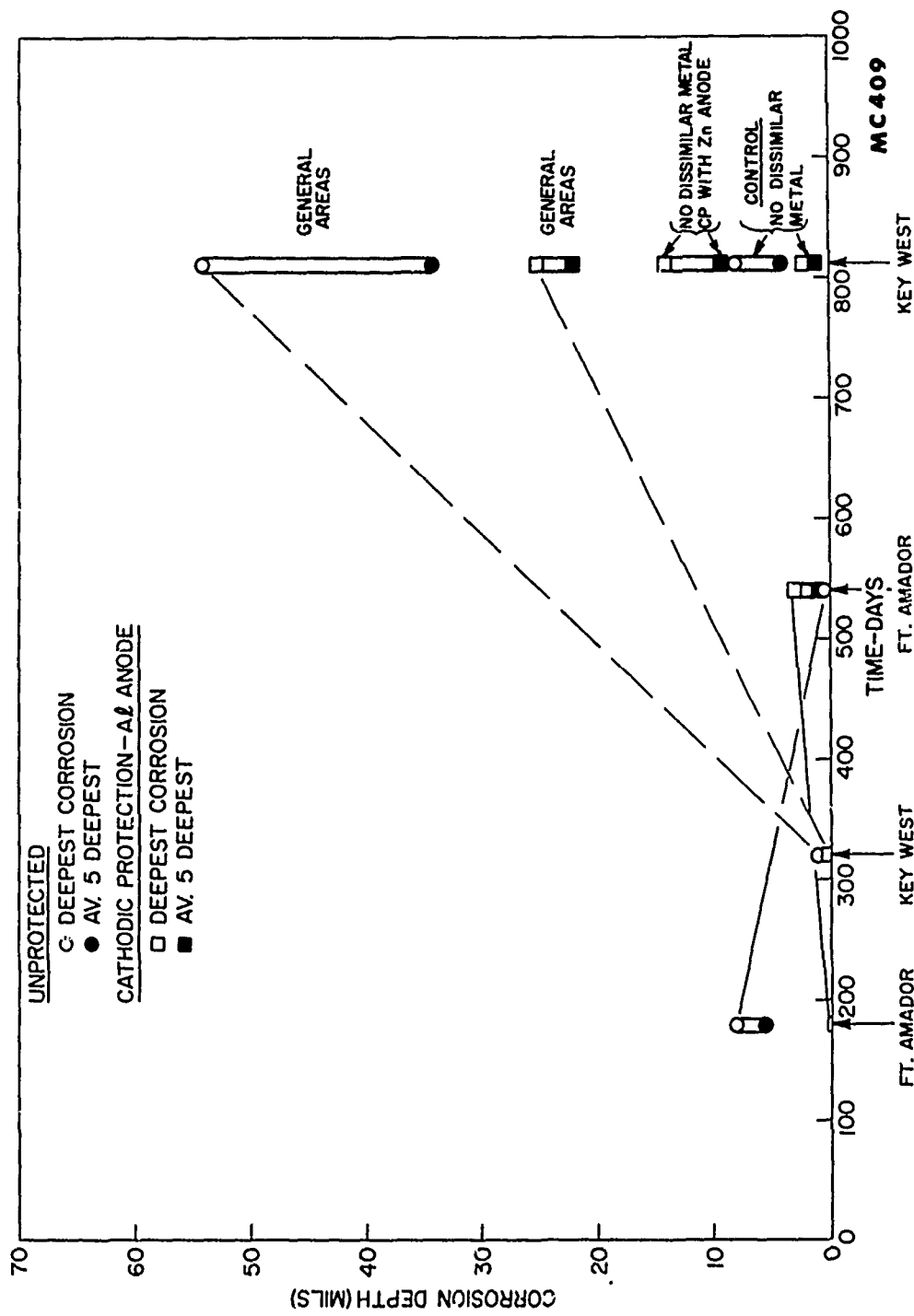


Fig. 20 - 5086-H32 aluminum coupled to copper nickel, 10%; with and without cathodic protection (CP). Data from various exposure times in seawater at Key West, Florida and Ft. Amador, Canal Zone.

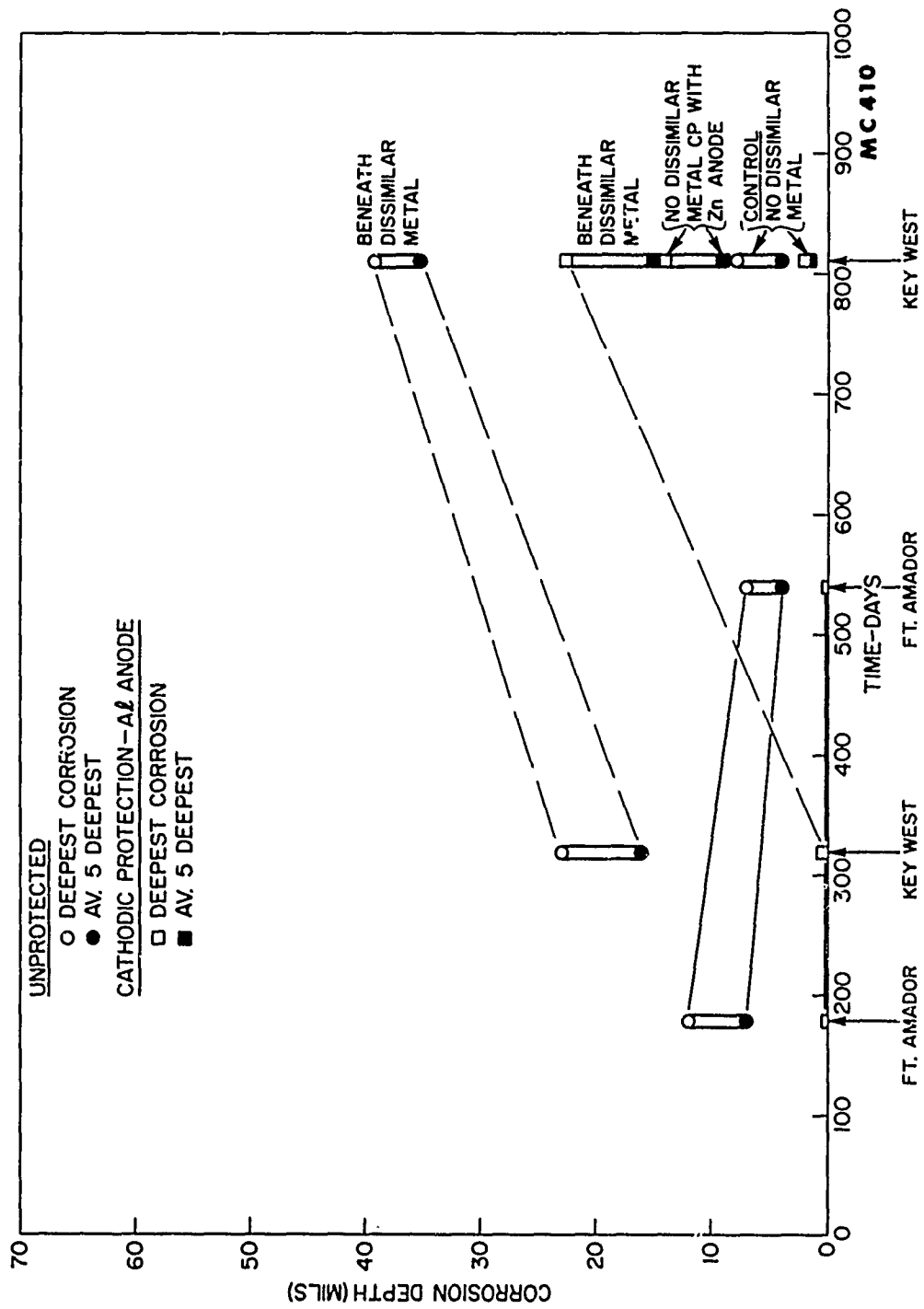


Fig. 21 - 5086-H32 aluminum coupled to yellow brass; with and without cathodic protection (CP). Data from various exposure times in seawater at Key West, Florida and Ft Amador, Canal Zone.

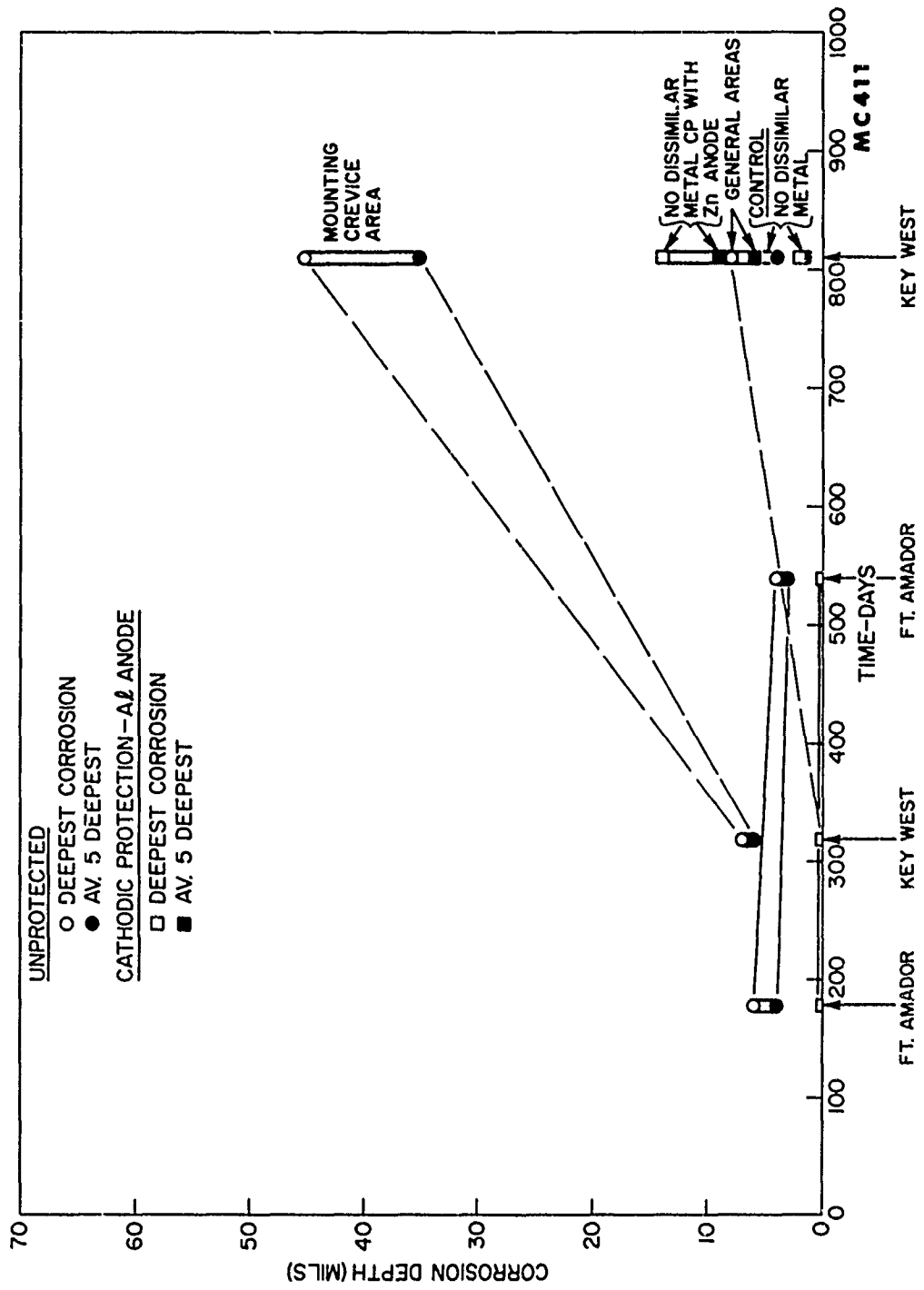


Fig. 22 - 5086-H32 aluminum coupled to 304 stainless steel; with and without cathodic protection (CP). Data from various exposure times in seawater at Key West, Florida and Ft. Amador, Canal Zone.

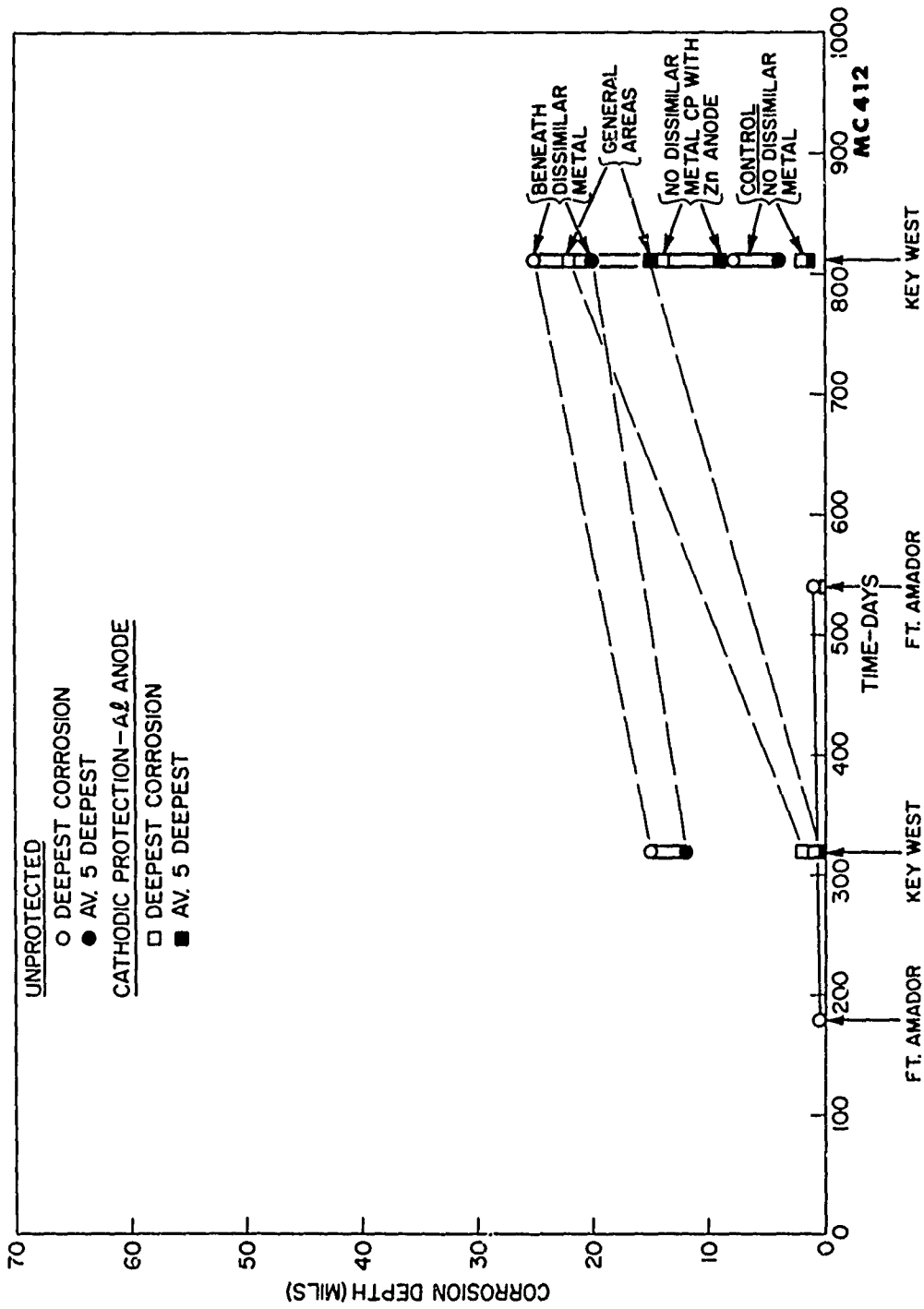


Fig. 23 - 5086-H32 aluminum coupled to mild steel; with and without cathodic protection (CP). Data from various exposure times in seawater at Key West, Florida and Ft. Amador, Canal Zone.

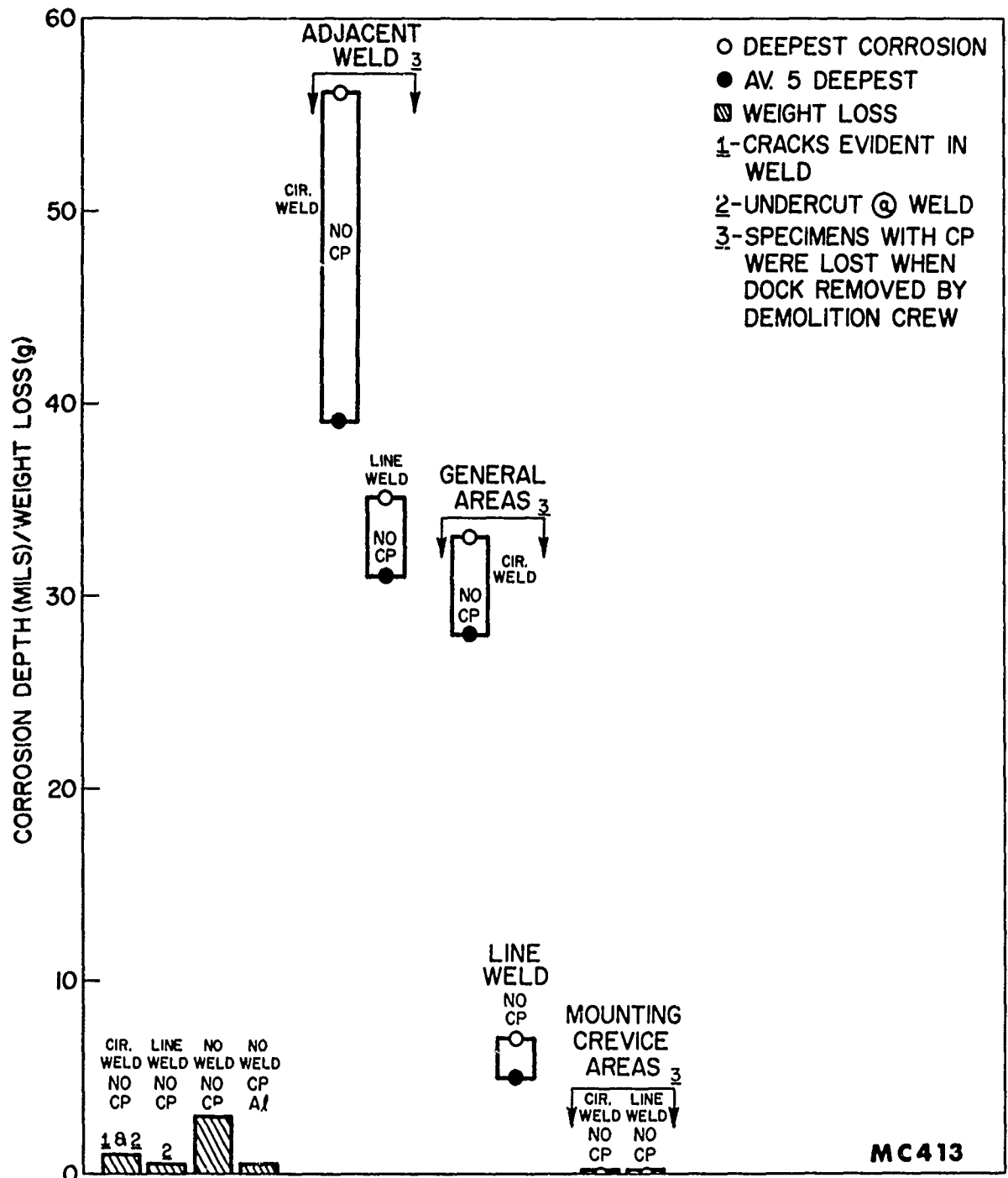
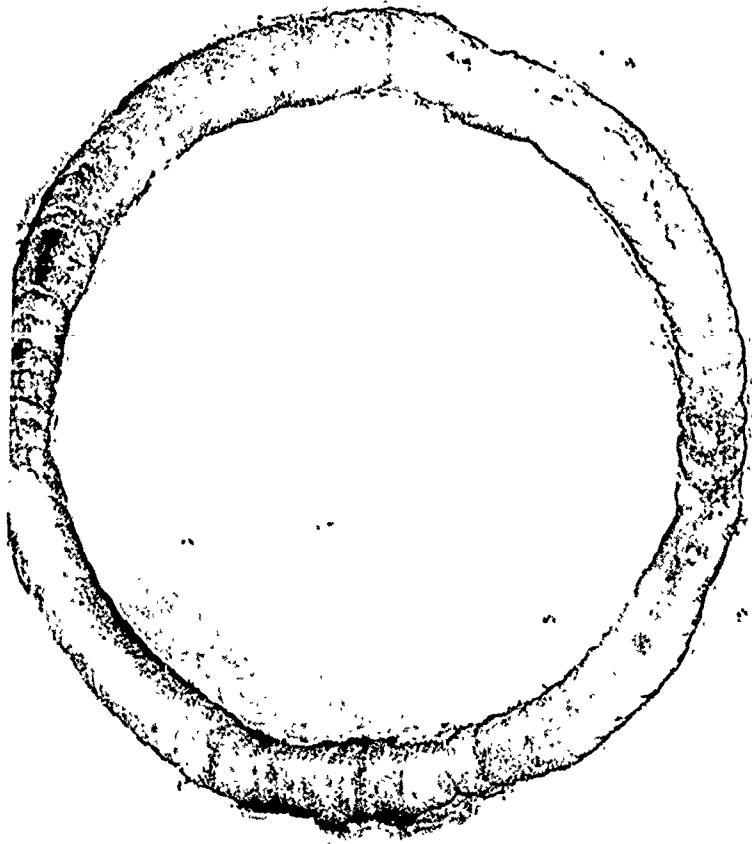


Fig. 24 - Welded 5086-H32 aluminum after 675 days in the Potomac River.



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Fig. 25 - Circular weld in 5086-H32 aluminum; without cathodic protection, 675 days in the Potomac River. Original magnification 1.25 X

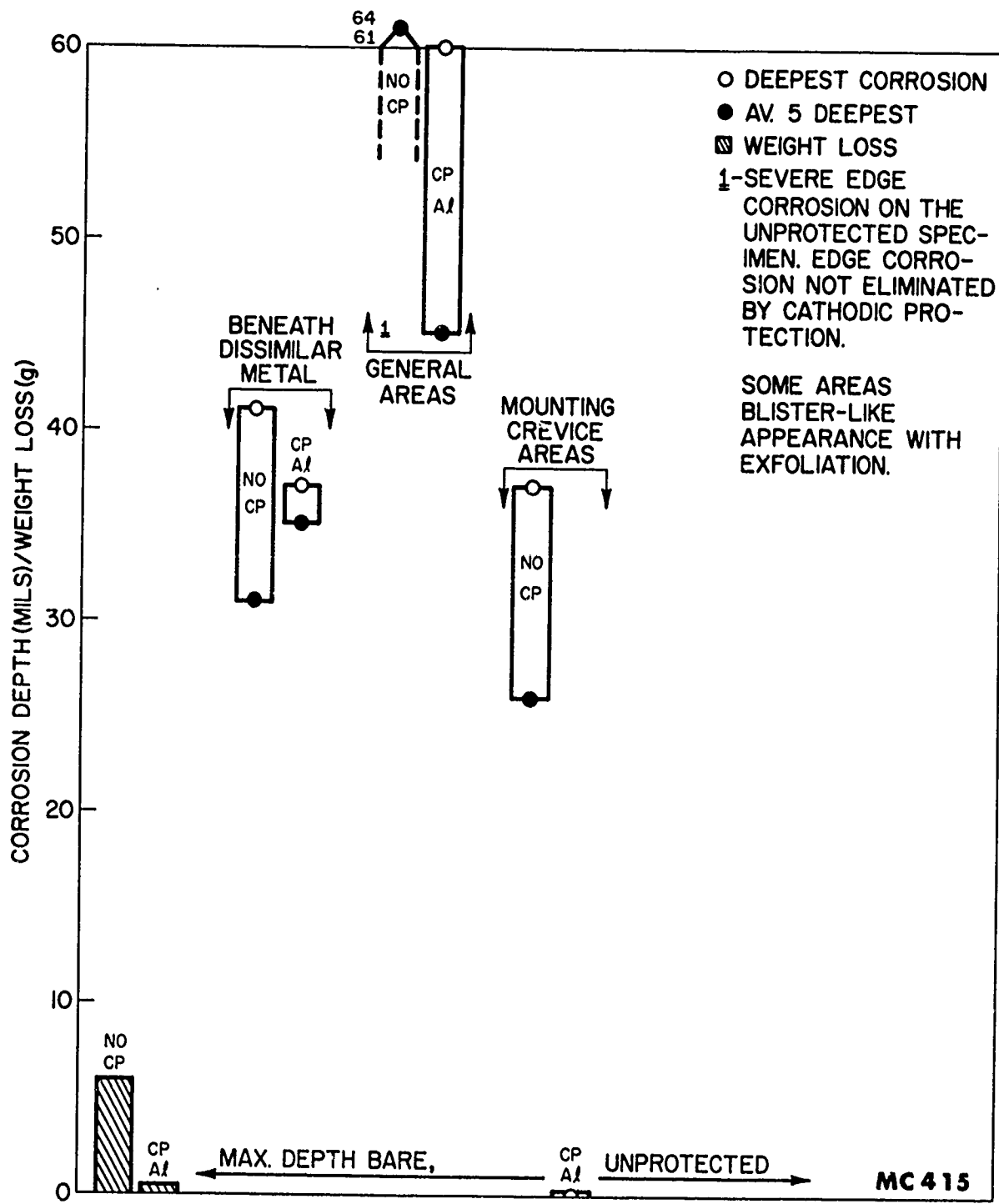


Fig. 26 - 5086-H32 aluminum coupled to copper nickel, 10%; with and without cathodic protection (CP), 675 days in the Potomac River.

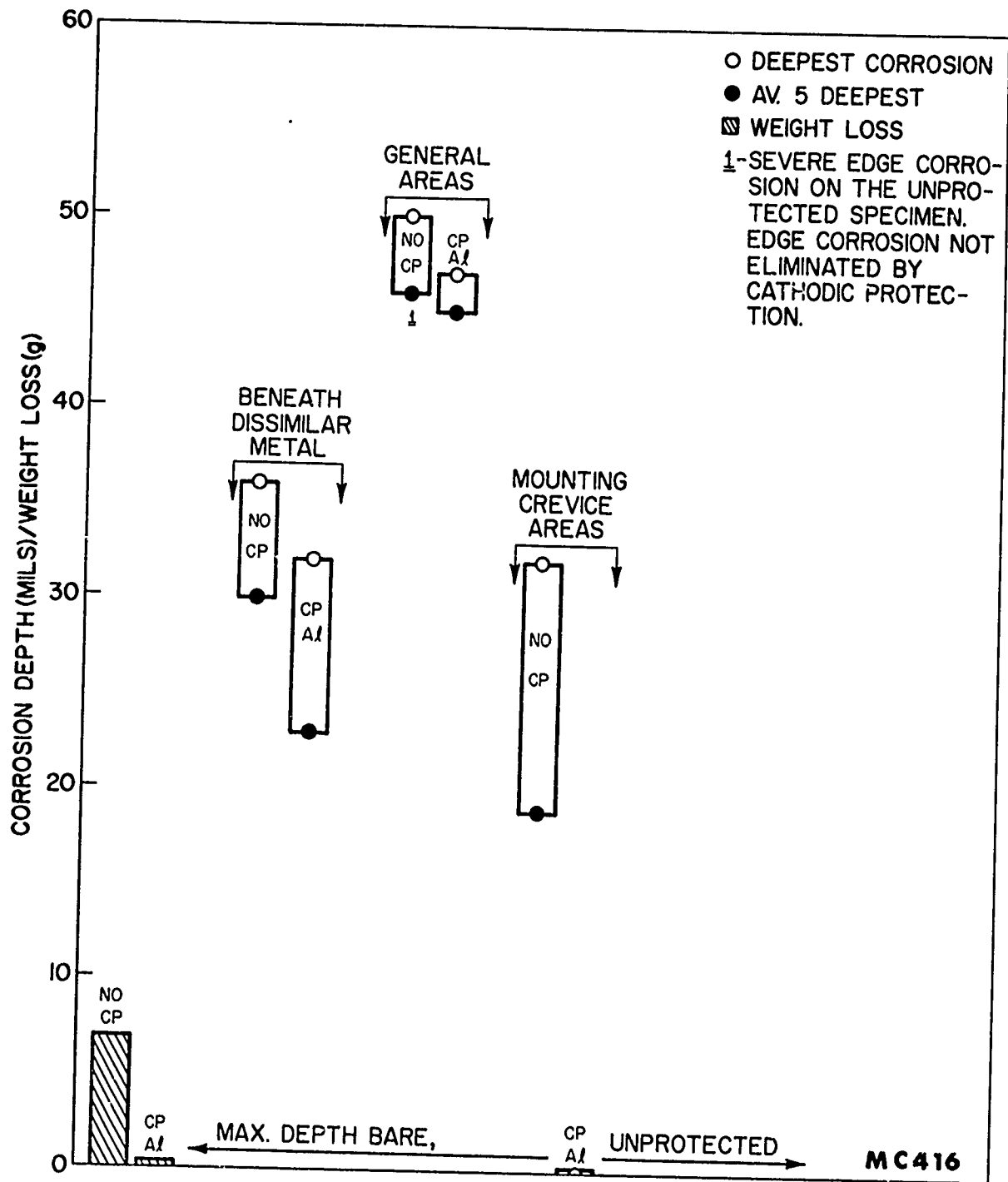


Fig. 27 - 5086-H23 aluminum coupled to yellow brass; with and without cathodic protection (CP), 675 days in the Potomac River.

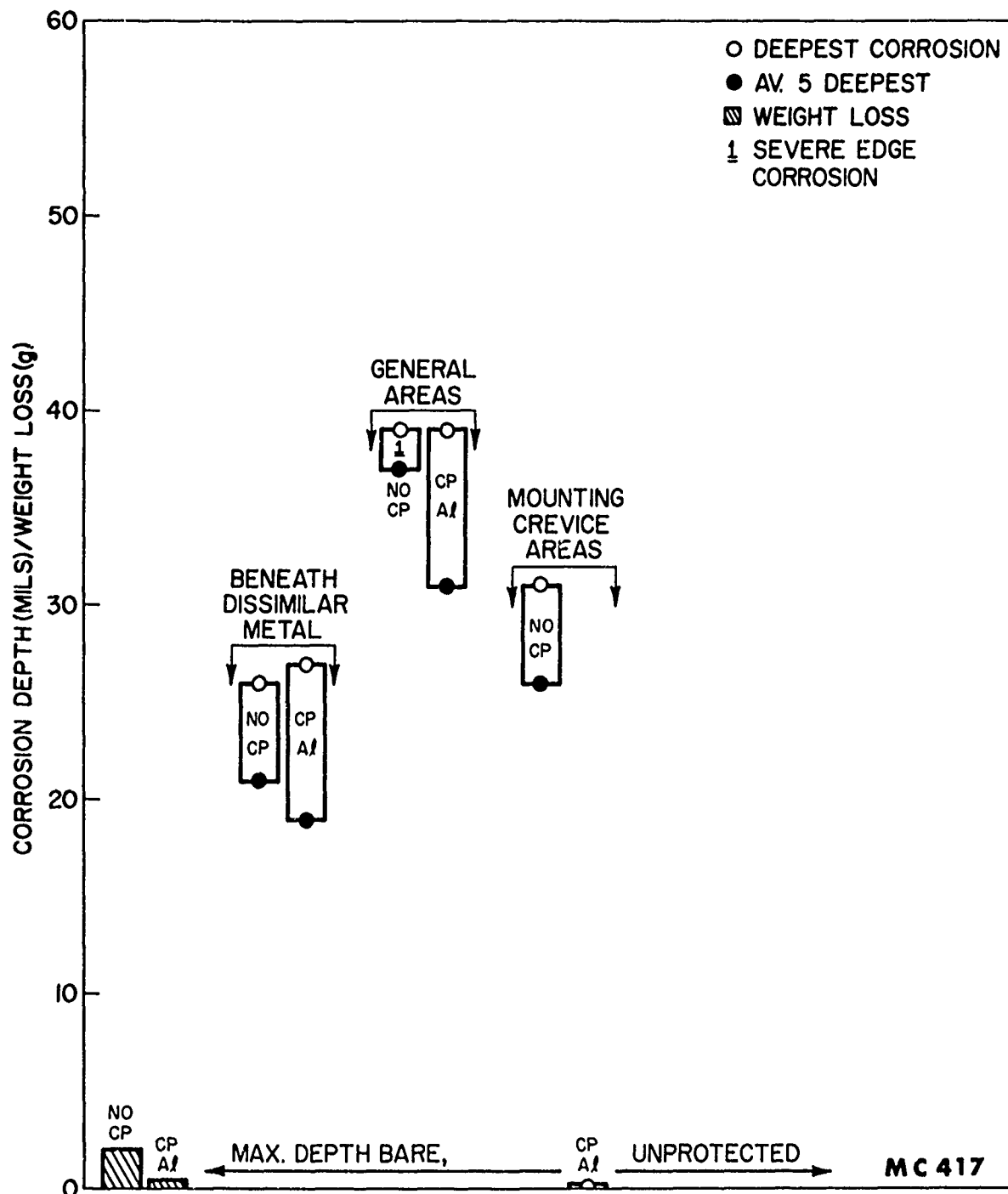


Fig. 28 - 5086-H32 aluminum coupled to 304 stainless steel; with and without cathodic protection (CP), 675 days in the Potomac River.

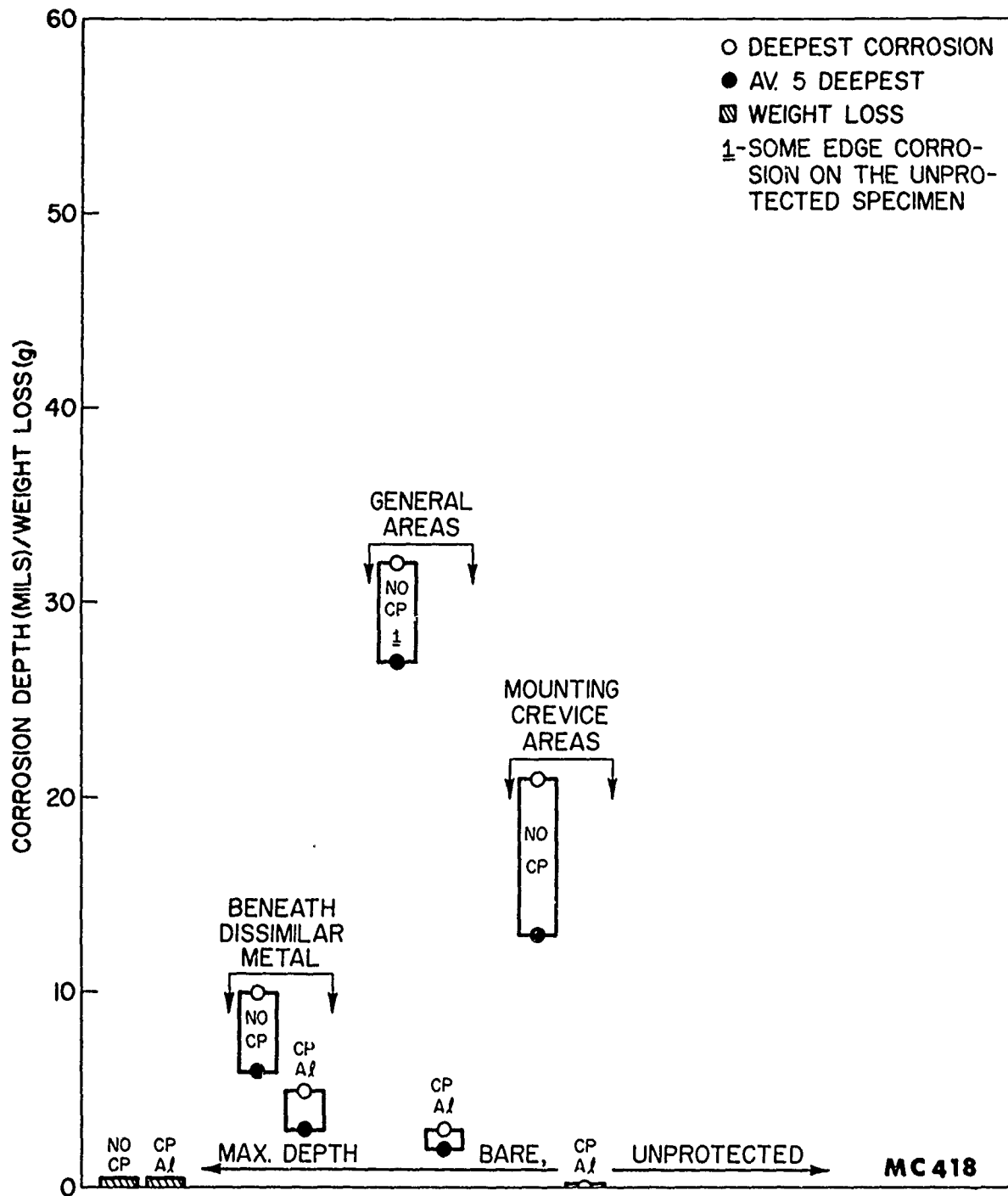


Fig. 29 - 5086-H32 aluminum coupled to mild steel; with and without cathodic protection (CP), 675 days in the Potomac River.

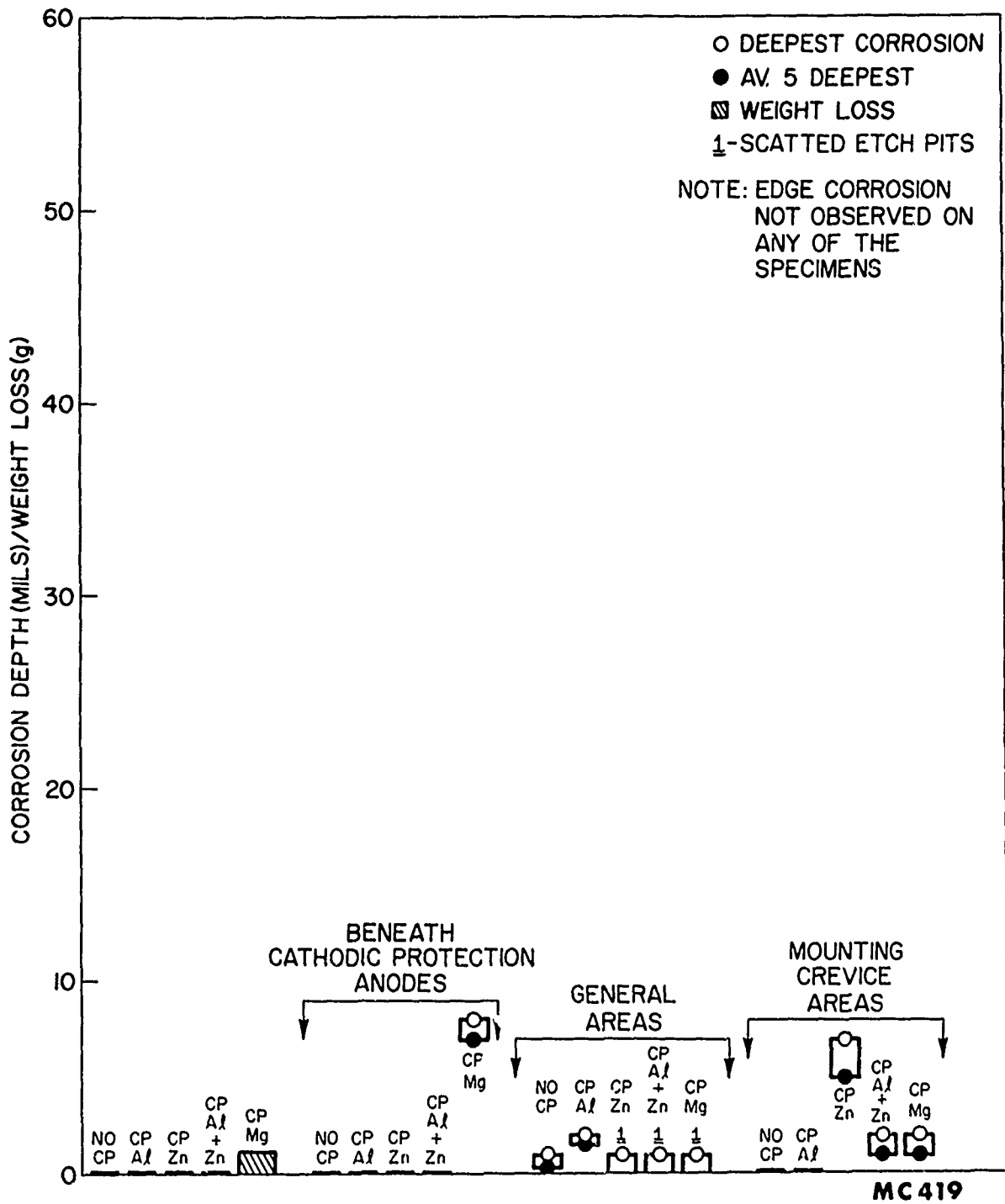


Fig. 30 - 5086-H32 aluminum; with and without cathodic protection (CP), 675 days in the Potomac River.

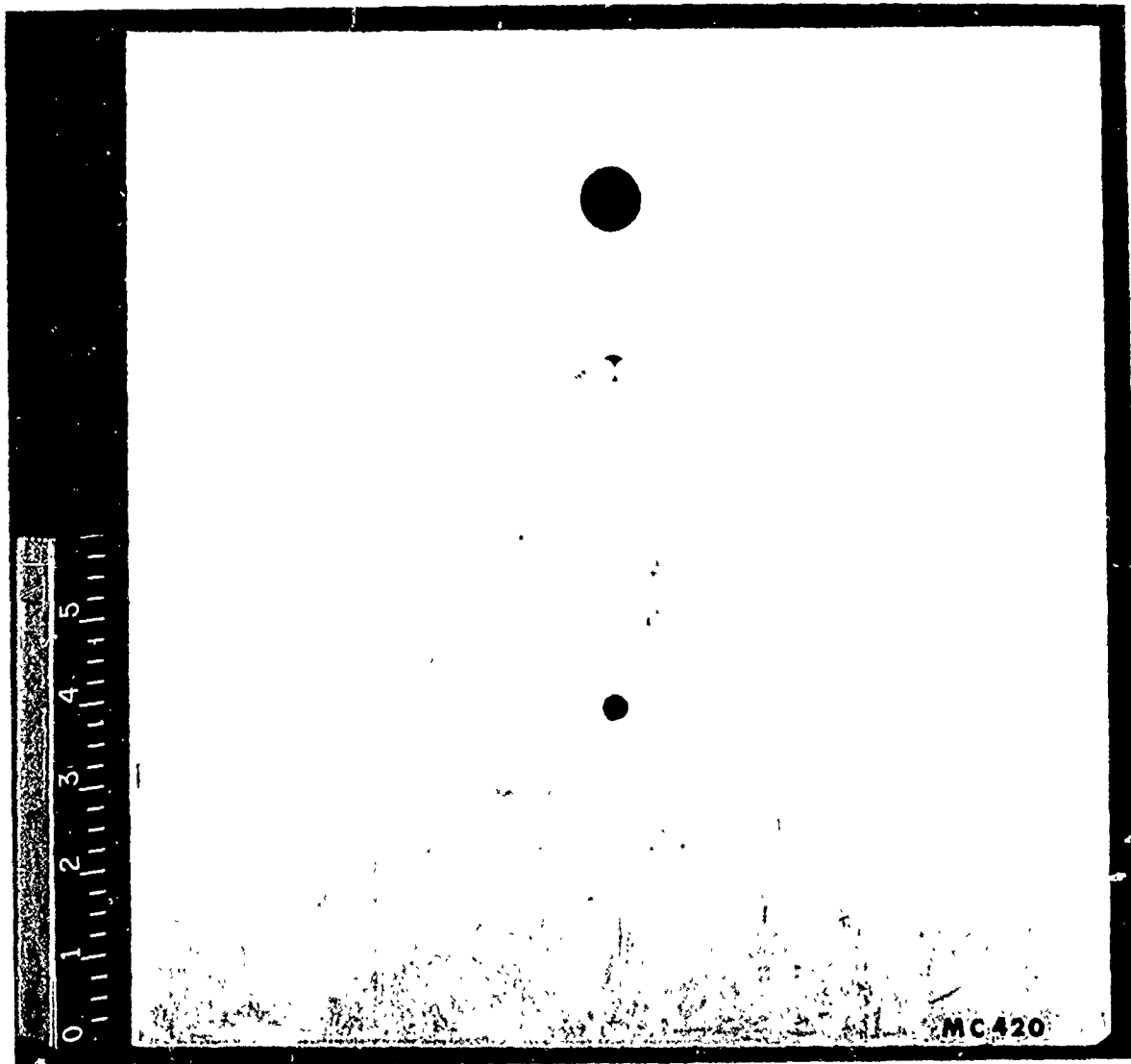


Fig. 31 - 5086-II32 aluminum coupled to copper nickel, 10°C; without cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

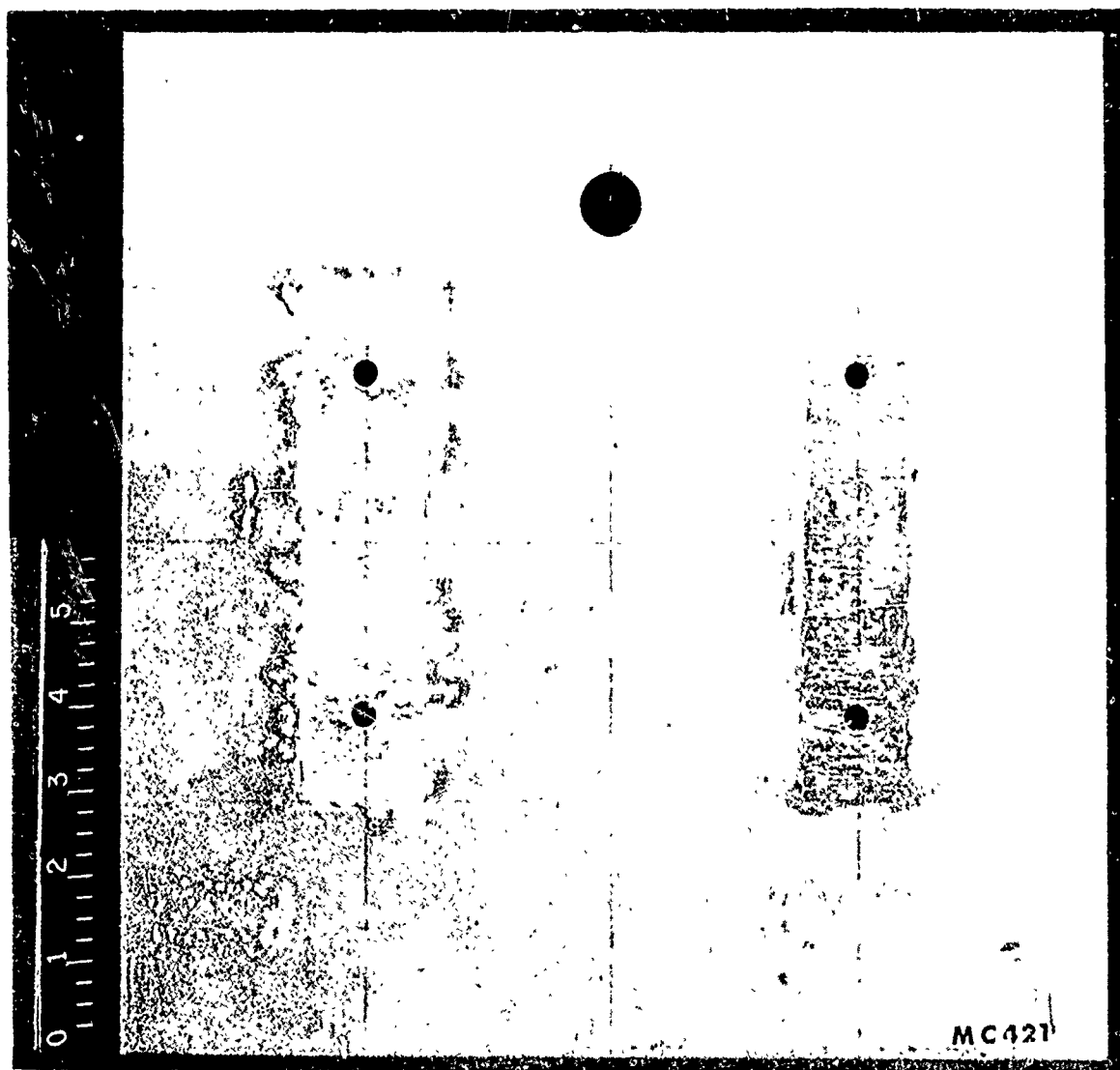


Fig. 32 - 5086-H132 aluminum coupled to copper nickel, 10%;
with cathodic protection, 675 days in the Potomac River.
Original magnification 0.5 X

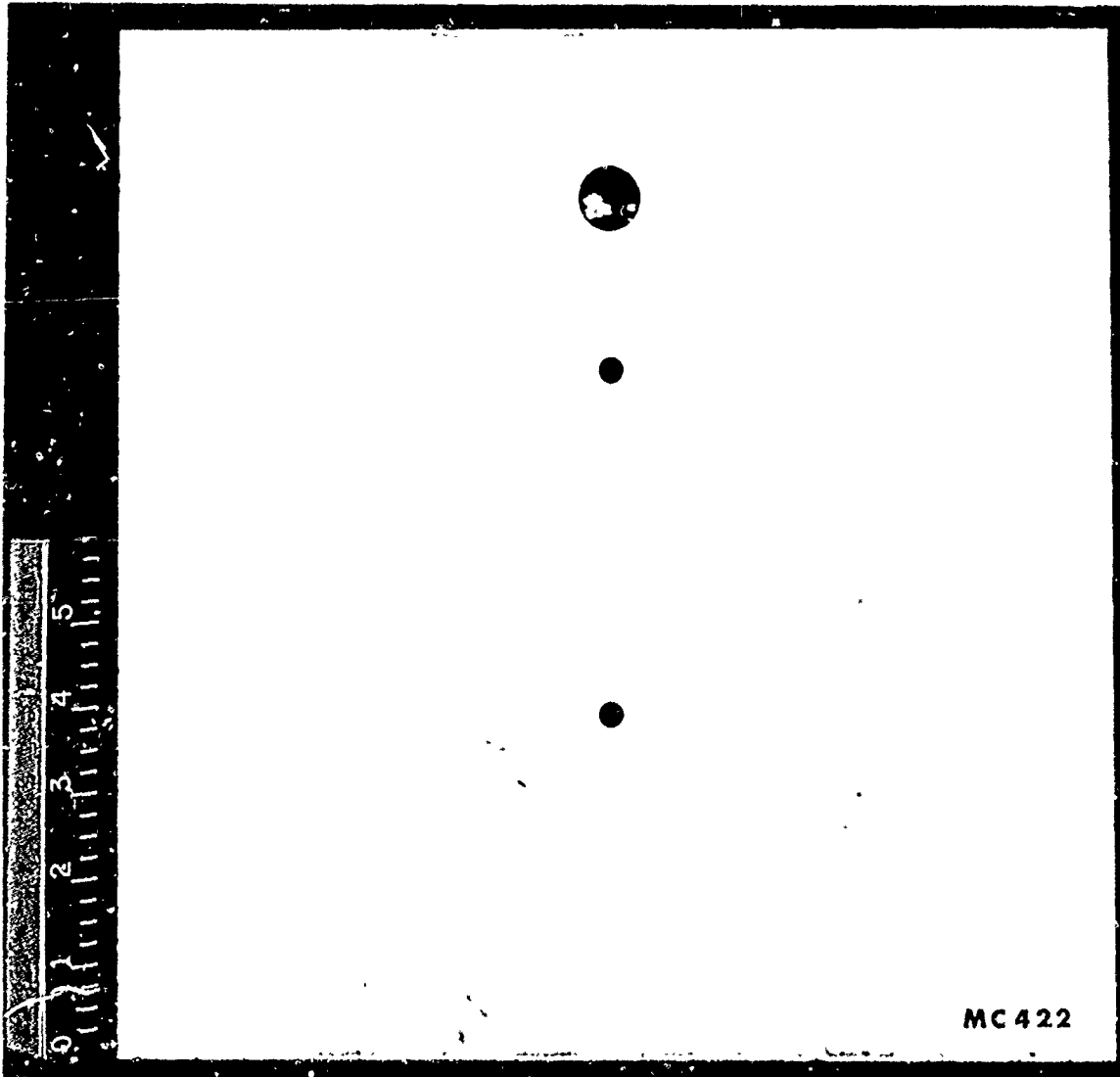


Fig. 33 - 5086-H132 aluminum coupled to yellow brass; without cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

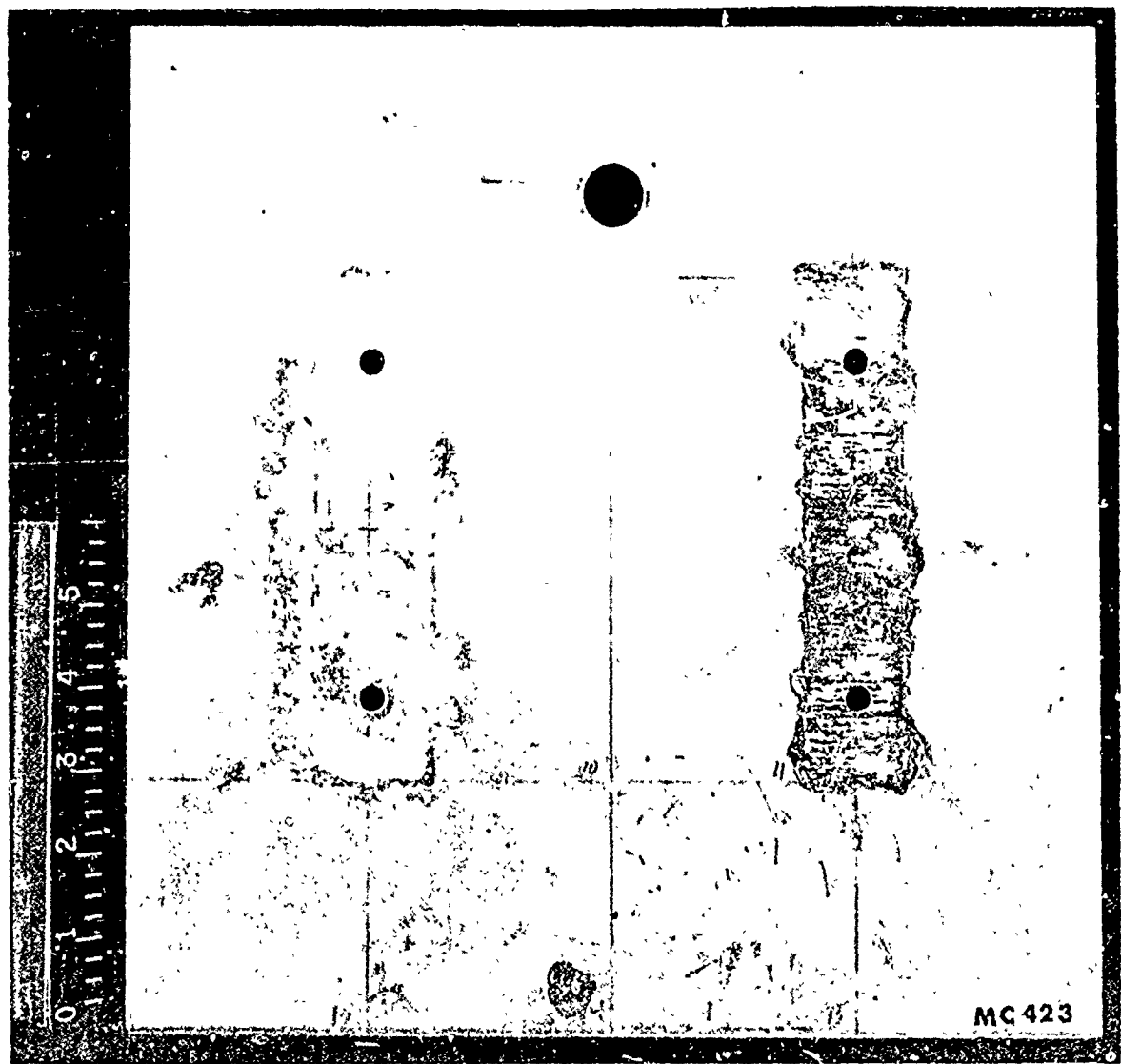


Fig. 34 - 5086-II32 aluminum coupled to yellow brass; with cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

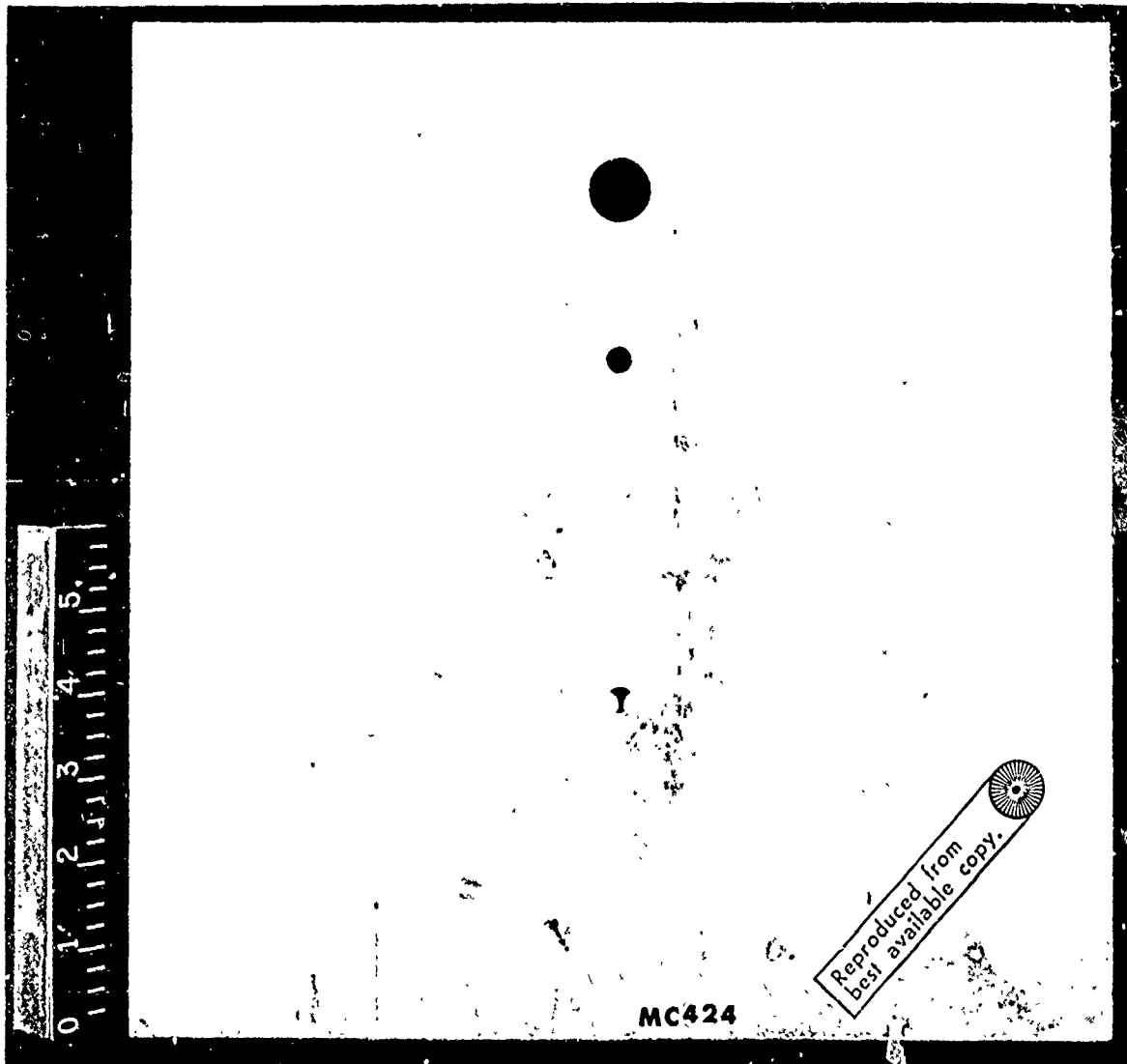


Fig. 35 - 5086-H32 aluminum coupled to 304 stainless steel; without cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

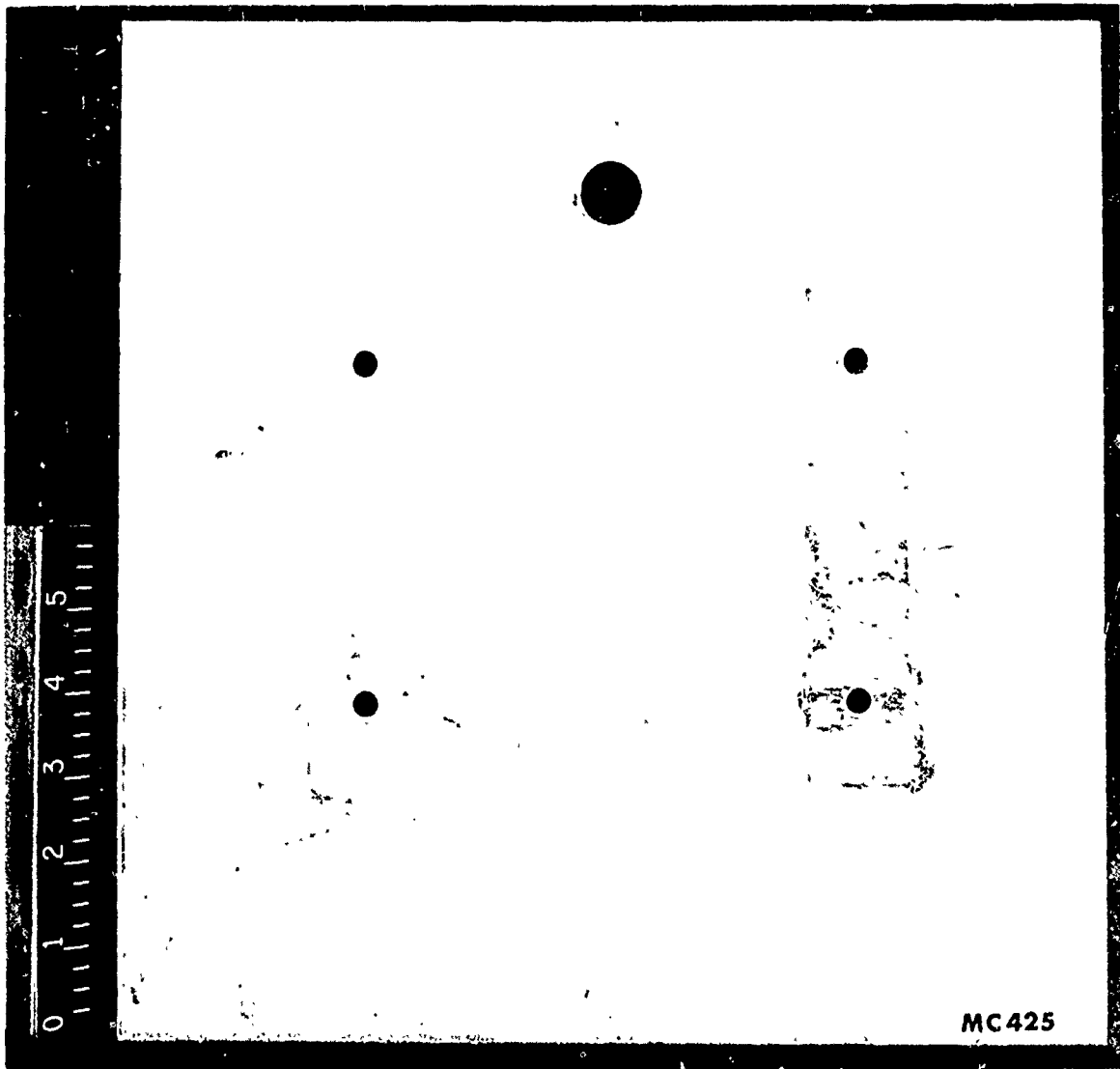


Fig. 36 - 5086-H32 aluminum coupled to 304 stainless steel;
with cathodic protection, 675 days in the Potomac River .
Original magnification 0.5 X

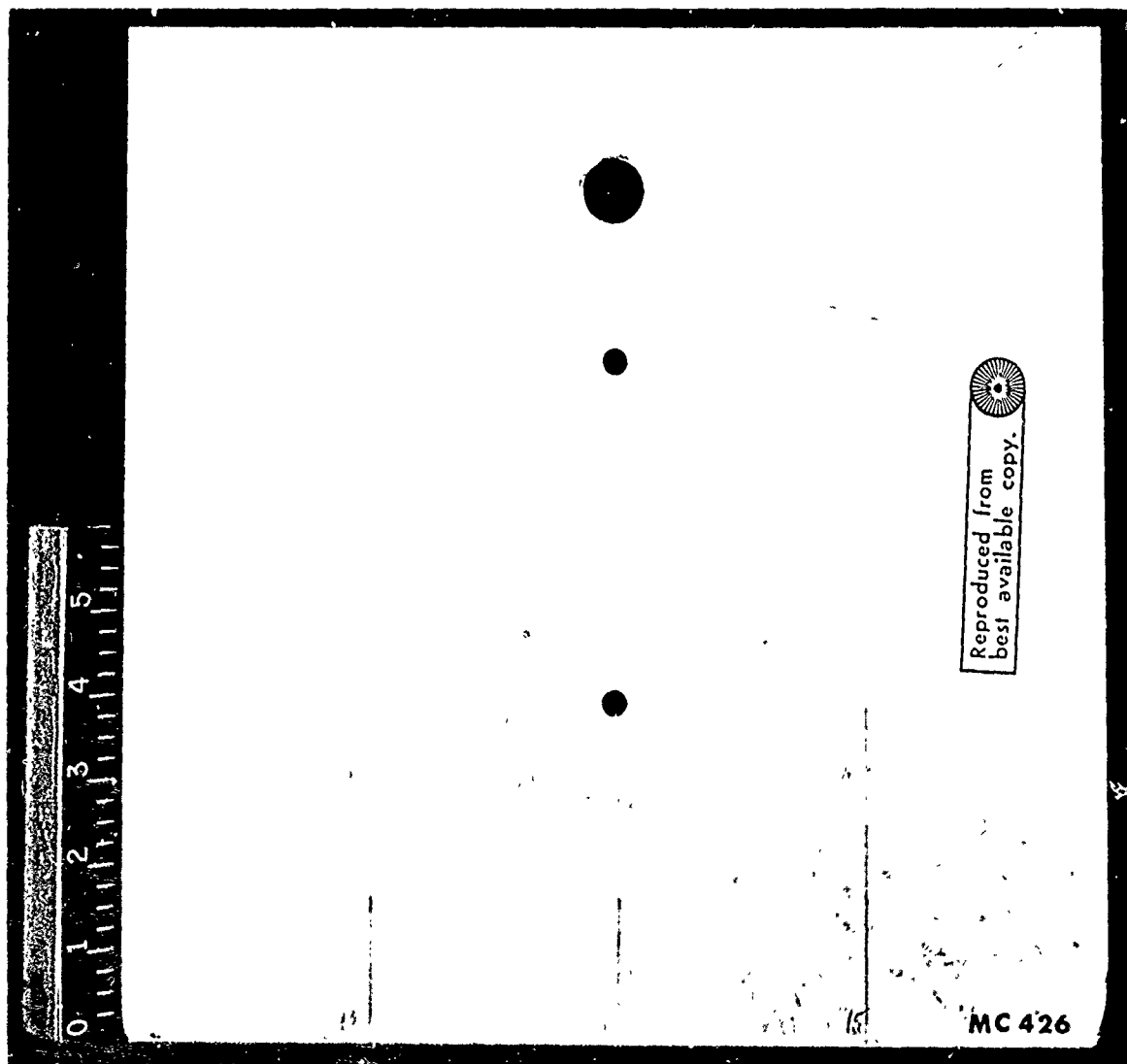


Fig. 37 - 5086-H32 aluminum coupled to mild steel; without cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

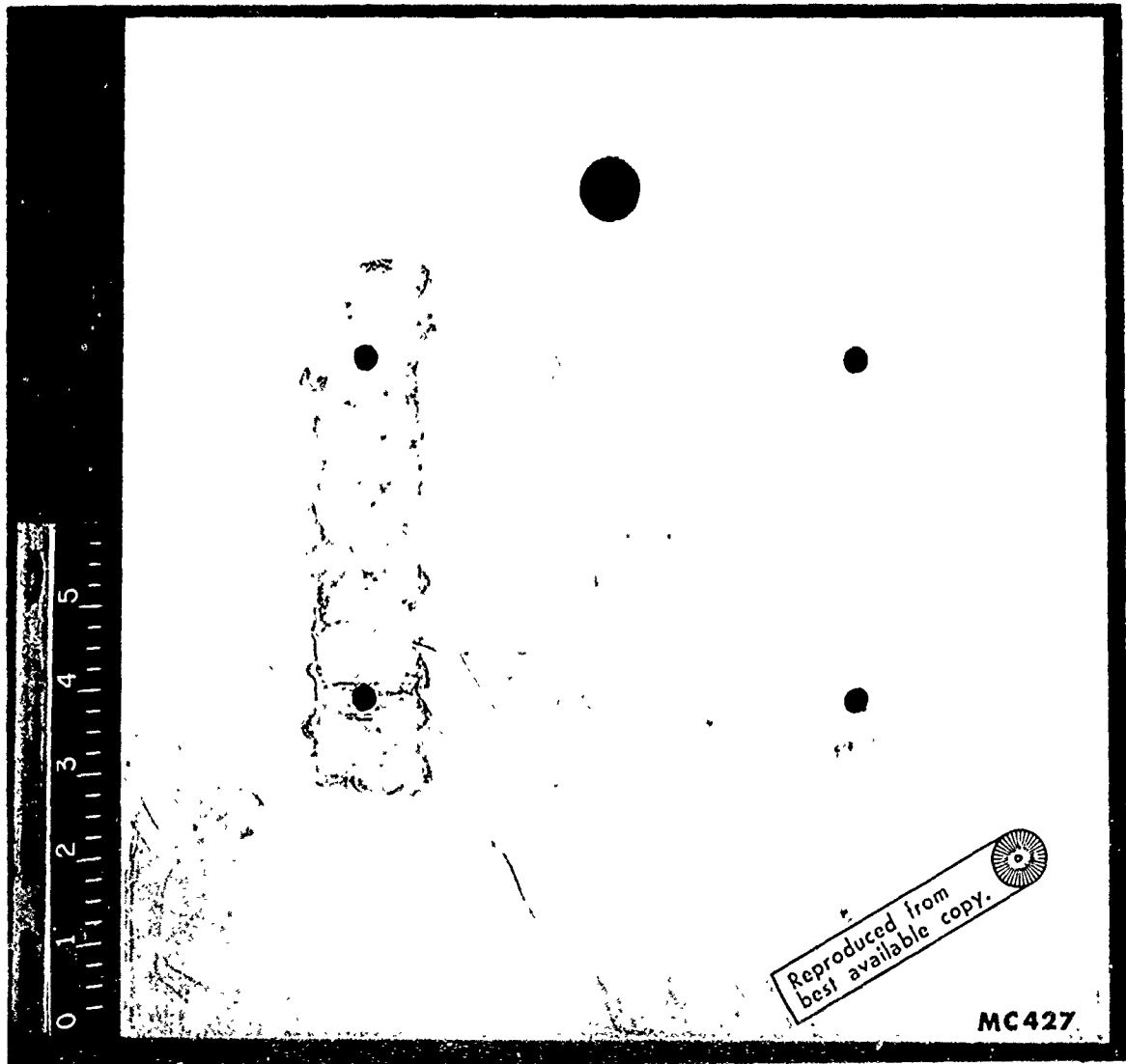


Fig. 38 - 5086-H32 aluminum coupled to mild steel; with cathodic protection, 675 days in the Potomac River. Original magnification 0.5X

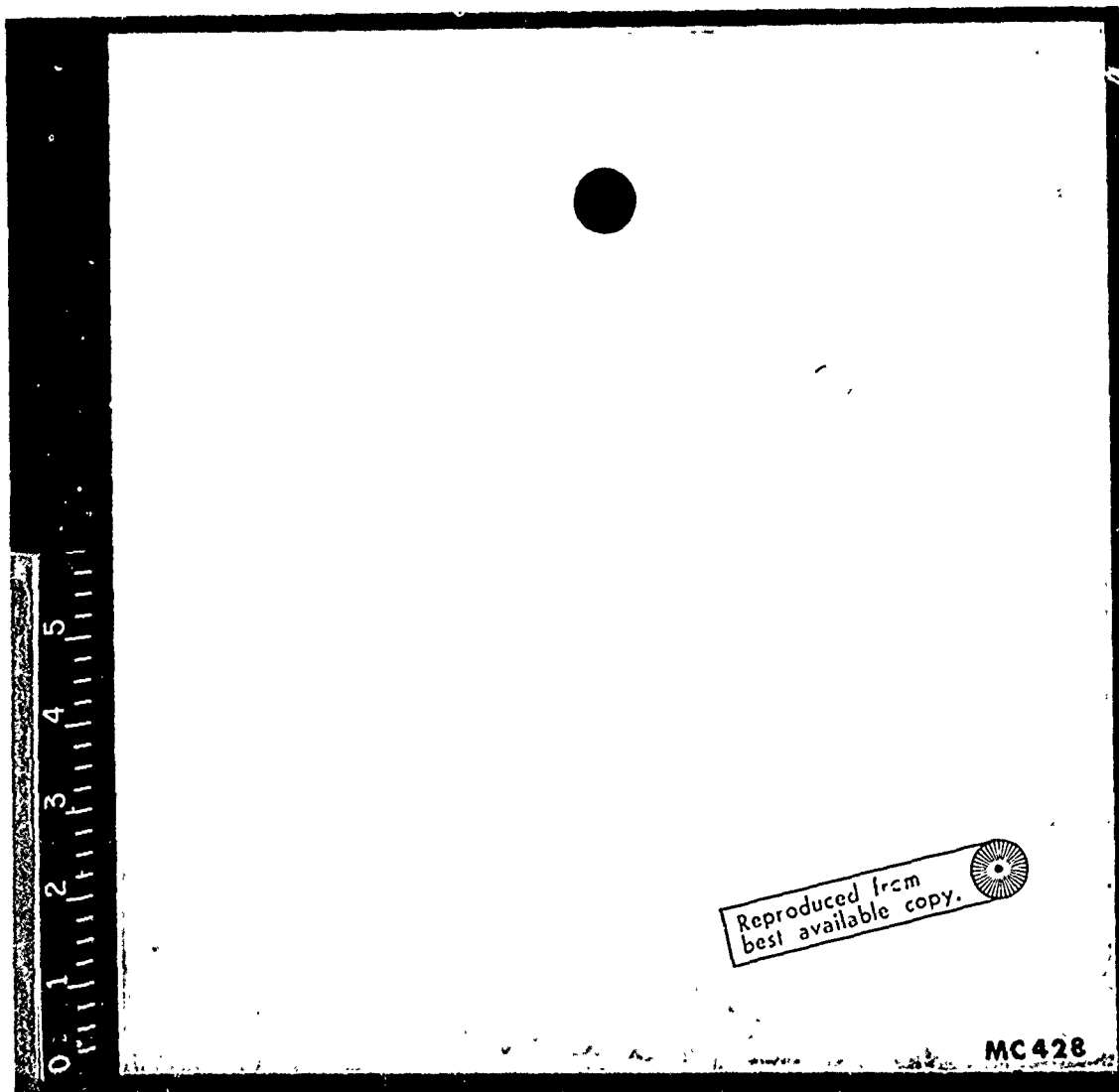


Fig. 39 - 5086-H32 aluminum; without cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

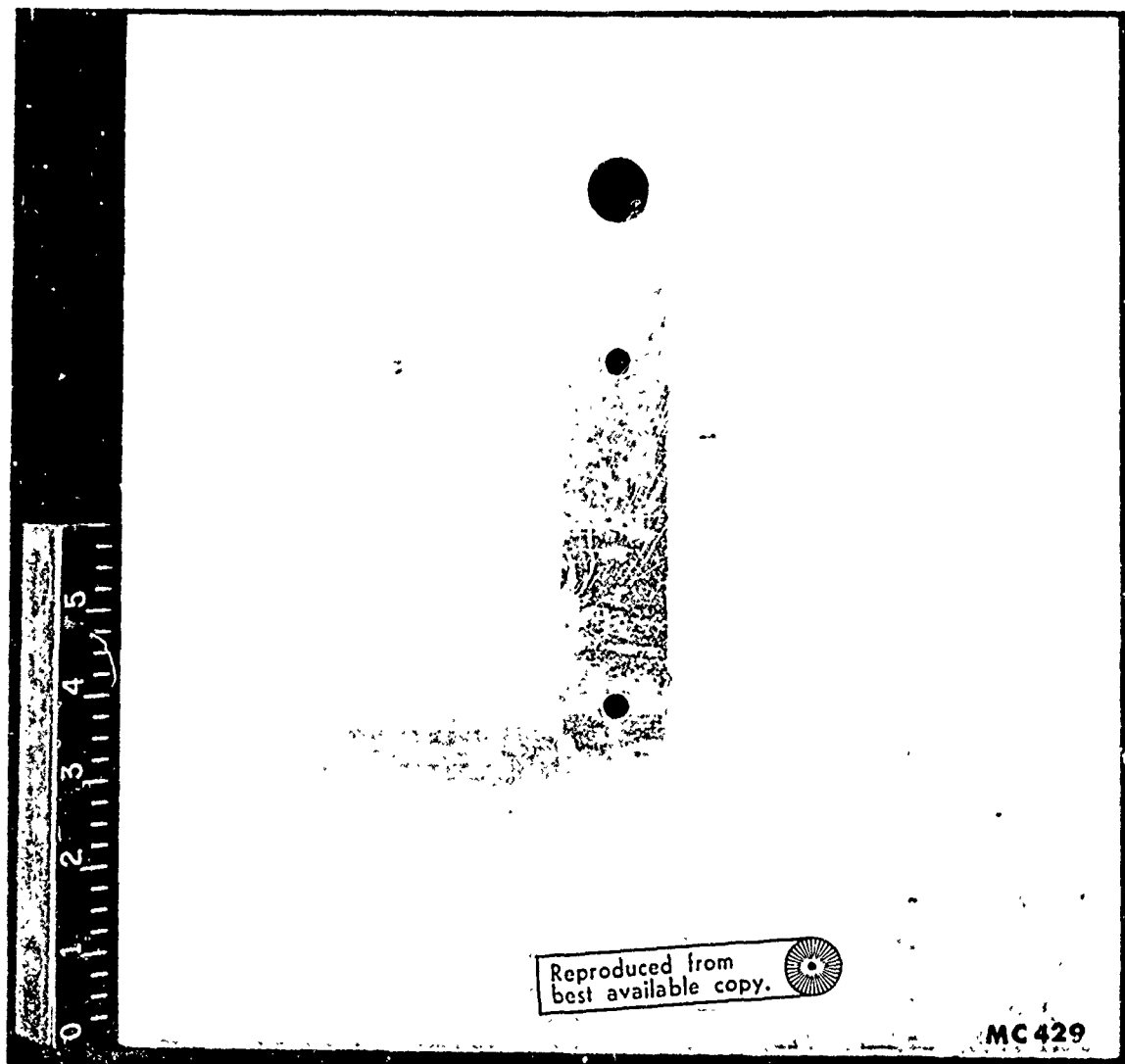


Fig. 40 - 5086-H32 aluminum; with cathodic protection, 675 days in the Potomac River. Original magnification 0.5 X

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Fig. 41 - 5086-H32 aluminum; with cathodic protection from a magnesium anode, 675 days in the Potomac River. Original magnification 1.2 X

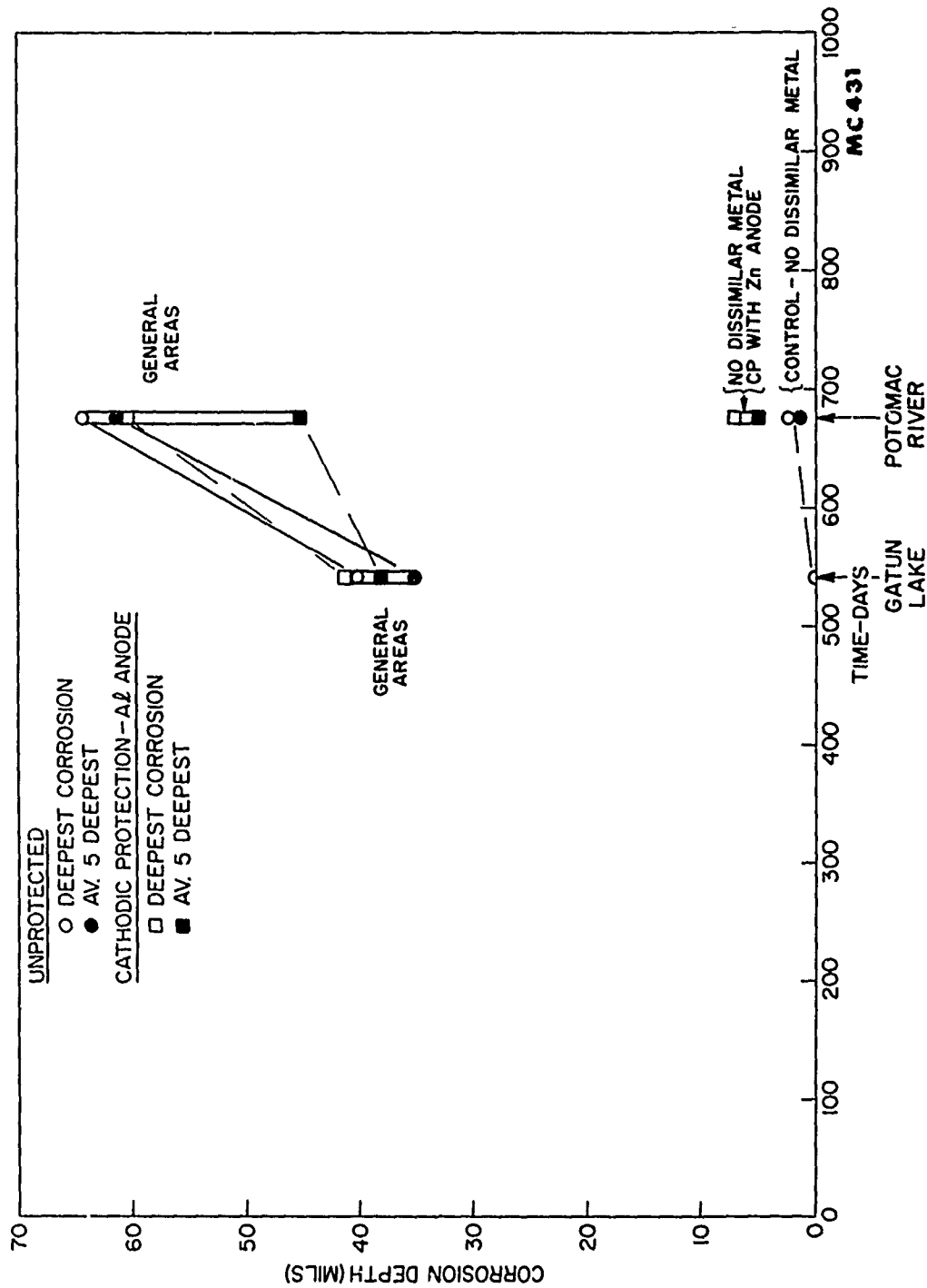


Fig. 42 - 5086-H32 aluminum coupled to copper nickel, 10%; with and without cathodic protection (CP). Data from Gatun Lake and the Potomac River exposures.

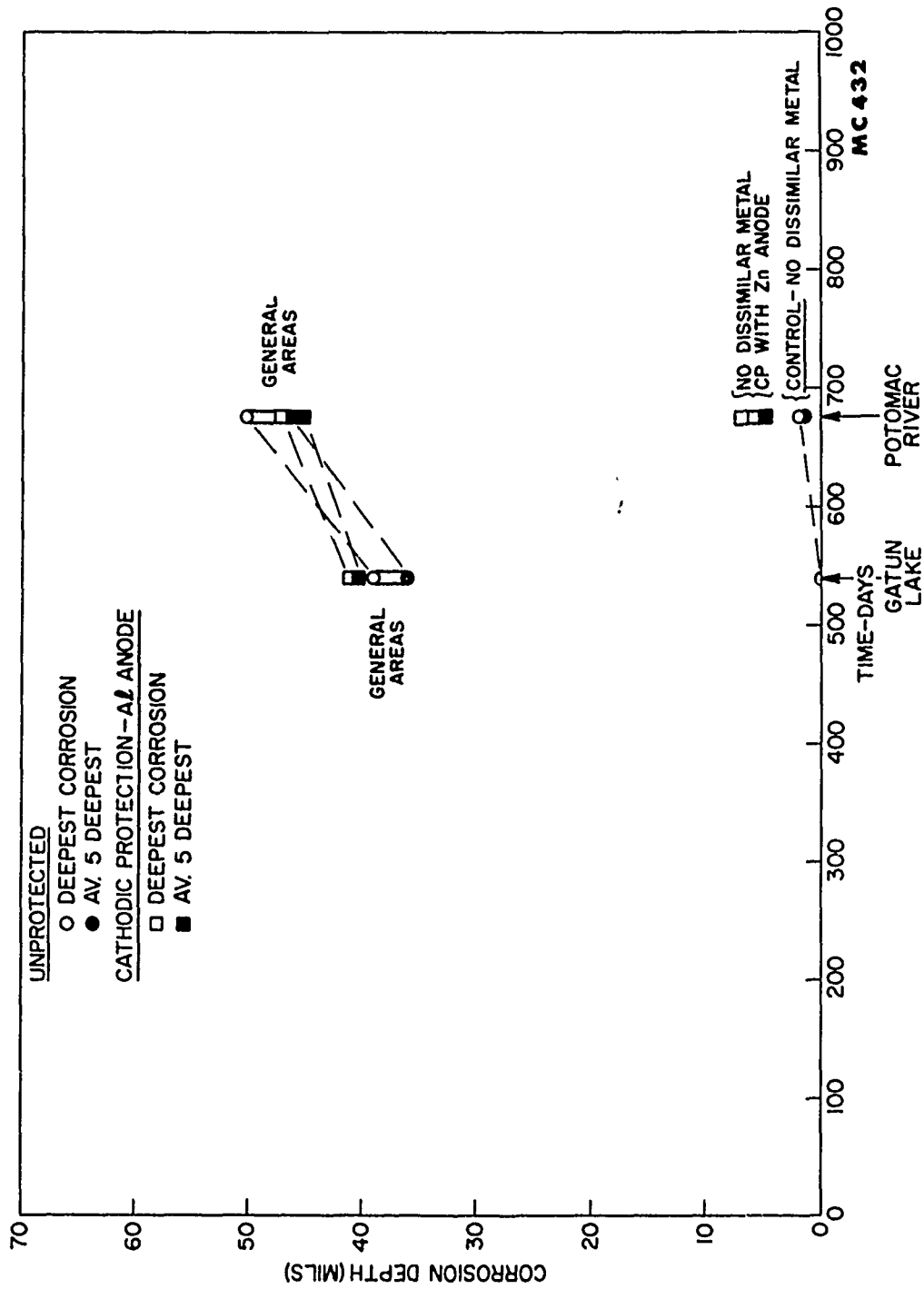


Fig. 43 - 5086-H32 aluminum coupled to yellow brass; with and without cathodic protection (CP). Data from Gatun Lake and the Potomac River exposures.

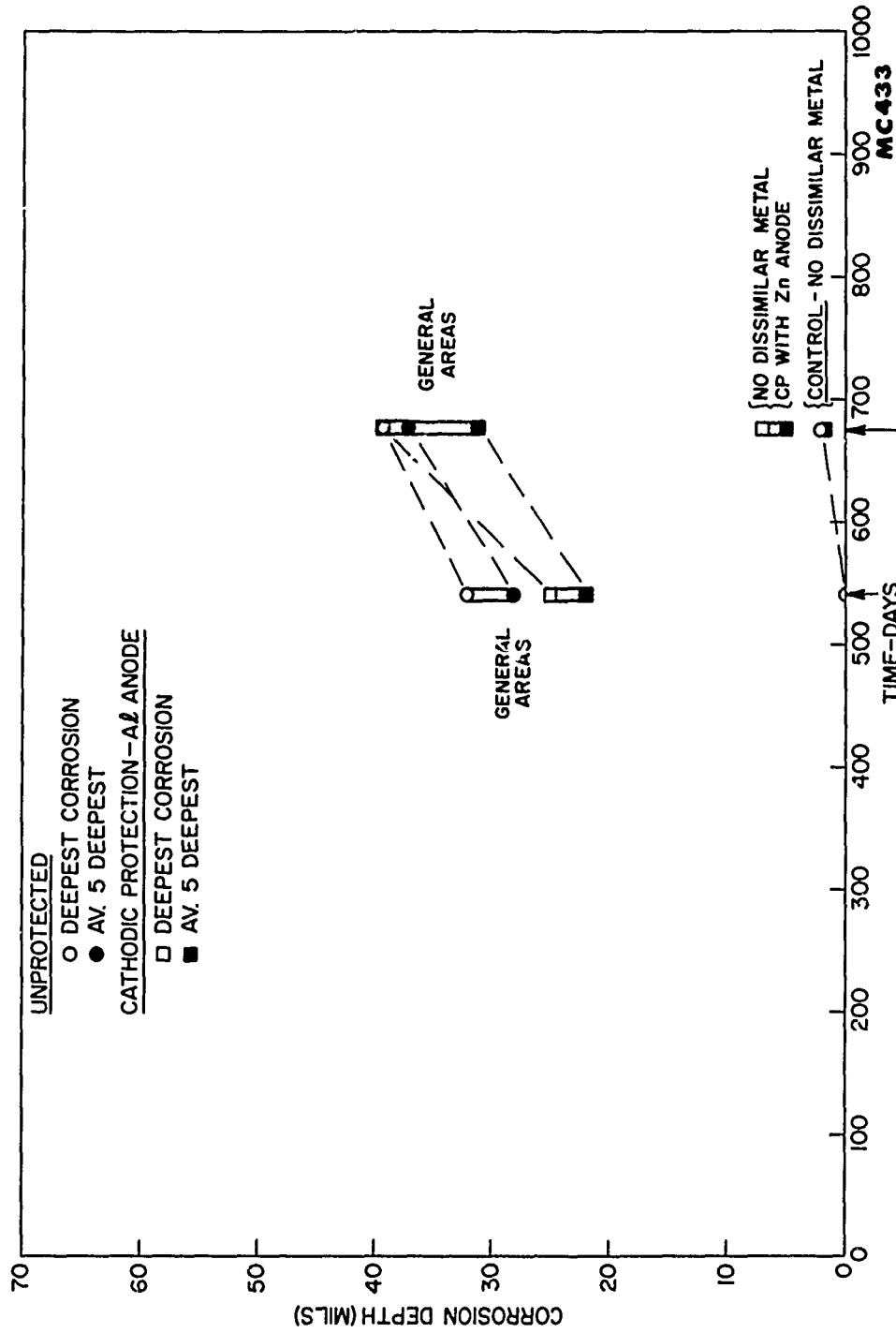


Fig. 44 - 5086-H32 aluminum coupled to 304 stainless steel; with and without cathodic protection (CP). Data from Gatun Lake and the Potomac River exposures.

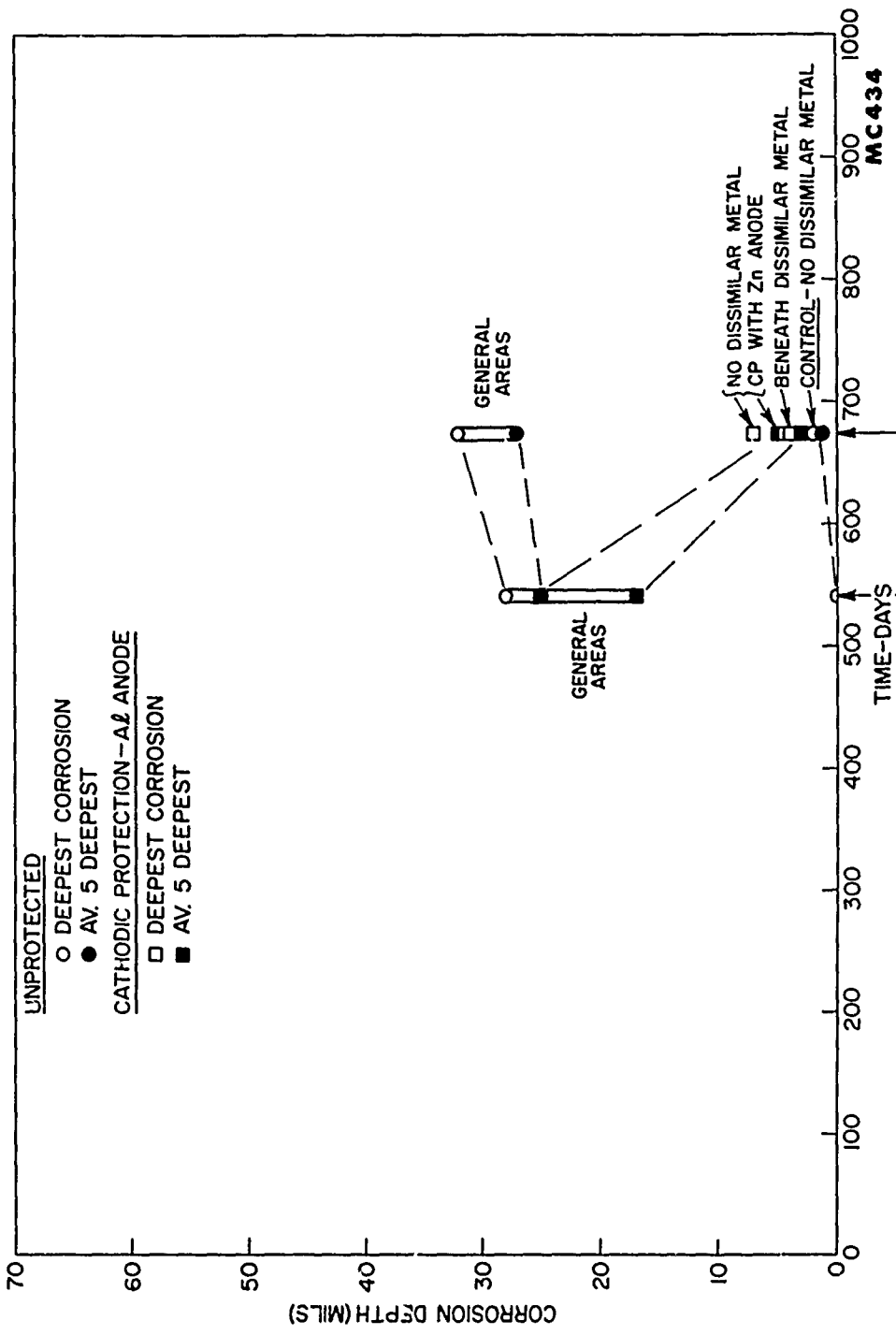


Fig. 45 - 5086-H32 aluminum coupled to mild steel; with and without cathodic protection (CP). Data from Gatun Lake and the Potomac River exposures.

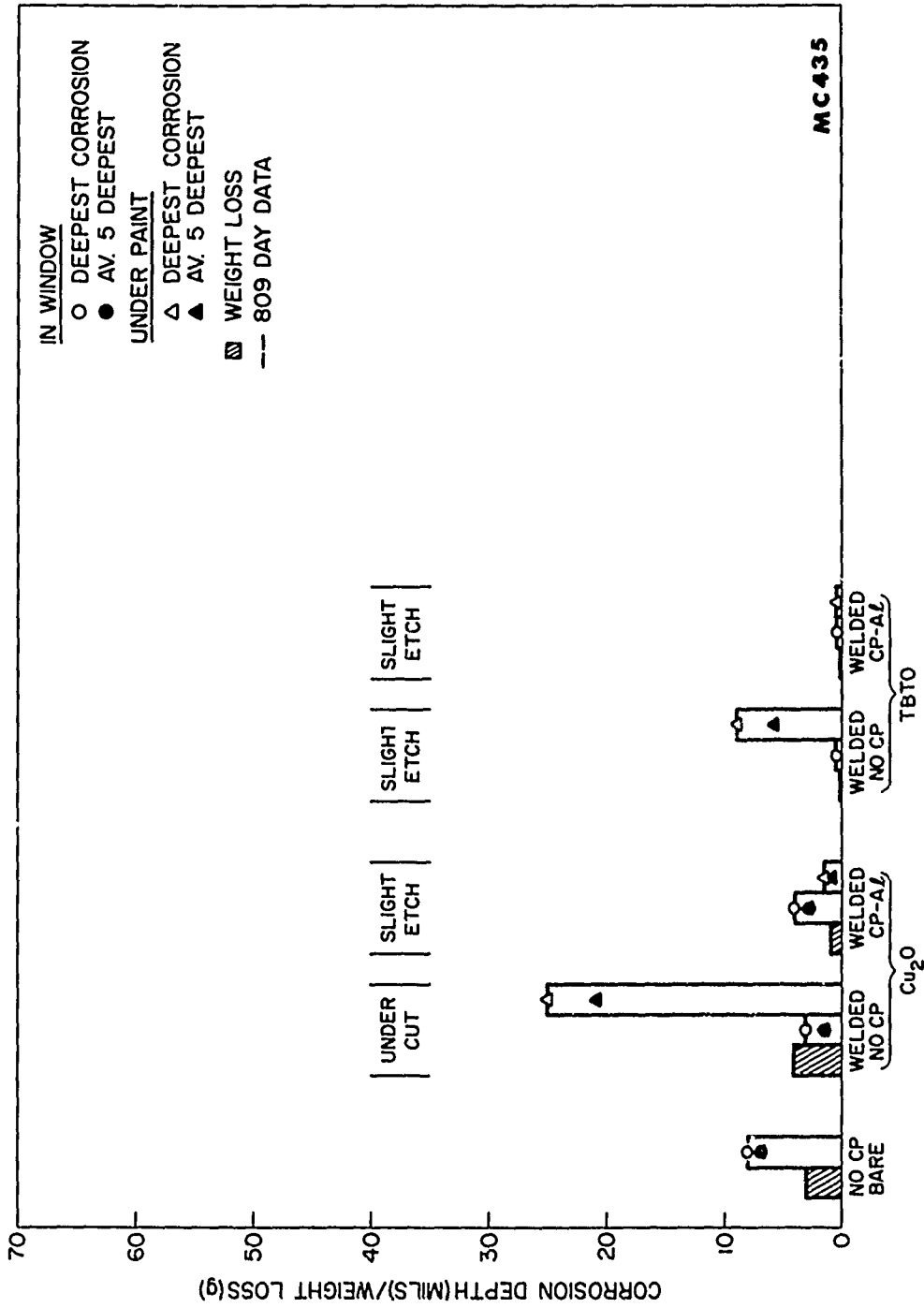


Fig. 46 - Welded 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O or TBTO Antifouling Toxicants; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida.



(a) No CP - Window Area,
magnification 2.2 X

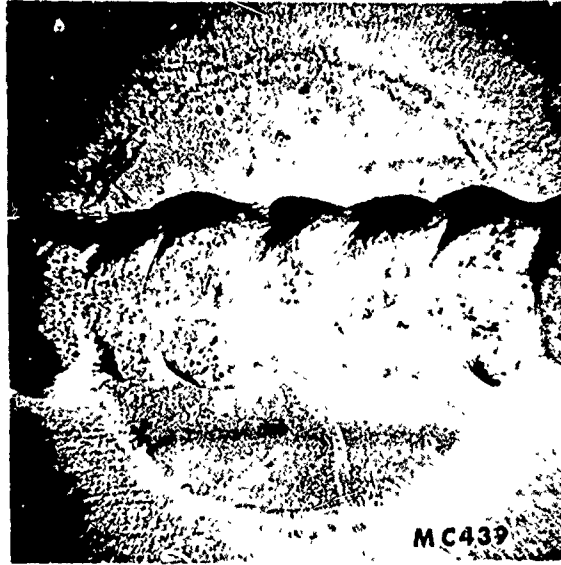


(b) No CP - Flat Area of Specimen,
magnification 2.2 X

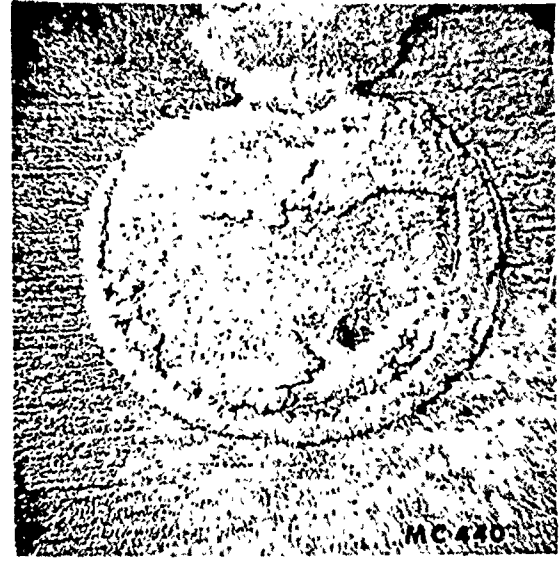


(c) CP Aluminum Anode -
Window Area,
magnification 3.1 X

Fig. 47 - Welded 5086-132 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O Antifouling Toxicant; with and without cathodic protection (CP). 1264 days in seawater at Key West, Florida. Figures reduced 15% in printing.



(a) No CP - Window Area,
magnification 3.1 X



(b) No CP - Near Mounting Hole,
magnification 6.2 X



(c) CP Aluminum Anode -
Window Area,
magnification 3.1 X

Fig. 48 - Welded 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida. Figures reduced 15% in printing.

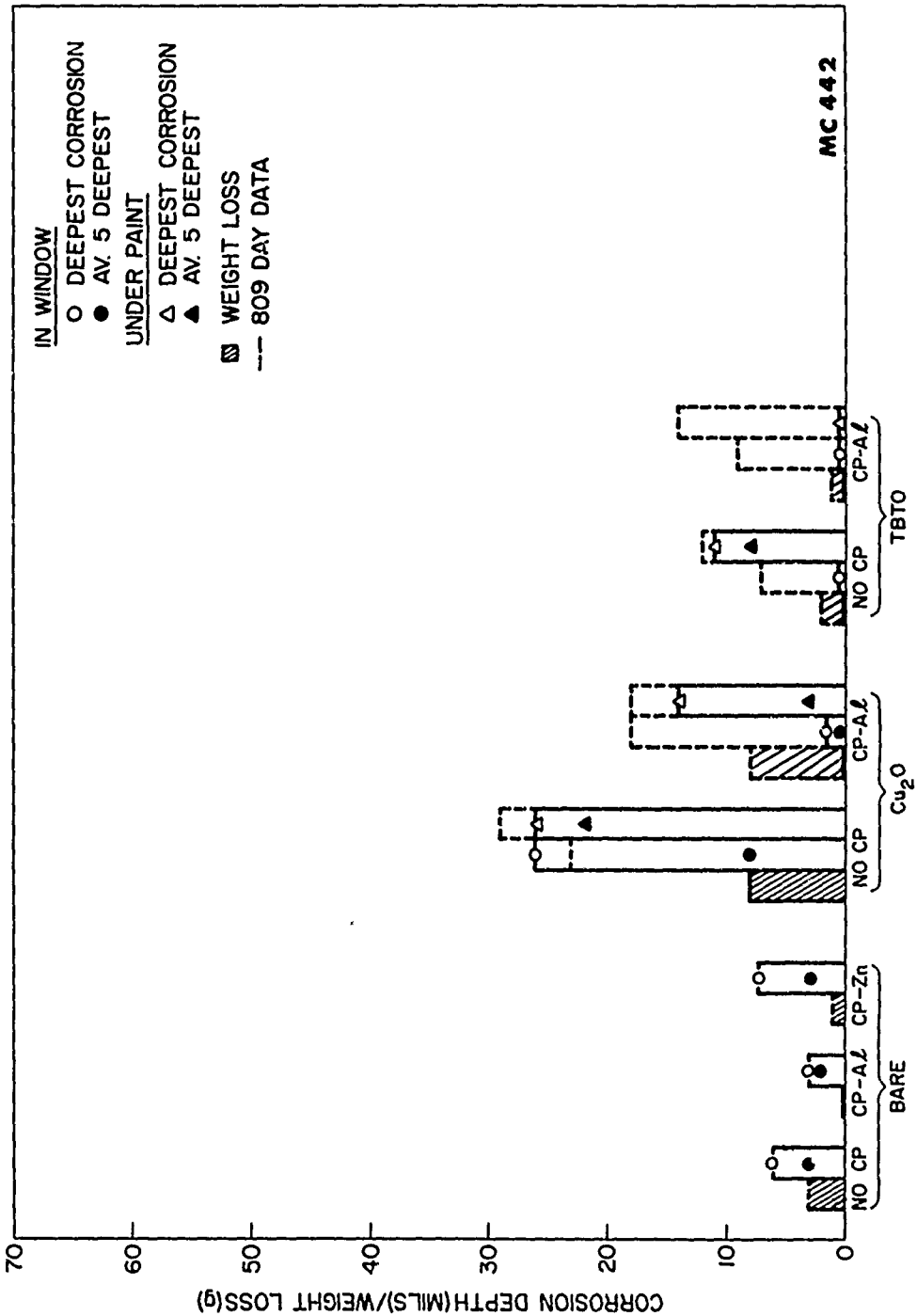
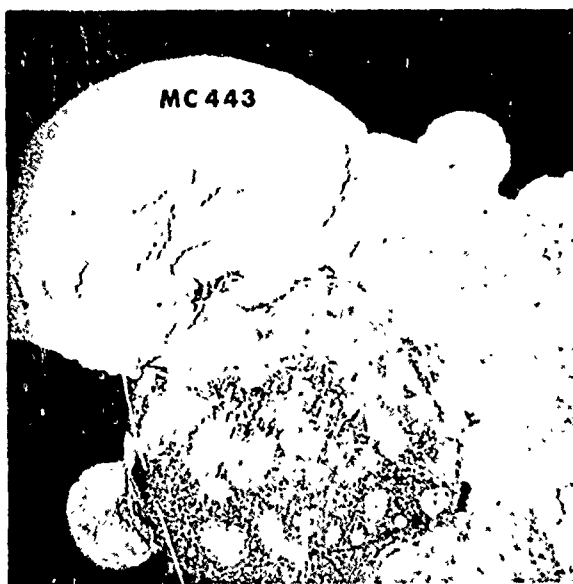
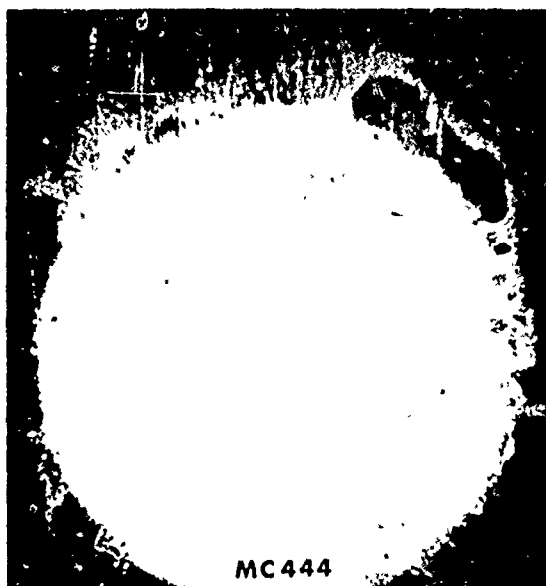


Fig. 49 - 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu₂O or TBTO Antifouling Toxicants; with and without cathodic protection (CP), 1264 in seawater at Key West, Florida.

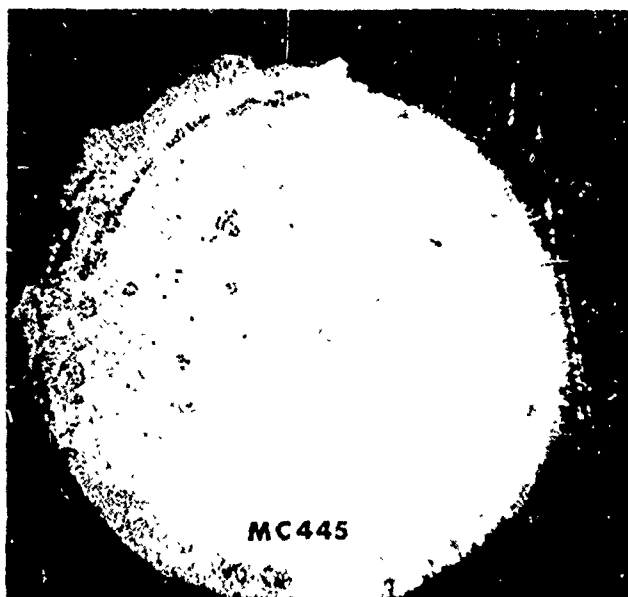


(a) No CP - Window Area,
magnification 2.2 X

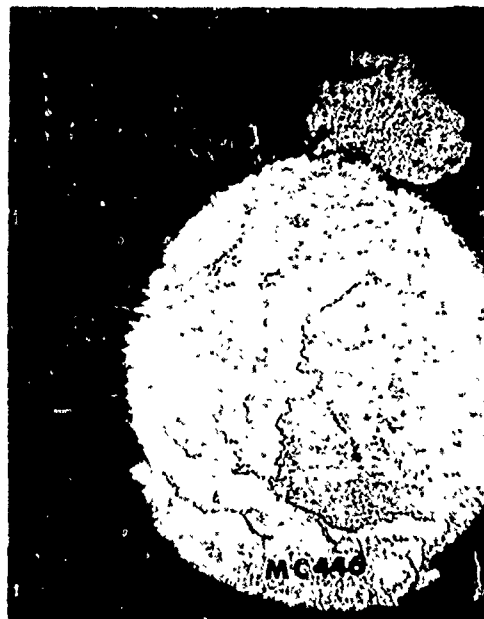


(b) CP Aluminum Anode - Window Area,
magnification 3.1 X

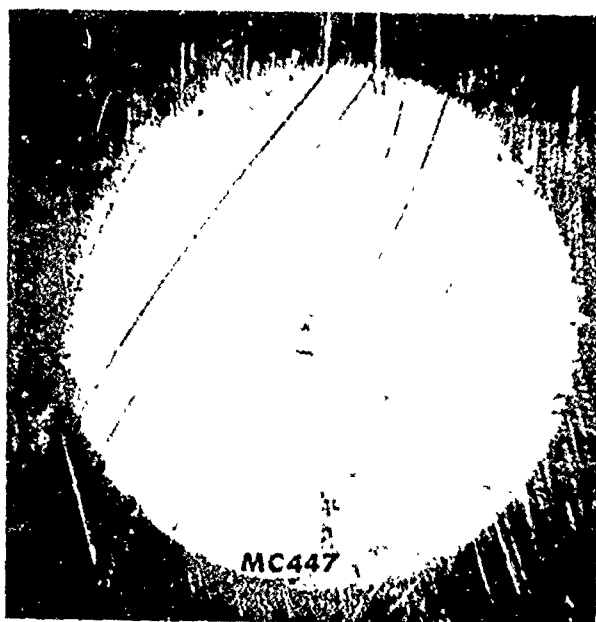
Fig. 50 - 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O Antifouling Toxicant; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida. Figures reduced 10% in printing.



(a) No CP - Window Area,
magnification 3.1 X



(b) No CP - Lower Corner,
magnification 3.1 X



(c) CP Aluminum Anode - Window Area,
magnification 3.1 X

Fig. 51 - 5086-H132 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida. Figures reduced 10% in printing.

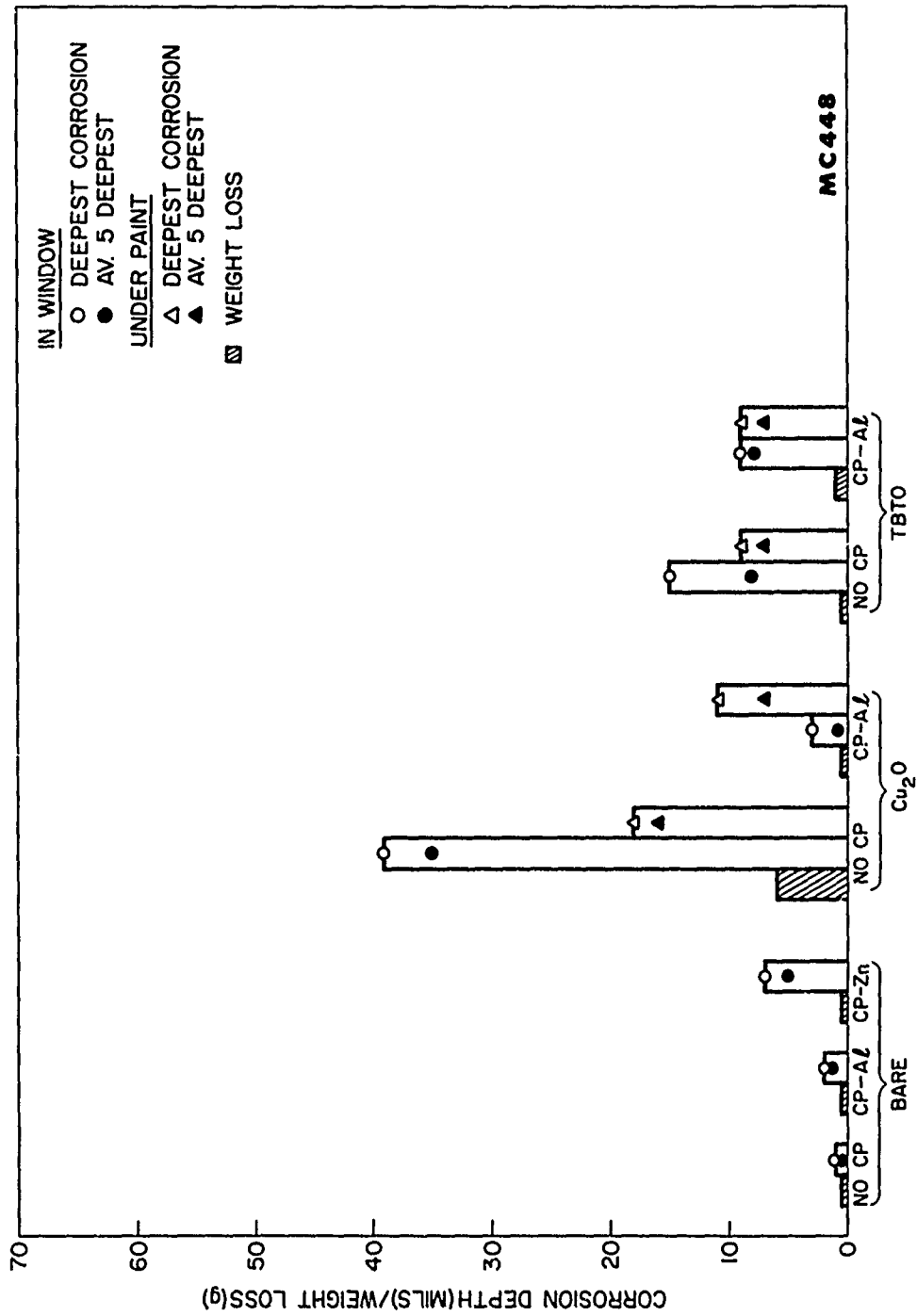
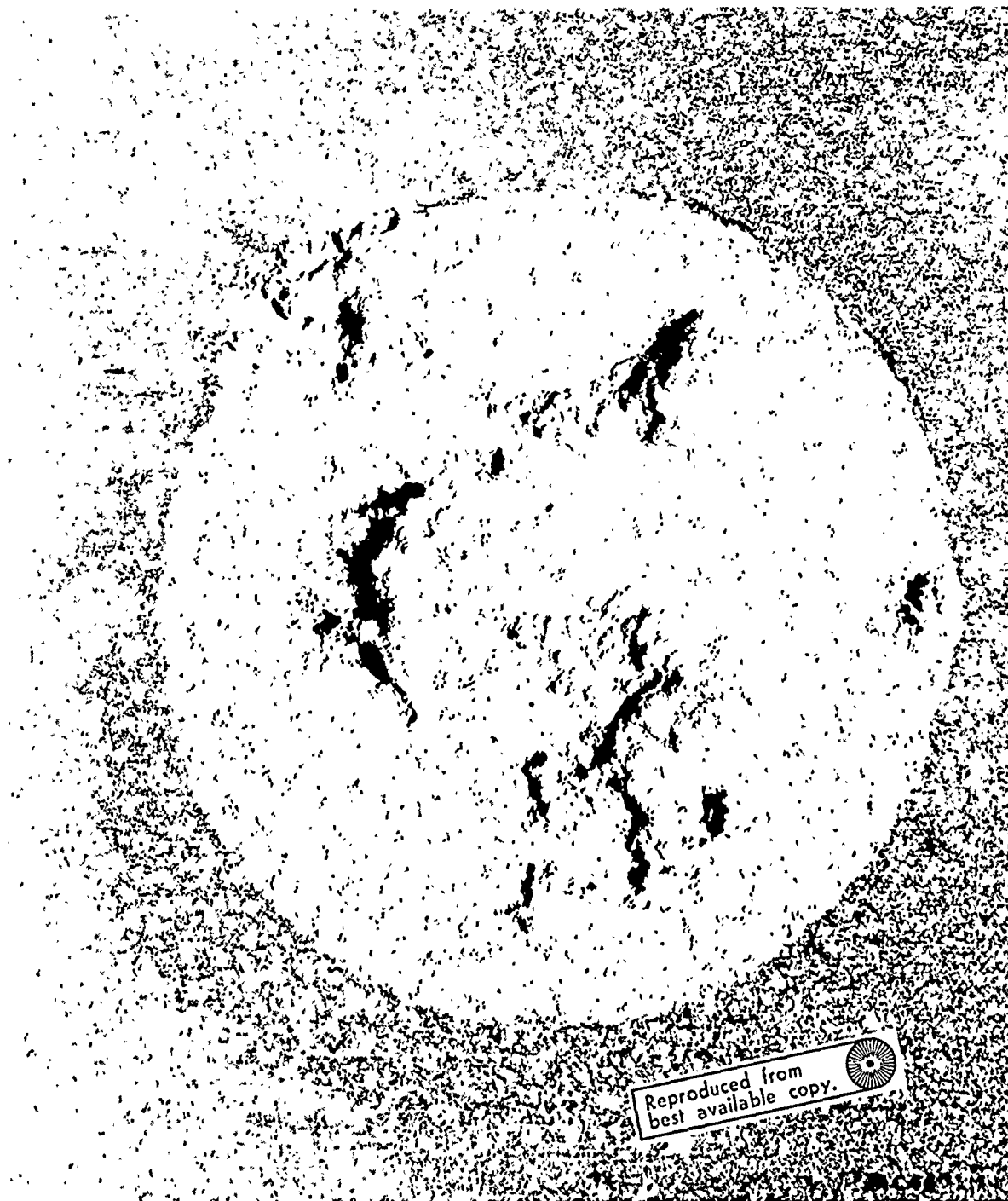


Fig. 52 - 5086-H32 aluminum coated with the Standard Navy Vinyl Anti-corrosive Barrier and Cu₂O or TBTO Antifouling Toxicants; with and without cathodic protection (CP), 675 days in the Potomac River.



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Fig. 53 - 5086-II32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O Antifouling Toxicant; without cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.

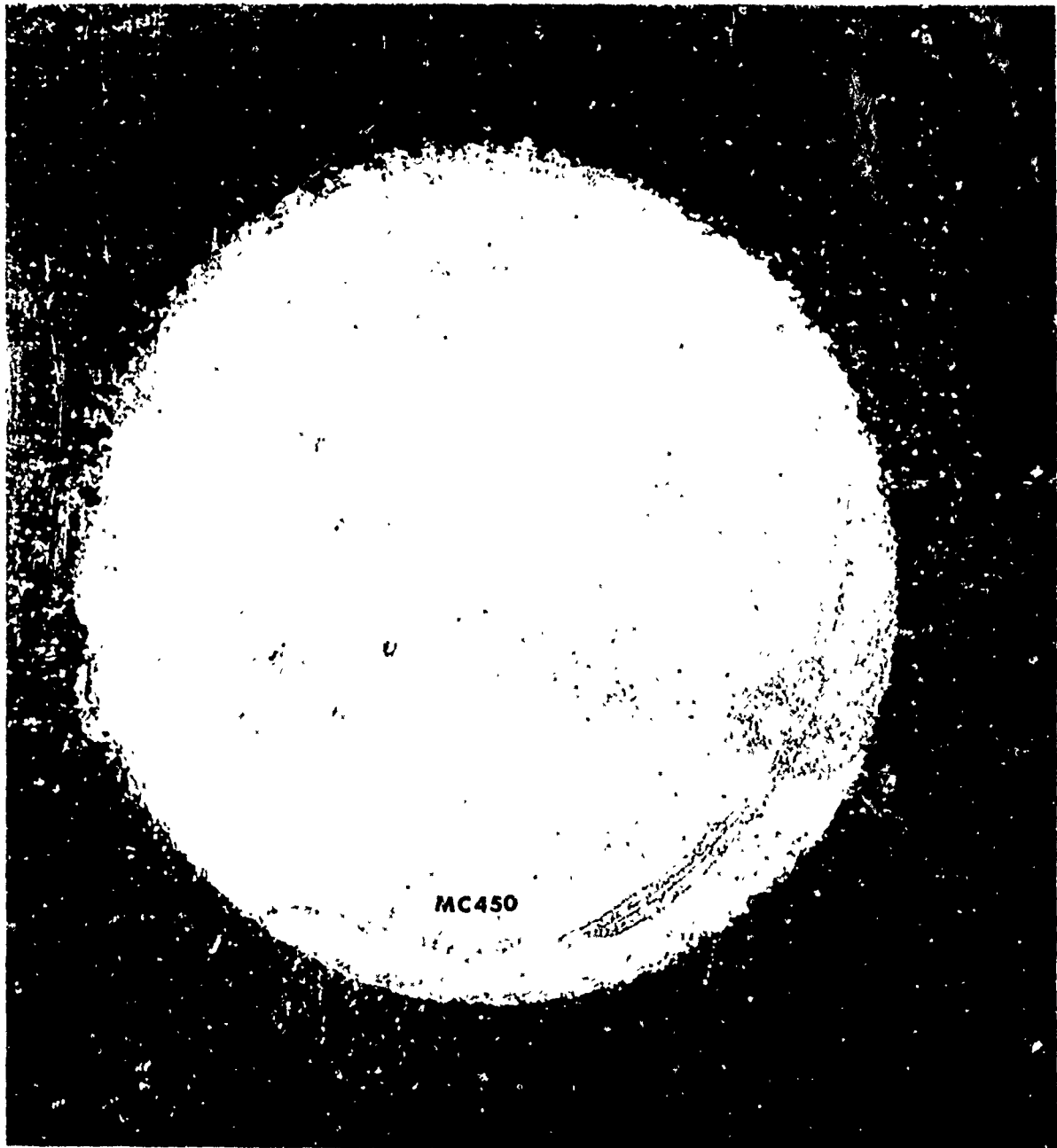


Fig. 54 - 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O Antifouling Toxicant; with cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.

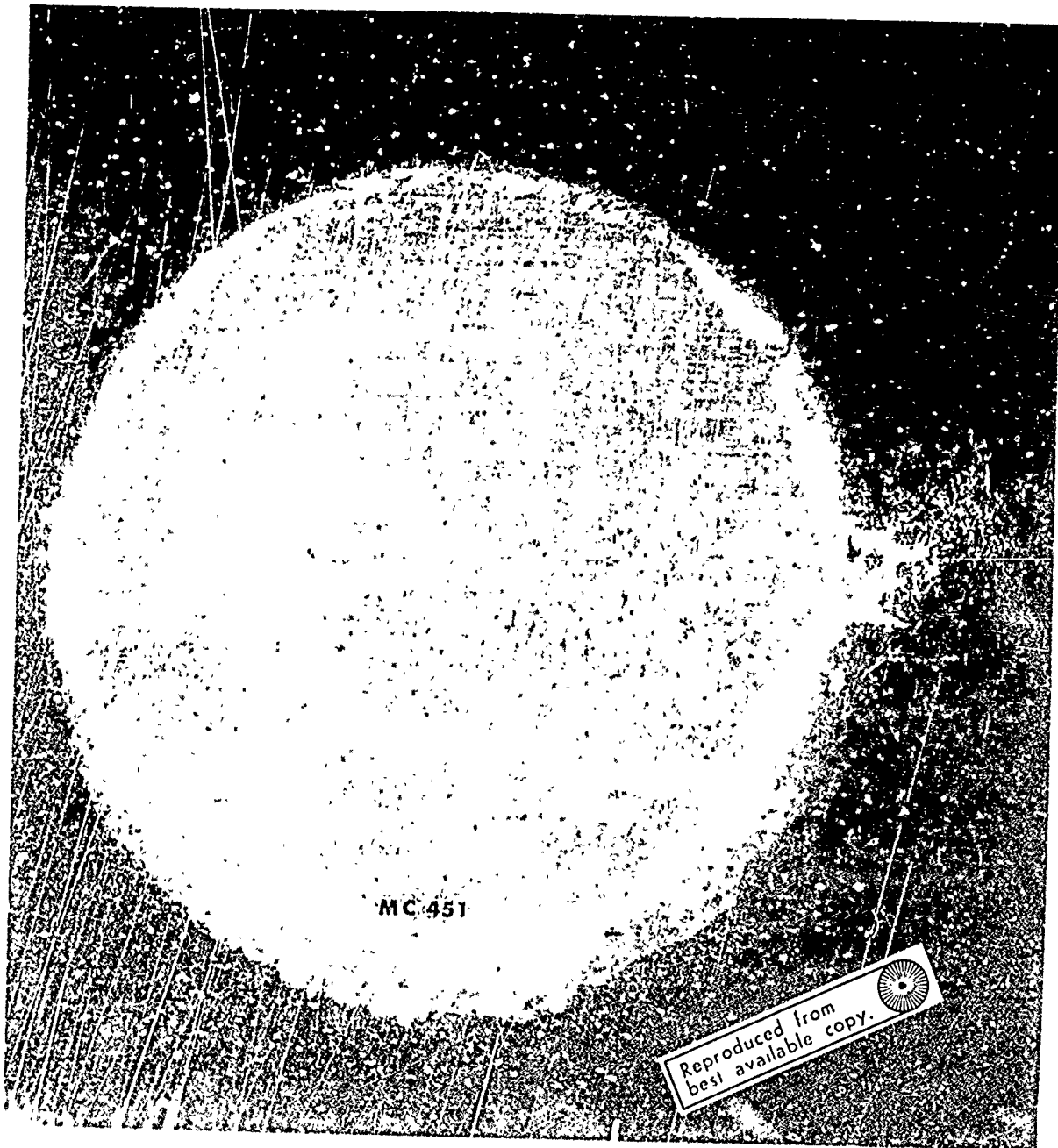


Fig. 55 - 5086-II32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; without cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.

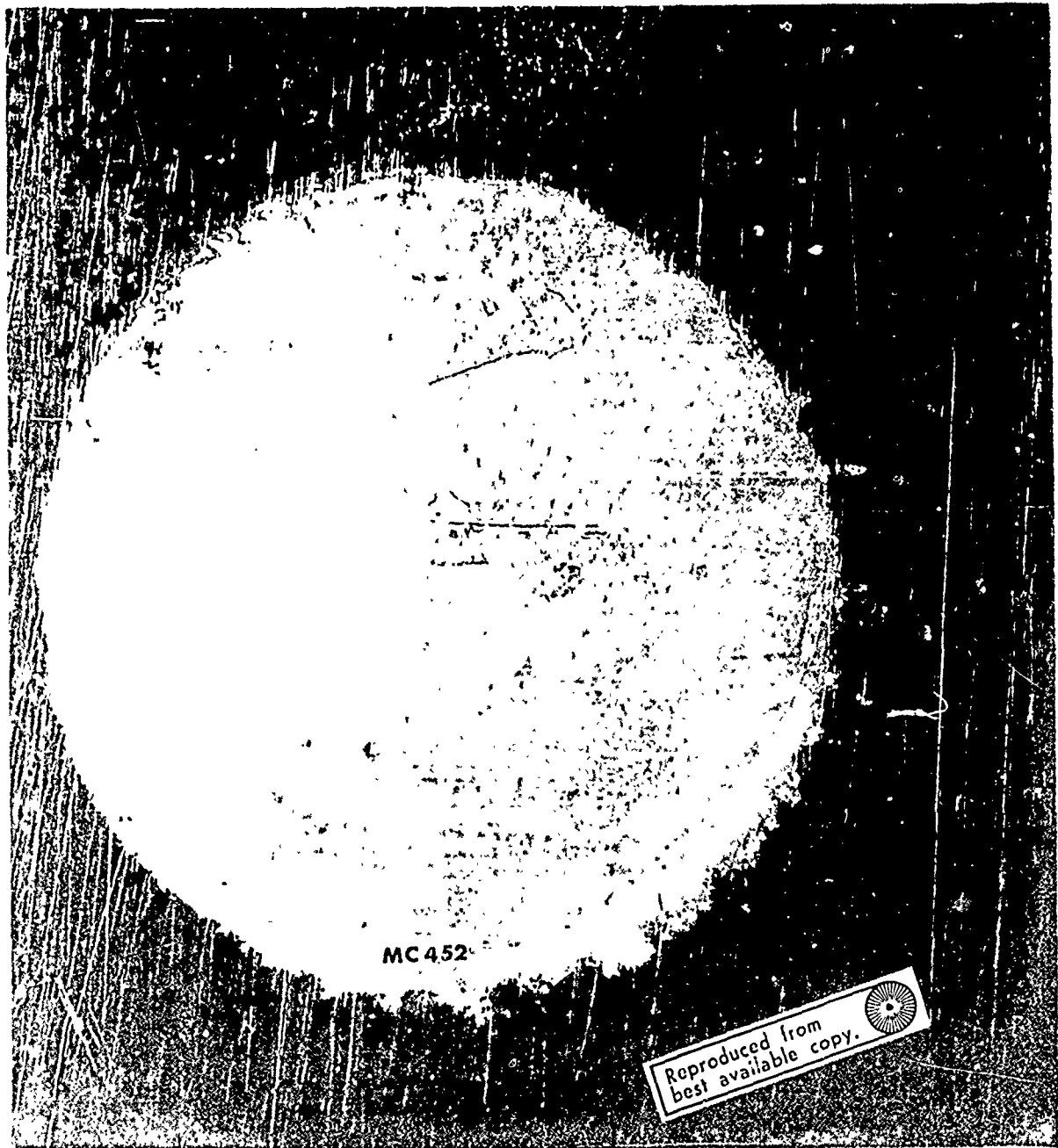


Fig. 56 - 5086-H32 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; with cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15" in printing.

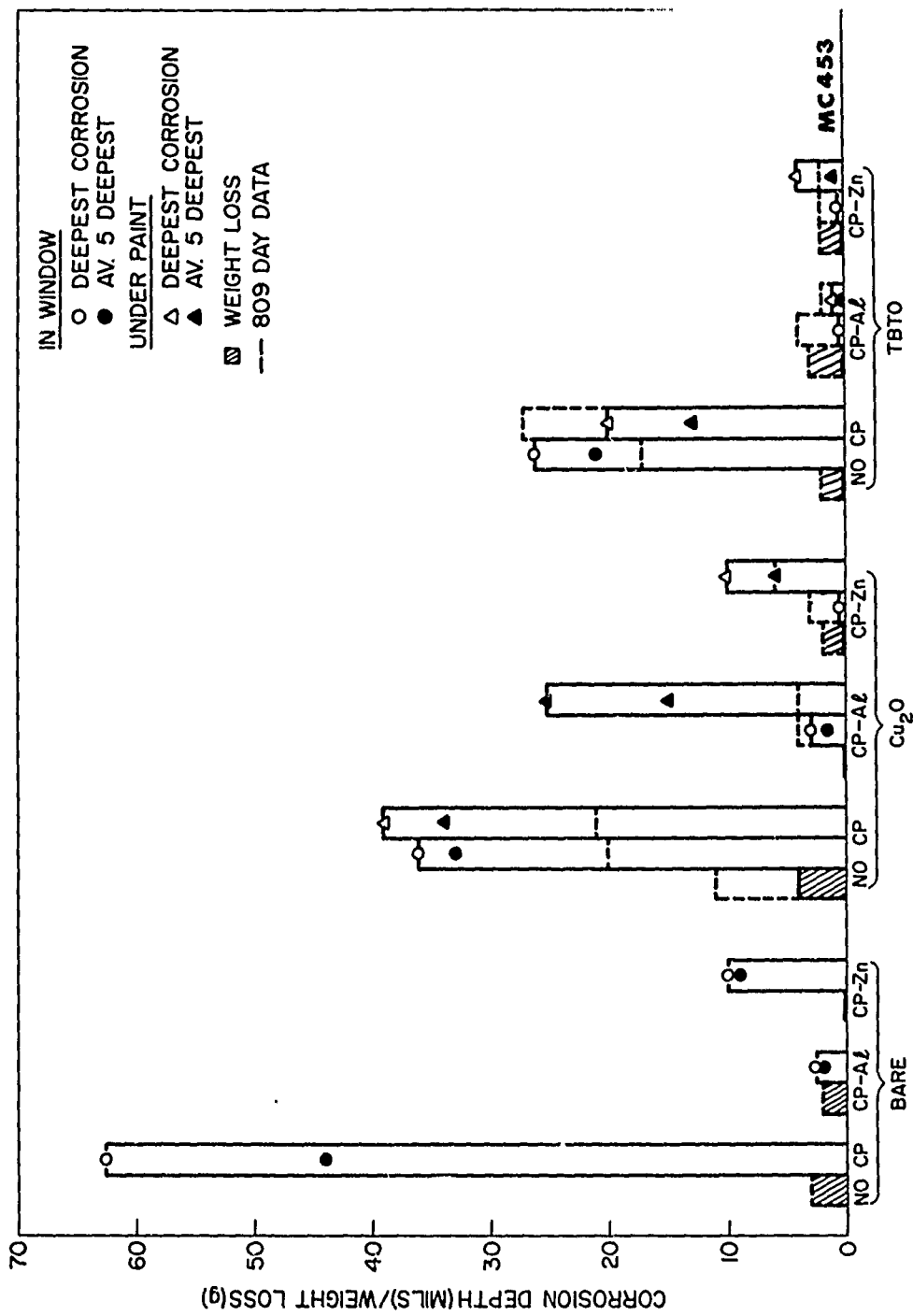
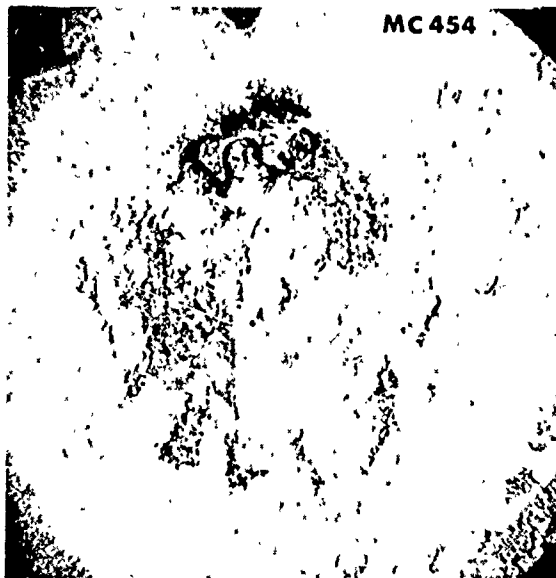


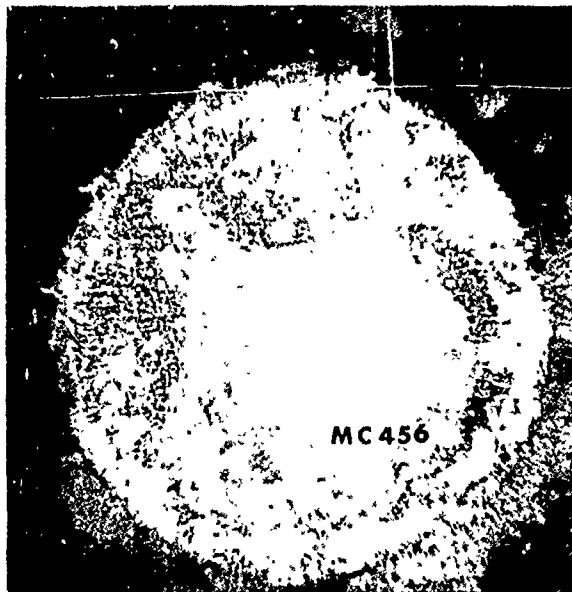
Fig. 57 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu₂O or TBTO Antifouling Toxicants; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida.



(a) No CP - Window Area,
magnification 2.2 X



(b) No CP - Near Mounting Hole,
magnification 2.3 X

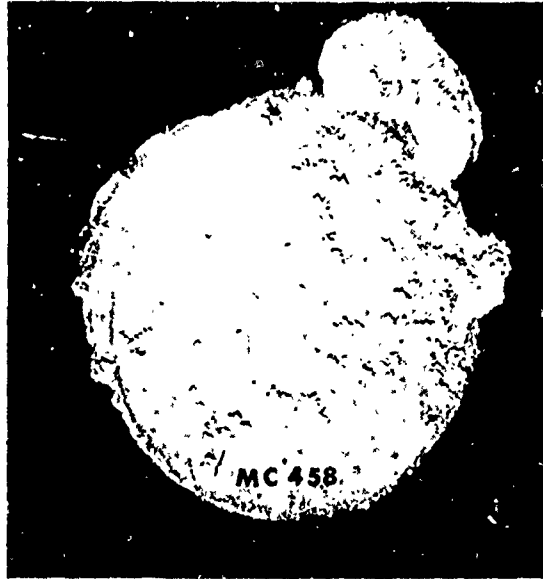


(c) CP Aluminum Anode - Window
Area,
magnification 3.1 X

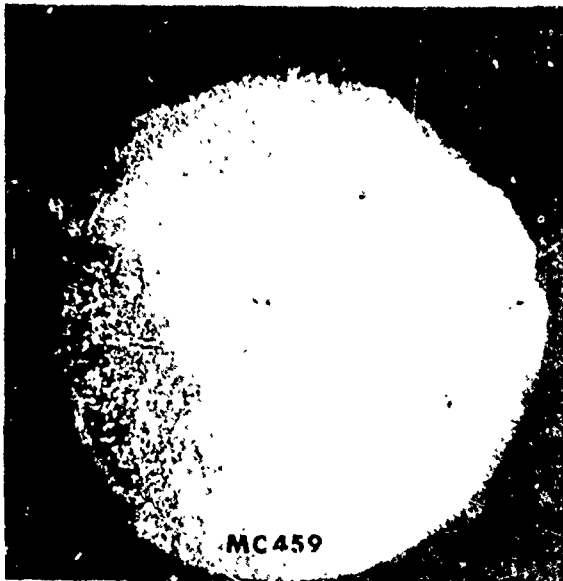


(d) CP Aluminum Anode - Near
Mounting Hole,
magnification 3.1 X

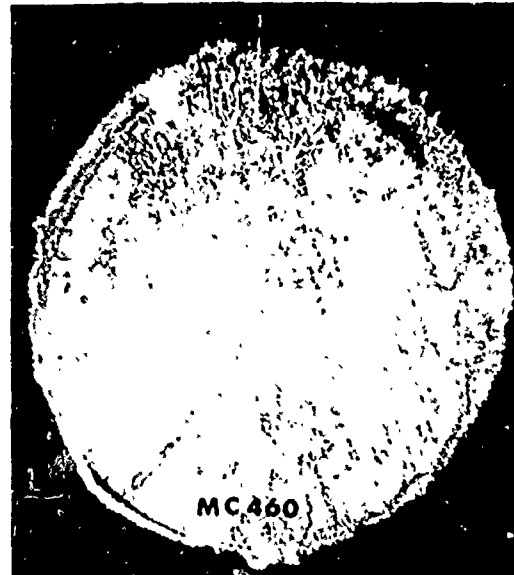
Fig. 58 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu_2O Antifouling Toxicant; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida. Figures reduced 15% in printing.



(a) No CP - Window Area,
magnification 2.5 X



(b) CP Aluminum Anode - Window Area,
magnification 3.1 X



(c) CP Zinc Anode - Window Area,
magnification 3.1 X

Fig. 59 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; with and without cathodic protection (CP), 1264 days in seawater at Key West, Florida. Figures reduced 15% in printing.

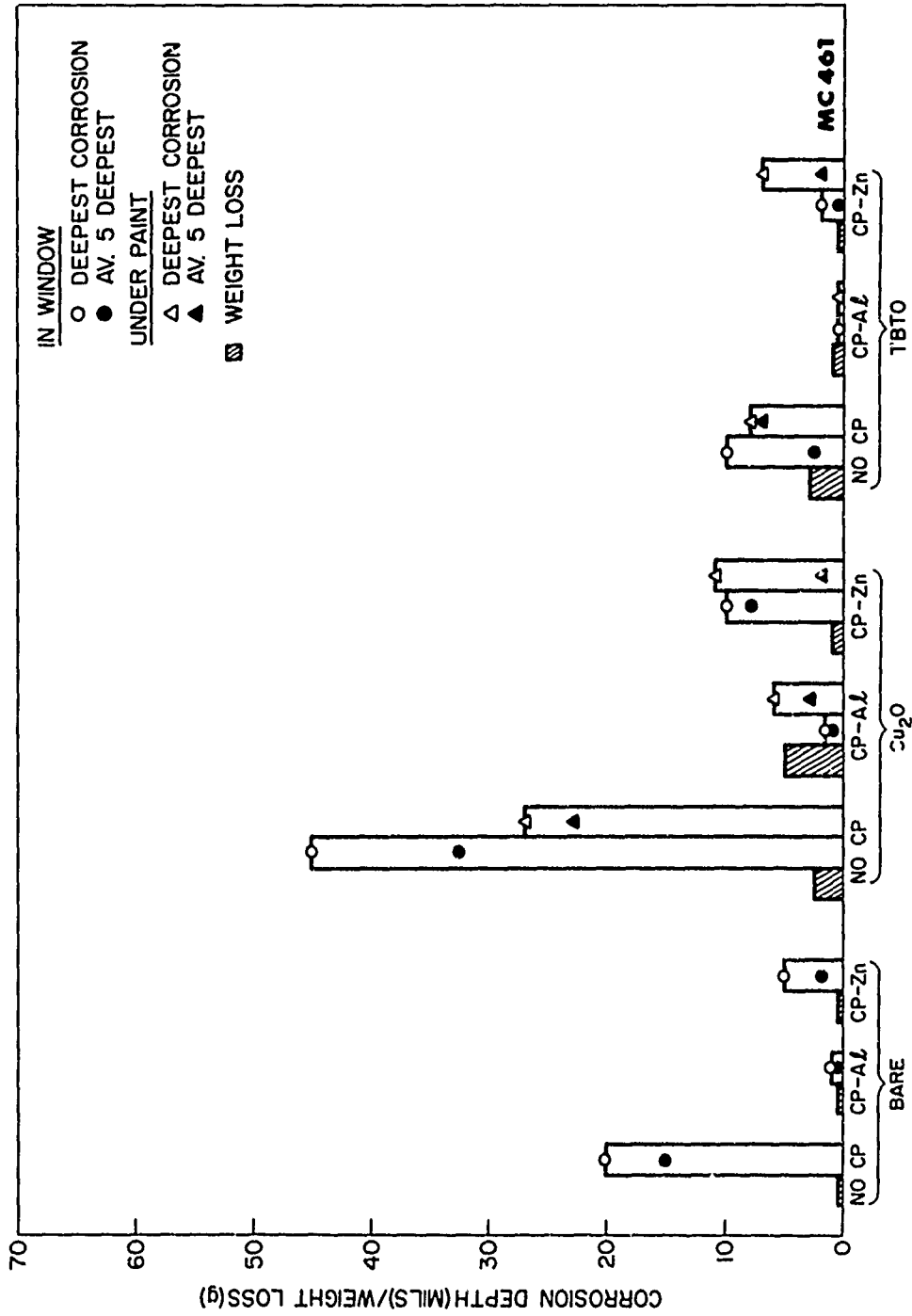


Fig. 60 - 6061T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu₂O or TBTO Antifouling Toxicants; with and without cathodic protection (CP), 675 days in the Potomac River.

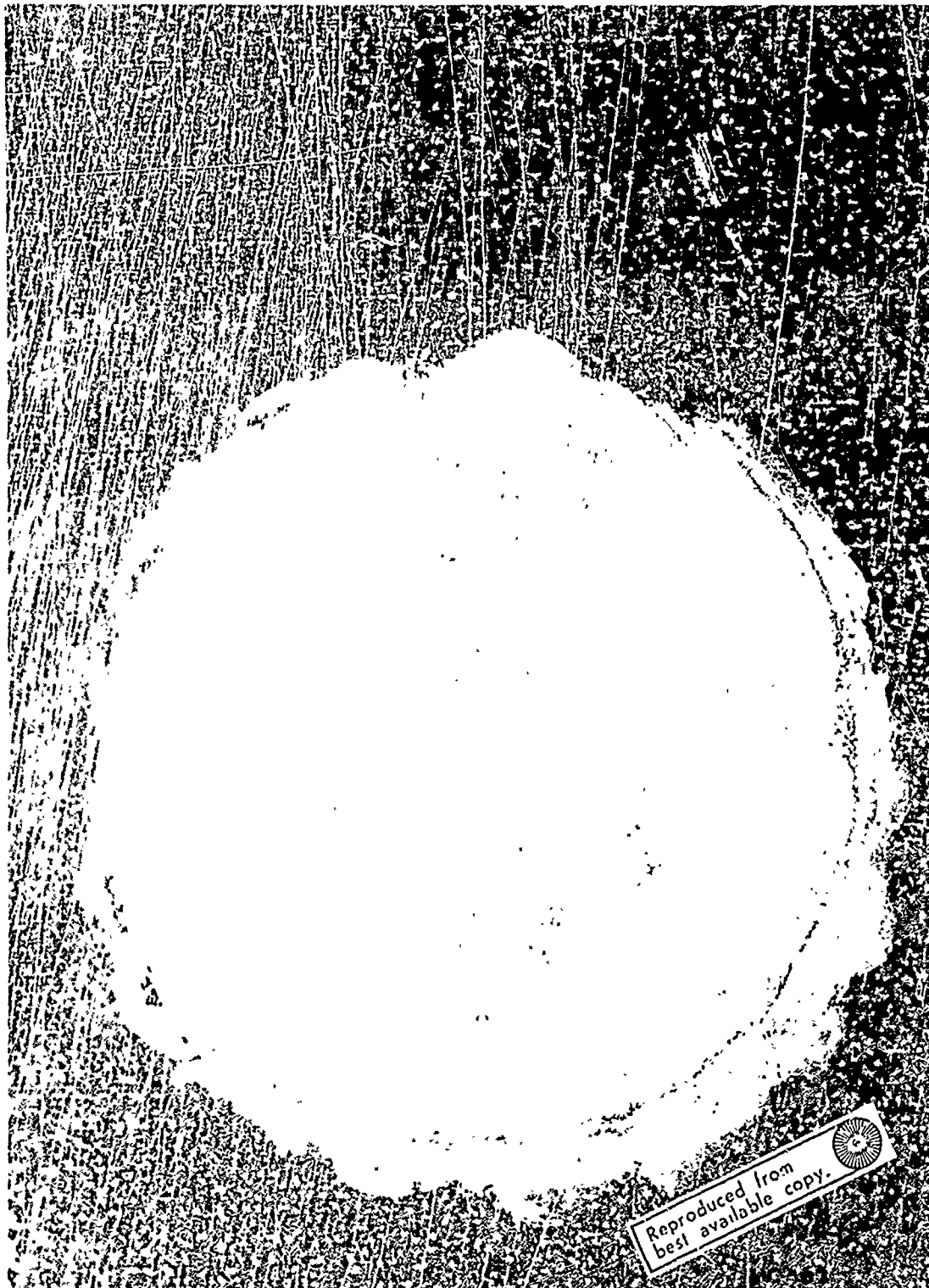


Fig. 62 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and Cu₂O Antifouling Toxicant; with cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.



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Fig. 63 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; without cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.

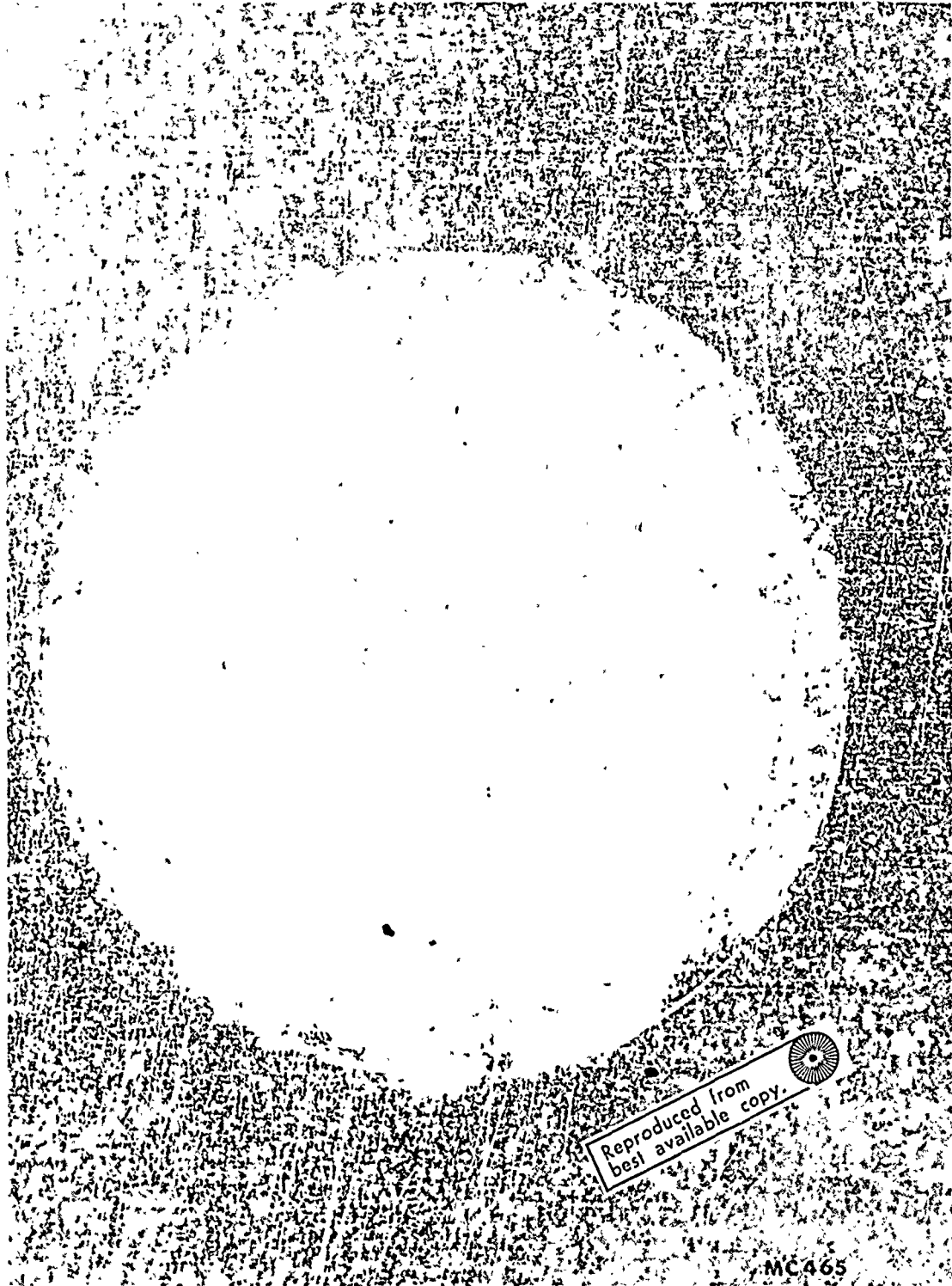


Fig. 64 - 6061-T6 aluminum coated with the Standard Navy Vinyl Anticorrosive Barrier and TBTO Antifouling Toxicant; with cathodic protection, 675 days in the Potomac River. Original magnification 6 X, reduced 15% in printing.