

Interaction of Antifouling Paints and Steel

The chief impetus for the development of anti-fouling paints came from the tendency of copper sheathing to corrode iron or steel hulls through galvanic action. Quite naturally suspicion has existed that copper and mercury paints may also accelerate the corrosion of ships' plates through some similar action. Atherton (2) stated that metallic copper, when introduced into antifouling compositions, sometimes does great injury to ships' plates, although paints of this type answer the purpose very well when used on small wooden yachts.

When metallic copper is in contact with iron or zinc, the solution of the copper and the attendant antifouling action is suppressed by galvanic action. Since the inhibition of antifouling action of copper is complementary to the increased corrosion of the baser metal in a galvanic couple, it is reasonable to expect that any corrosive action of the paint may also be accompanied by a destruction of the antifouling properties of the composition.

The present chapter contains a discussion of the available information on these two aspects of the interaction between antifouling paints and metallic structures. No attempt is made to consider the subject of anticorrosive coatings more generally.¹

ACCELERATED CORROSION DUE TO PAINT

The corrosive effects of copper paints have been investigated by Young, Seagren, Schneider, and Zehner (17). They exposed primed and unprimed steel panels coated with various paints containing either metallic copper or cuprous oxide to the sea for several months. The coatings were previously scribed diagonally. In one experiment in which a paint containing metallic copper was compared with one in which barytes was substituted for the toxic, it was found after eight months' immersion that there was somewhat more severe attack under the former, and this was increased on the unprimed panel.

¹ The material in this chapter was collected at the request of the Advisory Committee on Marine Coatings and Corrosion, and issued in substantially its present form as a report by Section II, N.D.R.C. (12). Acknowledgment is made to Stoner-Mudge, Inc., Multiple Industrial Fellowship in Protective Coatings at Mellon Institute for the preparation for the Committee of a report (9) on Accelerated Corrosion of Steel Coated with Antifouling Paints in which experiments by Drs. G. H. Young and G. W. Seagren are summarized. Other previously unpublished observations have been made available by the Bakelite Corporation, working under contract with Division II, N.D.R.C., and by Dr. F. L. LaQue of the International Nickel Co.

In other experiments, the unprimed panels showed much more severe pitting than the primed panels, but, in general, the distribution and severity of pitting under the paint coating away from the scribe marks appeared to be substantially independent of the toxic concentration and even of its type. The scribe marks were much more heavily pitted than the surfaces protected by paint. The depth of corrosion along the scribe mark was generally much greater in the unprimed than in the primed specimens. In both cases the corrosive action, as indicated by the depth of the scribed marks after four months' exposure, increased roughly in proportion to the concentration of copper in the dry paint film, as the figures in Table 1 show.

TABLE 1. Effect of Presence of Primer, and Type and Concentration of Copper Pigment on Corrosion at Interruptions of Paint Surface

Pigment	Copper in Pigment Weight %	Average Scribe Depth—mils	
		Primed Panels	Unprimed Panels
Cu powder	68	5.2	18.0
	43	3.3	5.2
	14.5	2.1	0.7
Cu paste*	55	4.4	14.5
	38.5	5.3	9.4
	12	2.7	3.6
Cu ₂ O#	38	4.4	7.2
	33.5	1.4	5.2
	22	1.7	4.5

* Proprietary metallic copper pigment—Phelps Dodge Corporation.
Cu₂O and ZnO in equal proportions.

These experiments appear to demonstrate that copper paints accelerate corrosion, at least at localized bare areas of steel. The attack was actually as severe with cuprous oxide paints as with those containing metallic copper, when the per cent of copper in the paints was comparable.

Similar experiments have been conducted by the Woods Hole Oceanographic Institution at Miami Beach, using a series of modifications of the metallic copper paint AF23. One series of panels was painted with coatings in which the percentage of metallic copper was progressively reduced. The other series was coated with paints in which cuprous oxide was substituted for metallic copper so as to give the same quantities of copper as those present in the corresponding members of the first series. The paints were applied to steel

TABLE 2. Effect of Type and Concentration of Copper Pigment on the Corrosion of Steel in Scribe Marks through the Paint Surface

% Cu by Dry Weight	Average Depth of Scribe (mils)	
	Metallic Copper Pigment	Cuprous Oxide Pigment
76.2	35.8	18.0
57.2	27.0	18.0
38.2	20.4	13.8
27.7	16.6	12.4
19.1	20.2	8.6
11.8	6.6	8.6
7.6	12.2	3.8
3.8	5.4	—

panels primed with one coat of PS primer and were each scribed longitudinally before immersion in the sea. The average depths of corrosion in the scribe marks after 112 days' exposure are given in Table 2

The results confirm the conclusion that depth of corrosion is related to the concentration of copper in the film. It is clear, however, that with these paints, metallic copper is more active in accelerating corrosion than is cuprous oxide, particularly with the higher loadings.

Previously, Hudson (5) had reported an experiment which showed that a $\frac{1}{2}$ -inch bare spot in a panel painted with red lead and red oxide corroded to a depth of 80 mils on 15 months' exposure to the sea, a rate greatly in excess of the normal corrosion rate of 5 mils per year. He also described numerous cases of localized corrosion of steel ships which were attributed to accelerated action on areas from which the paint has been accidentally scraped off.

British investigations (8) have also demonstrated increased corrosion of holidays on steel panels coated with a variety of antifouling compositions applied over the usual anticorrosive systems. These experiments showed that the depth of attack varied widely, depending on the character of the

painting scheme. The causes for these differences were not analyzed.

The Mellon Institute investigation (10, 19) confirmed these observations, using a paint system consisting of one coat of Navy standard zinc chromate primer, 52P18, and two coats of S-1471 anticorrosive, a blue lead pigmented oleo-resinous phenolic paint. It was found that the depth of corrosion in a holiday decreases as the area of unpainted surface is increased. After six months' exposure, the results recorded in the first two columns of Part A in Table 3 were obtained. It should be noted that, below a certain size, the inverse relation of area to depth of corrosion does not hold, as shown by the reduced attack in a scribe mark.

When antifouling paints containing metallic copper or cuprous oxide were substituted for the second coat of anticorrosive, results were obtained which depended on the paint formula. A paint containing metallic copper (S-1379B) caused greatly accelerated corrosion of the bare areas of all sizes. The smaller holidays were completely penetrated. The cuprous oxide paint (ER-169) caused somewhat less corrosion, yet definitely more than did the nontoxic surface. The Navy cold plastic, on the other hand, gave no evidence of corrosive action greater than that due to the nontoxic surface. (See Table 3, Part A.)

When deliberate contact was made between the metal and the antifouling coating which might establish a galvanic couple between the paint and the steel, it was found that the corrosive effect was increased with the coating containing metallic copper but not with those containing cuprous oxide. (Compare Parts A and B, Table 3.)

In another experiment, the effect of the size of the holiday on the depth of corrosion occasioned by a paint system topped with the metallic copper

TABLE 3. Depth of Corrosion of Bare Metal Areas after 6 Months' Immersion at Daytona Beach. Steel Panels 3/32-Inch Thick Coated with One Coat 52(P)18 Primer, One Coat S-1471 Anticorrosive and Topped with the Coating Indicated.

	Top Coating Toxic	Paint System			
		S-1471 None	S-1379B Metallic Cu	ER-169 Cu ₂ O	Navy 143E Cu ₂ O
	Size of Holiday Inches	Average Depth of Corrosion in Mils			
Part A	0.25×0.25	28-22	P 0.5×0.5	P 0.25×0.25	20-0
	0.85×0.85	10-11	28-26	14-5	5-4
	1.90×1.90	4-4	9-8	10-3	7-3
	Scribe Mark	6-2	14-12	9-8	5-3
Part B	0.25×0.25	—	P 0.5×0.5	P 0.13×0.13	11-6
	0.85×0.85	—	P 1.0×1.0	16-9	13-5
	1.90×1.90	—	19-13	8-5	4-4
	Scribe Mark	—	24-20	7-7	4-4

Part A: No deliberate contact between antifouling coat and steel.

Part B: Deliberate contact between antifouling coat and steel.

P indicates panel penetrated by corrosion. The following numbers indicate dimension of the hole in inches.

antifouling composition S-1379 was studied more extensively (10, 19). In one series of tests, a single holiday of varying size was left on each panel. In another test, holidays of the various sizes were all included on a single panel. The resulting corrosive attack is recorded in Table 4.

When the holidays were on separate panels, the depth of attack varied inversely with the size of the exposed area down to areas as little as 1/16-inch wide. A very narrow area (1/64-inch), like a scribe mark, was less deeply corroded. When the holidays were all on the same panel, the relation between depth of corrosion and area is no longer apparent, and all areas appear to corrode more or less equally.

Similar experiments have been conducted at Miami Beach, using standard or experimental Navy paints containing metallic copper or cuprous

TABLE 4. Average Depth of Corrosion on Bare Areas of Steel Panels Coated with 2 Coats Navy 52 P18, 1 Coat Stoner-Mudge ER-173, and 1 Coat S-1379 Copper Metal Antifouling Paint. Area of Panel: 6×12 inches

Dimensions of Holidays		Average Depth of Attack (Mils)	
Dimensions inches	Area square inches	Holidays on Separate Panels	Holidays on Same Panel*
1/8 × 8	4	4.5	7
1/16 × 8	3	7	6
1/32 × 8	2	5	4
1/64 × 8	1	6.5	3
1/16 × 1/2	1/16	9	4
1/32 × 1/2	1/32	13	5
1/64 × 1	1/64	13	4
1/64 × 8	1/8	2	—

* Total area of all holidays 10 3/16 square inches.

oxide as pigment. The paints were applied over a single coat of P8 primer to steel panels 8 by 10 inches in area. Holidays about 7 inches long and of different widths were left in the center of each panel. The results obtained after 112 days' exposure at Miami are shown in Table 5.

With all four paints the depth of corrosion decreases as the area of the holiday increases, except that in holidays of 1/16-inch width or less, corrosion is stifled presumably by its own products, as described by the Mellon Institute investigators.

The results again demonstrate the greater corrosive effect of metallic copper. The cuprous oxide paints, regardless of the type of matrix, all produce much less corrosion in a holiday of the same size. There is no clear evidence that the amount of corrosion produced by these cuprous oxide paints is related to the percentage of copper in the coatings. This may be because of differences in the matrices of the several paints.

TABLE 5. Effect of Dimensions of Holiday on Corrosion

Paint Pigment % Cu (dry wt.)	AF23	AF14	143E	16X
	Cu	Cu ₂ O	Cu ₂ O	Cu ₂ O
	76.2	74.7*	36.3*	46.3*
	Average Depth of Corrosion (Mils)			
Width of Holiday				
Knife scribe	36.0	8.8	16.8	5.0
1/16 inch	30.2	—	19.8	7.6
1/8 inch	40.4	14.6	6.4	13.4
1/4 inch	33.6	—	6.8	11.0
1/2 inch	17.6	7.8	6.8	8.8
1 inch	11.6	4.6	3.8	6.6

* Computed as copper, not as Cu₂O.

THE MECHANISM OF CORROSIVE ACTION OF PAINT

It is important to understand the mechanism responsible for the corrosive effects of copper paints if measures are to be taken to eliminate them. The corrosion of a bare area through the influence of neighboring painted surfaces involves some sort of "action at a distance." Two hypotheses present themselves.

One hypothesis assumes that copper ions, dissolving from the paint, diffuse across the surface and are deposited as metallic copper by electrochemical displacement on the exposed steel of the holidays (18). Localized galvanic cells are set up between the metallic copper deposited on the holiday and the steel, and this results in corrosion of the latter. This view is plausible because of the demonstrated fact that copper diffuses from active paint surfaces in sufficient concentration to inhibit fouling over a distance of one-half centimeter or more (see Chapter 14). On the other hand, it is difficult to see why the presence of a priming coat should interfere with an action of this sort. It is also difficult to understand the area relations which are so clearly demonstrated.²

The alternative hypothesis would assume some sort of electrochemical interaction between paint and bare steel. This view would be quite adequate in the case of metallic copper paints if it could be shown that the metallic copper particles actually contacted one another and the steel, so as to develop a bimetallic couple. It would have the advantage of explaining adequately the area relations, for it is known that in a copper/iron couple the galvanic activity is limited by the area of the cathode (13). This would be represented by the

² Young and Seagren (18) have advanced in support of this hypothesis the observation that steel coupons attached to wood panels painted with metallic copper and cuprous oxide paints, but carefully insulated from the paint surface, corrode at a rate approximately five times that considered normal to steel in sea water. This observation is at variance with the results recorded in Table 6 in which galvanized iron strips attached to cuprous oxide paints and certain metallic paints corroded no faster than control strips attached to bare wood. Quite aside from theoretical considerations, the degree to which bare or galvanized iron structures are endangered by the proximity of copper paint surfaces is an important one which deserves further examination.

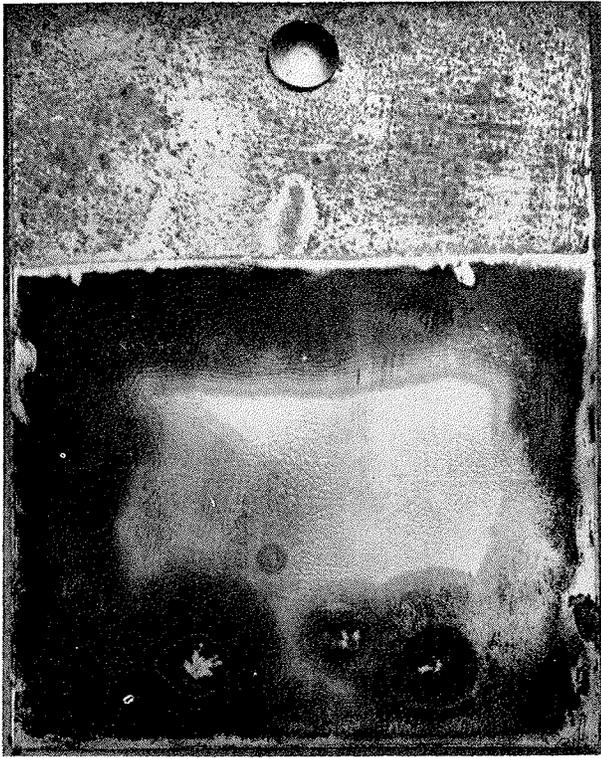


FIGURE 1. Coppery deposit formed under a commercial yacht paint applied directly to zinc. The paint has been removed with organic solvent. Exposure 4 weeks, upper third of panel unpainted.

area of the panel and would be essentially the same, regardless of the area of a small holiday. Consequently, the current density would be inversely proportioned to the area of the bare spot, and corrosion would be deeper in the smaller holidays. On the same grounds, equal corrosion of areas of different size, when these are on the same panel, is to be understood, since these all are subject to attack by the same current density, being a part of the same galvanic system. The protective effects of priming coatings, and the increased corrosion observed when the metallic copper composition was in contact with the steel, are also understandable, since these factors would influence the resistance of the galvanic circuit.

Young, Seagren, and Zehner (19) appear to doubt the possibility that the usual metallic copper paint surfaces can form gross galvanic couples with the steel, because of resistance measurements which they have made which they consider to preclude sufficient current flow. Alexander and Benemelis (1) have also measured the resistance of films of highly pigmented metallic copper paints, and have confirmed the conclusion that even such films do not possess sufficiently low resistances to perform as a cathode where coupled

to steel. A more compelling difficulty is the impossibility of explaining the corrosive action of cuprous oxide on these grounds.

Young and Seagren have presented a theory which, by combining features of the two hypotheses discussed above, appears to account for most of the observations. They propose that the copper pigment dissolves within the paint film and, on coming in contact with the underlying metal, is deposited on it as metallic copper by galvanic displacement. In this way, a bimetallic cell is formed in which the uncoated area is the anode, and it corrodes in consequence. The corrosion which takes place under the surface of uninterrupted coatings or when ineffective priming systems are employed, could result from inequalities in the copper deposit, which would cause localized galvanic reactions, pitting, and blistering.

Young, Seagren, and Zehner (19) have shown that a thin "flash" of copper deposited on the steel prior to painting will accelerate the corrosion in holidays in the same way that copper paints do. In order to test whether copper is actually deposited under paint, as required by the hypotheses, the following experiment was made at Woods Hole. Unprimed steel and zinc panels were painted with cuprous oxide paints, leaving an unpainted area on the panel to accentuate galvanic action. When, after a week or more of exposure in the sea, the paint was removed with organic solvent, a granular coppery deposit was found on the surface which had been painted. In the case of the steel panels the deposit was light, and the possibility that the deposit consisted of a residue of the paint film was not precluded. In the case of the zinc, the deposit was much heavier and had every appearance of metallic copper.

Figure 1 shows the deposit formed under the paint coating of a zinc panel. The deposit is heaviest near the margin of the unpainted area and near the edges of the panel where presumably the paint film was broken.

Young and Seagren's theory does not, by any means, exclude the possibility that metallic copper compositions may also accelerate corrosion by direct galvanic coupling. They have demonstrated that a steel coupon directly contacting a metallic copper coating, applied to wood, corrodes more rapidly than a similar coupon carefully insulated from the paint surface (18). A number of experiments performed at the Woods Hole Oceanographic Institution's testing station at Miami show very clearly that metallic copper paint films may cause severe corrosion of iron under condi-

tions which have every resemblance to bimetallic galvanic coupling.

When iron (or galvanized iron) strips are attached to wood surfaces painted with metallic copper paints, very severe corrosion of the strip may follow immersion in the sea.³ The result of one experiment is recorded in Table 6. Similar results have been noted with some commercial bronze yacht paints and with the Navy formula AF23. It should be noted that some commercial paints reputed to contain metallic copper have failed to produce accelerated corrosion. Paints containing cuprous oxide did not increase the corrosion of galvanized iron in this experiment.

The rate of corrosion has been found to depend upon the concentration of metallic copper in the paint film, as shown by the experiment summarized in Table 7. It is interesting to note that the corrosive action parallels the leaching rate of

TABLE 6. Weight Loss of Galvanized Iron Strips Attached to Painted Wood Panels during Immersion at Miami Beach

Paint	Toxic	Weight Loss (grams)	
		0-30 days	30-60 days
PT 10	Cu Metal	7.3	3.5
AF 12	Cu Metal	9.7	7.0
Commercial Paint "A"	Cu Metal	0.1	0.1
Commercial Paint "B"	Cu, Cu ₂ O etc.	0.1	0.1
AF 22	Cu ₂ O	0.1	0.1
143	Cu ₂ O	0.1	0.1
Bare wood	None	0.1	0.1

TABLE 7. Weight Loss of Steel Coupons (area 3 square inches) Coupled to Dilutions of AF12, a Metallic Copper Paint, after One Month's Immersion at Miami

Paint	% Copper	Weight Loss grams	Leaching Rate* $\mu\text{g./cm.}^2\text{/day}$
12	90	14.6	19
121	67	16.5	19
122	45	23.4	21
123	31.5	16.0	21
124	22.5	11.0	15
125	13.5	2.4	4.8
126	9.0	2.1	1.9
127	4.5	2.0	0.7

* Leaching rate of uncoupled paint surface.

the uncoupled panel closely, and that both drop abruptly when the per cent of copper falls below about 22 per cent. It is thought that at about this concentration the metallic particles are no longer effectively in continuous contact, and thus their participation in the bimetallic couple, as well as the rate of dissolution of the paint surface, is hindered.

The rate of corrosion is also influenced by the area of the paint surface with which the metal is in contact, as would be expected if the system acts

³ The experimental set up is shown in Figure 3, which illustrates also the attendant fouling phenomena.

TABLE 8. Weight Loss of Steel Coupons $3\frac{3}{8} \times 1 \times \frac{1}{8}$ Inch in Size Attached to Surfaces of Varying Length Painted with AF23. Exposure 92 Days

Length of Painted Surface, Inches	Weight Loss of Steel Coupon, Grams
1	1.05
2	1.09
4	1.38
8	1.21
16	2.05
32	1.92
64	1.37

Control on unpainted wood lost 0.35-0.64 gram.
Control on copper sheet 5 inches long lost 2.74 grams.

like a copper/iron galvanic couple. In an experiment in which steel coupons were fastened across the middle of wood surfaces painted with AF23 and exposed to flowing sea water, the weight loss of the steel due to corrosion increased with the length of the painted surface, as shown in Table 8. The influence of the painted surface evidently decreased with its distance from the steel, since corrosion was not increased by painted areas greater than 16 inches long—i.e., by paint more than 8 inches from the metal.

Metallic copper paint appears to lose its tendency to attack iron rapidly after exposure to the sea. If the paint is soaked for some time prior to the attachment of the iron, it is found that the rate of attack is diminished and may be negligible after a period of two months. In an experiment to test this point, made by C. M. Weiss, the results shown in Table 9 were obtained, using the standard Navy AF23 metallic copper paint.

This phenomenon may be due to an increased resistance of the paint film on soaking such as that observed in some of the experiments of Young, Seagren and Zehner (19). Dr. Young suggests that it may result from the breaking of the contacts between pigment particles by the swelling and gelatinization of the vehicle, or to the conversion of their metallic surfaces to a nonmetallic condition as they corrode (personal communication).

These experiments appear to indicate that the corrosive action of metallic copper paints is due

TABLE 9. Effect of Soaking a Metallic Copper Paint on the Corrosion of Galvanized Iron Subsequently Attached

Days of Soaking Prior to Attachment of Iron Strip	Weight Loss of Strip in 30 Days (Grams)
0	13.1
15	10.8
30	8.1
30	5.0
45	2.5
60	2.1
60	0
75	0
90	0

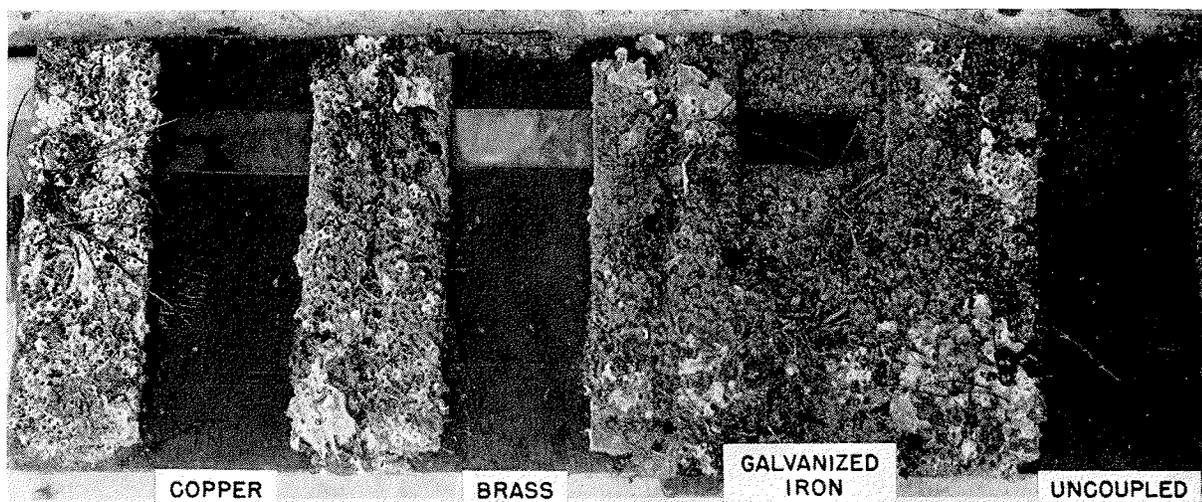


FIGURE 2. Fouling of a commercial brand of yacht paint when coupled with galvanized iron. Surfaces coupled with copper and brass and uncoupled remain unfouled. Exposure 60 days.

to the formation of galvanic couples with iron. Discussion will be delayed until the effect of such couples on the fouling of the paint is described, since these effects afford additional evidence of the nature of the phenomenon.

INACTIVATION OF ANTIFOULING PAINTS ASSOCIATED WITH CORROSION

Many metallic copper paints when applied to a wood panel lose their antifouling action completely if the paint is in contact with iron or zinc. This has been demonstrated by exposures at Miami using three commercial brands of yacht paint, four different metallic copper paints submitted for use on PT boats, and Bakelite Corporation AF12 and AF23 (14, 15, 16). Figure 2 shows the fouling on one brand of yacht paint induced by contact with galvanized iron after 60 days' immersion. The Stoner-Mudge S-1379, used in an experiment described by Young and Seagren (11, 18), was also inactivated for a distance of two inches about an attached steel coupon.

TABLE 10. Weight Loss of Iron Strips Applied to Paints over Wood, and Distance, Measured from the Iron Strip, over Which Antifouling Action was Inactivated

Paint	Pigment	Period of Immersion days	Weight	Inactivation Distance
			Loss of Iron Couple grams	
PT 10	Cu	135	18.8	10
AF 12	Cu	135	34.5	36
AF 22	Cu ₂ O	180	0.5	none
143	Cu ₂ O	180	0.7	none
Commercial Paint "A"	Cu	135	0.3	none
Commercial Paint "B"	Cu, Cu ₂ O, etc.	135	0.4	none
Control	—	180	0.4	none

A number of metallic copper paints fail to be inactivated when coupled with iron or zinc. This has been the experience at Miami Beach with a commercial paint and with one sample of PT paint tested. There is a close relation between corrosion of the coupled metal and inactivation of the paint; paints which increase corrosion are inactivated, while paints which do not increase corrosion are not inactivated.

In none of the experiments conducted at Miami Beach has a paint known to contain only cuprous oxide as a toxic been inactivated by contact with an iron or zinc strip, except where heavy deposits of rust spread out over the paint from the metal.

These relations between corrosion and inactivation are demonstrated in Table 10 and illustrated in Figure 3.

Young and Seagren (9) suggest that to produce such gross inactivation effects as have been described, the coating would have to be an exception rather than an orthodox paint. However, the effects have been observed not only on three ordinary commercial bronze yacht paints but also on

TABLE 11. Fouling Resistance of Coupled and Uncoupled Surfaces of Diluted Samples of AF23 and Weight Loss by Corrosion of the Coupled Steel Coupon in 30 Days

No.	Per Cent Copper (dry weight)	Fouling Resistance#		Weight Loss of Steel Couple (grams)
		Uncoupled	Coupled	
23	76	100	0	25.1
231	57	100	0	24.6
232	38	100	0	18.1
233	26.6	92	*	4.7
234	19	91	91	3.4
235	11.4	0	0	2.2
236	7.6	0	0	2.1
237	3.8	0	0	2.6

* Paint fouled only close to steel strip.
100 = no fouling 0 = complete fouling.

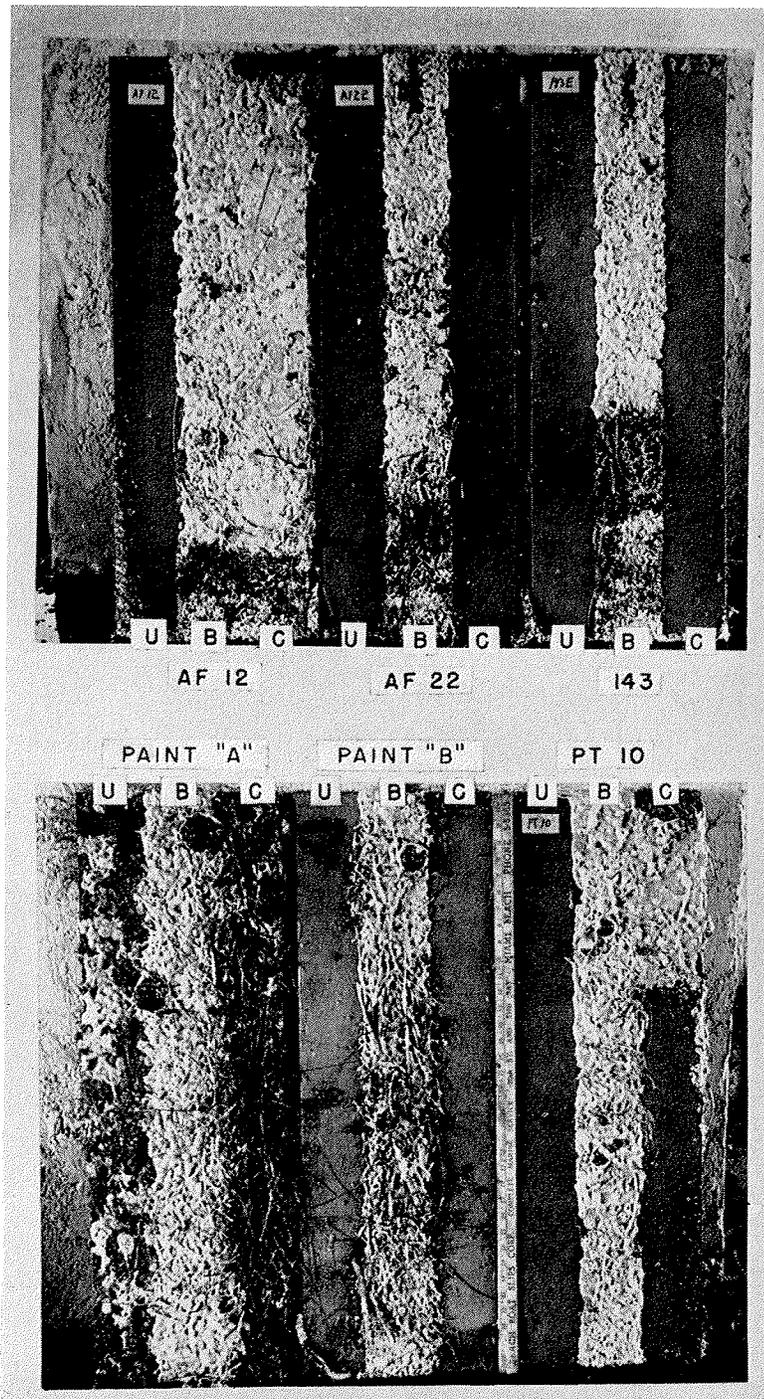


FIGURE 3. Inactivation of antifouling action of metallic copper paints, PT10 and AF12 when coupled to galvanized iron. No inactivation occurs with the cuprous oxide paints AF22 and 143E or with Commercial Paint "B". Commercial

Paint "A" fouled whether coupled or not. Exposure 91 days. U, uncoupled B, bare wood, C, coupled.

AF23, a paint at one time used by the Navy, and on a number of paints, such as PT10, submitted by the industry for use on high-speed wooden vessels.

The occurrence of inactivation can be shown to be associated with high pigment loading. Table

11 shows the result of an experiment in which the relative proportions of pigment and binder were varied, with the result that both corrosion and inactivation of the antifouling action dropped abruptly when the per cent of copper in the dry paint film was reduced to about 25 per cent. A

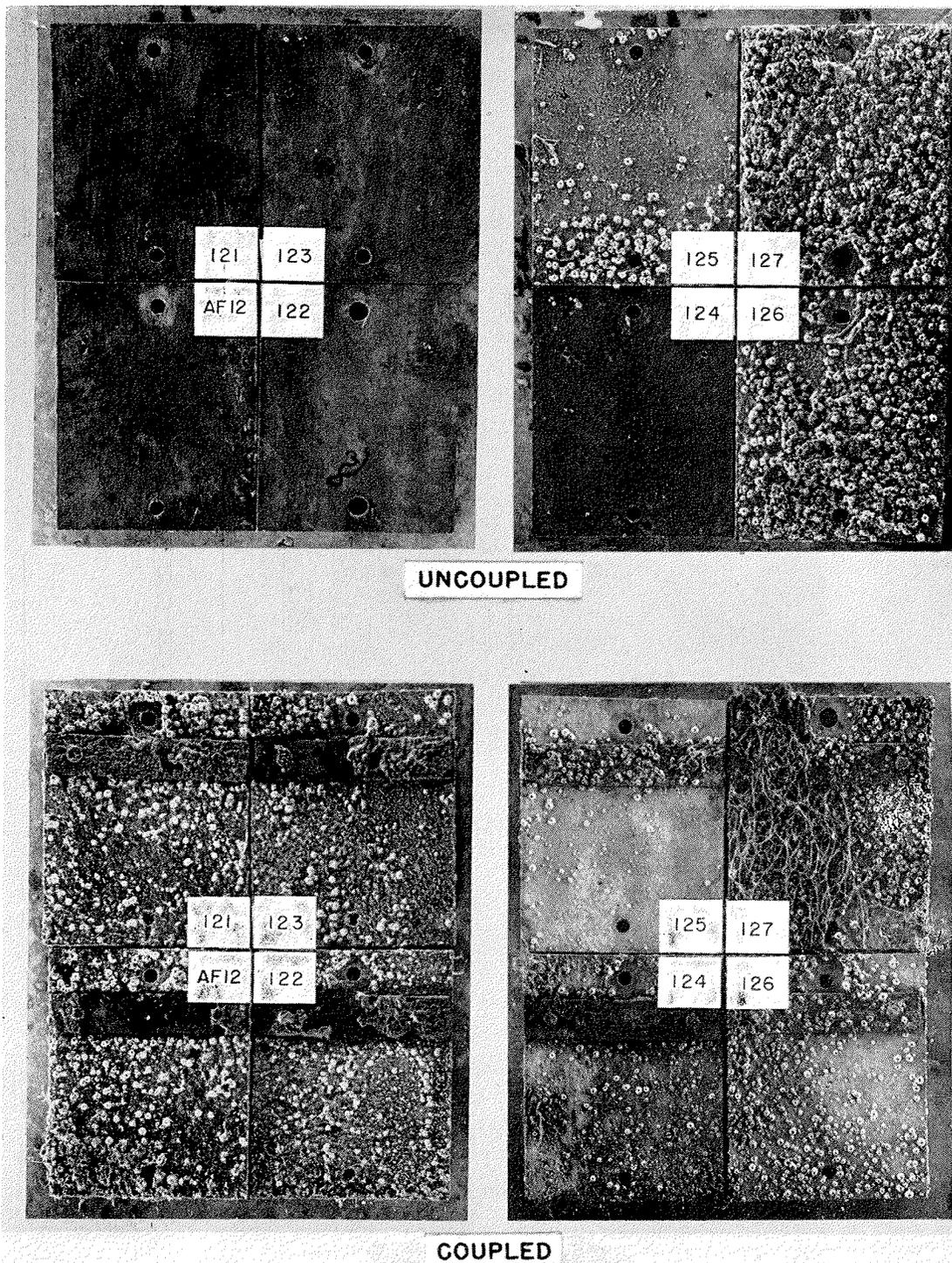


FIGURE 4. Fouling of series of dilutions of metallic copper paint, AF12, applied to wood when uncoupled and when coupled to steel. The more heavily loaded samples, AF12 to AF124, are inactivated by coupling. Exposure 30 days.

very similar relation was demonstrated in the experiment recorded in Table 7 in which AF12 was employed, the results of which are recorded in Figure 4. Inactivation was evident in all samples containing 22.5 per cent of Cu or more.

The distance over which inactivation extends from the metal strip also appears to depend very largely on the loading of the paint with metallic copper. Figure 5 illustrates the extent of inactivation in a series of dilutions of AF23. In Table 12,

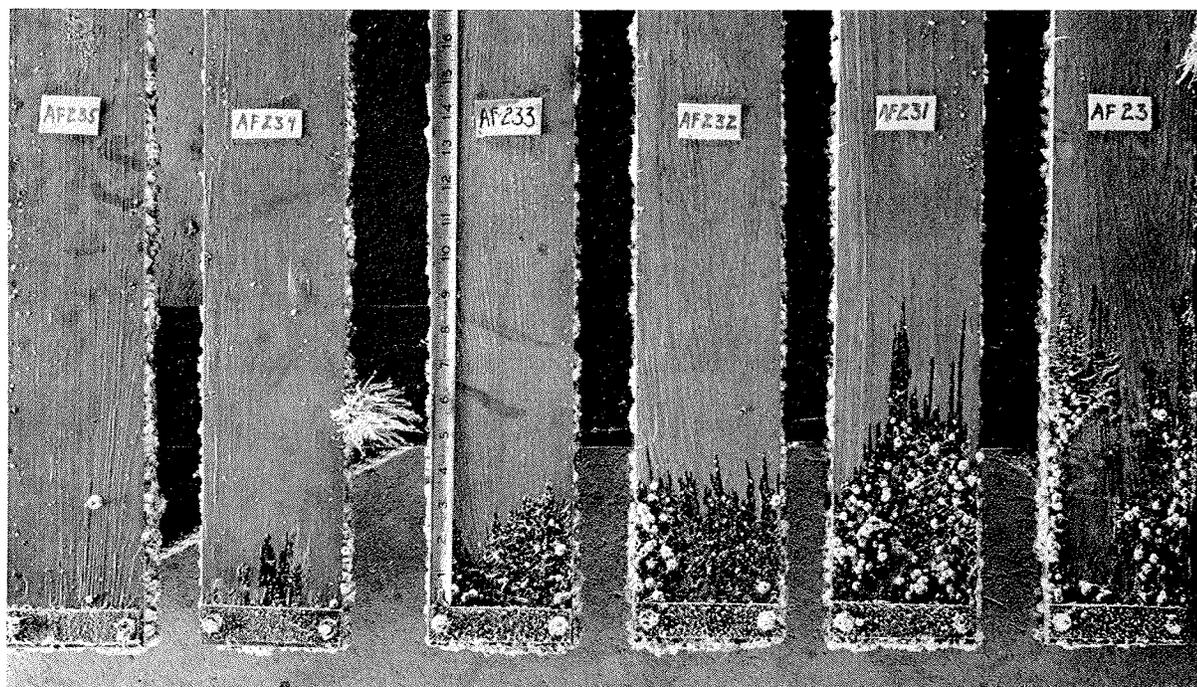


FIGURE 5. Distance of inactivation of a series of dilutions of AF23 containing various amounts of metallic copper. Dilution increases from right to left.

observations on a number of paints are recorded which also demonstrate this relation. Irregularities in the correlation are, no doubt, due to differences in the matrix and perhaps to other causes, such as the characteristics of the metallic copper pigment used in the various paints. Figure 6 illustrates the extreme effect observed in which inactivation extended for 9 feet from the galvanized iron strip.

The great distances over which these effects may occur, the dependence of the result on the loading, and hence, presumably, on the conductivity of the film, and the absence of the effect when cuprous oxide is employed, all point to the phenomenon being one of bimetallic galvanic coupling in which the solution of the copper is suppressed in proportion to the increased corrosion of the anodic metal.

In addition, it has been found that similar results are not obtained if strips of copper or brass are applied to the metallic copper paint instead of a more base metal (see Figure 2). Inactivation is not obtained if the iron is not in contact with the metallic copper paint film. If a 2-inch band of cuprous oxide paint, such as 143, separates the iron from the metallic copper paint AF12, the latter is completely protected from inactivation, though without this protection it would foul for a distance of several feet. The corrosion of the metal is also reduced to normal values by this degree of insulation. Thus, the results shown in Table 13

were obtained in an experiment of 115 days' duration, and are illustrated in part in Figure 7. This and other experiments show that wood does not contribute effectively to completing the supposed galvanic circuit.

Young and Seagren (11, 18) also found that when the metal piece was insulated from the paint surface (S-1379) by plastic insulators, the paint was not inactivated, as it was on direct contact.

When strips of iron or zinc are attached to metallic paints, the surface of the paint becomes darkened in the immediate neighborhood of the metallic strip on exposure to sea water. The darkened area gradually extends to some distance depending on the galvanic activity of the paint and the composition of the metallic strip. Figure 8 illustrates this effect. Darkening has just commenced about the iron coupon, but has spread for

TABLE 12. Metallic Copper Content and Distance of Inactivation by Galvanic Coupling

Paint	% Cu	Distance of Inactivation
AF 12	90	9 feet
AF 23	76	2.5 feet
Commercial Paint "C"	—	1.5 feet
Pt 10	—	1 foot
S-1471	40	2 inches
Commercial Paint "D"	—	>8 inches
AF 232	38	>8 inches
AF 233	26.6	1 inch
AF 234	19	0 inches
AF 125	13.5	0 inches
Commercial Paint "A"	—	0 inches

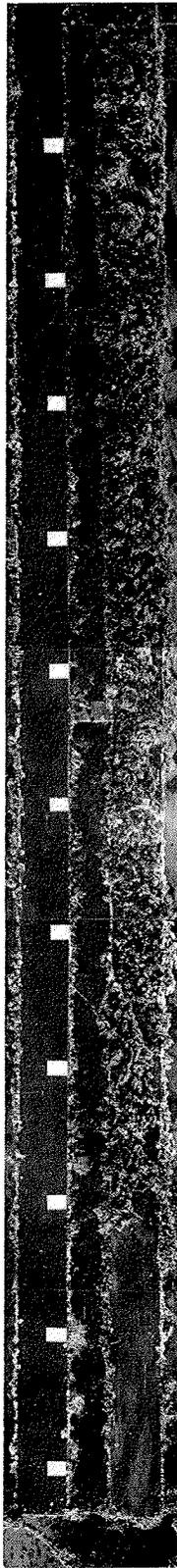


FIGURE 6. Inactivation of metallic copper paint AF12 extending more than 9 feet from galvanised iron coupon. The coupon was attached at the upper end of the right plank. The uncoupled plank, to which marks are attached at one-foot intervals, has not fouled. Exposure 3 months.

several inches from the galvanised iron coupon, and has covered the entire panel to which zinc was attached. This darkening has proved to be an invariable precursor to the subsequent fouling of the paint. The correspondence between the darkening and the subsequent extent of fouling is illustrated in Figure 9. Metallic copper paint when applied to wood is also frequently observed to blister severely near an attached strip of iron or zinc.

It has also been demonstrated that the electrical resistance of the paint films becomes greatly re-

TABLE 13. Effect of Insulating a Metallic Coupon from Metallic Copper Paints by a Protective Band of Cuprous Oxide Paint, 143

Paint	Protective Band of 143	Weight Loss of Iron	Fouling of Metallic Paint
AF 23	present	0.4 gram	none
AF 23	absent	108. grams	fouled heavily
AF 12	present	0.7 gram	none
AF 12	absent	130. grams	fouled heavily
143	—	0.5 gram	none

duced in the inactivated regions marked by the dark discoloration. This may be demonstrated by applying the terminals of an ohmmeter to the surface of a painted panel which has been removed from the sea water. In exploring the surface it is found that the resistance drops abruptly as the margin of the discolored zone surrounding the iron or zinc coupon is crossed.

If a piece of glass is set into the face of the panel and covered by a coating of metallic paint, and a zinc coupon contacts the paint surface, the same effects are observed. This shows that the phenomenon does not depend on the conductivity of the underlying wood, and that it is the lateral resistance of the paint layer which is altered. The magnitude of these effects and the time required for their development are illustrated by Table 14.

These observations suggest that inactivation accompanies a redeposition of metallic copper in the cathodic paint film surrounding the anodic coupon, and that this process spreads across the paint, aided by the improved conductivity of the portions of the deposit already laid down nearer to the anodic area. In this way an iron or zinc coupon alters the structure of the paint in its neighborhood so that it forms the cathodic member of a very effective galvanic couple.

This conclusion is supported by studies by Alexander and Benemelis of the electrical properties of films of metallic copper paint (1). They observed that when films having a pigment volume ratio of 30 or 35 per cent metallic copper were coupled to steel and soaked in artificial sea water, a galvanic

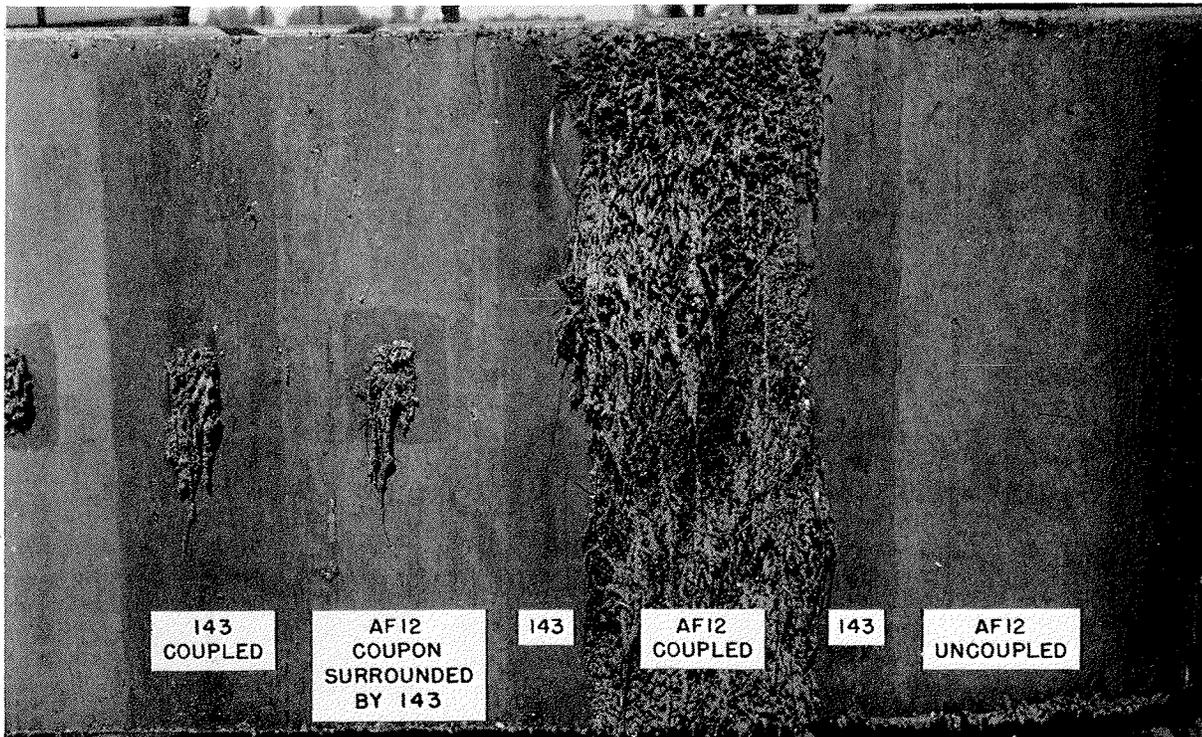


FIGURE 7. Protection of metallic copper paint, AF12 from inactivation by a galvanized iron coupon by surrounding the coupon with an area painted with the cuprous oxide coating 143E. Exposure 60 days.

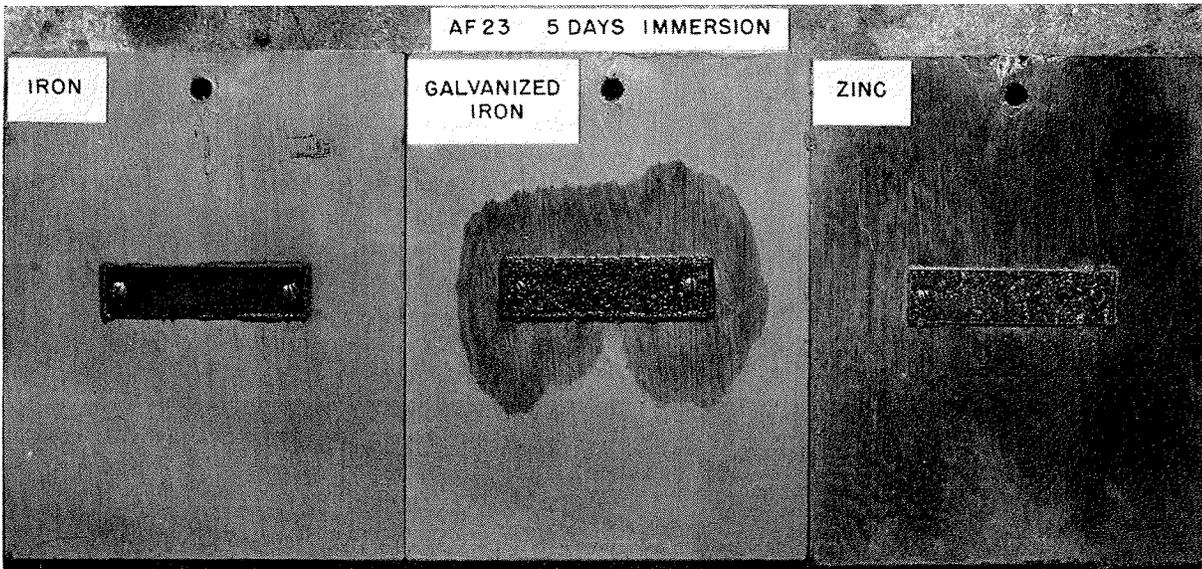


FIGURE 8. Discoloration of metallic copper paint AF23 surrounding coupons of iron, galvanized iron and zinc. Exposure 5 days.

TABLE 14. Resistance of Metallic Copper Paint Films Discolored by Coupling to Metallic Zinc. Resistance, in Ohms, between Points about 1 Inch Apart.

Paint	AF 23			Commercial Paint "C"		
	24 hours	48 hours	10 days	24 hours	48 hours	10 days
Resistance of unchanged portion of paint over wood	3-5,000	1,5-2,500	*	15,000	5,000	*
Resistance of discolored portion of paint over wood	250	50-250	10-25	0-5	0-5	0-5
Resistance of portion of paint over glass	50,000	5-10,000	100-150	70,000	0-5	0-5

* No unchanged paint areas left for measurement.

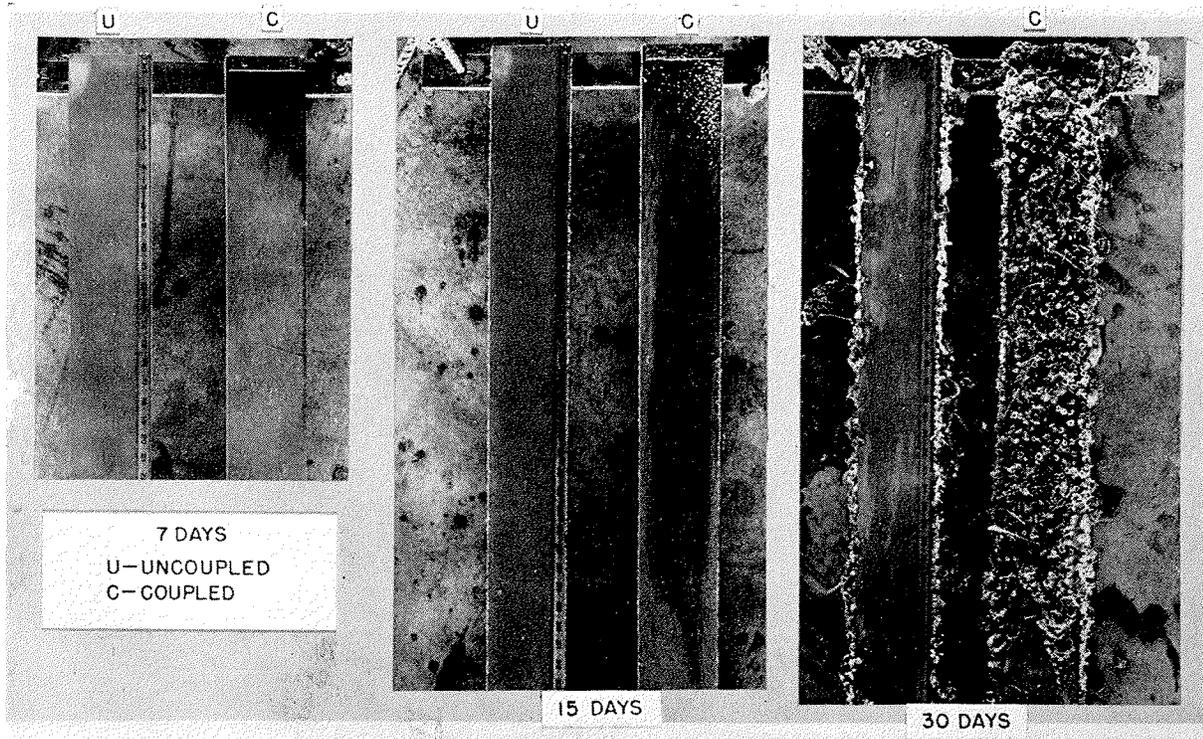


FIGURE 9. Discoloration of metallic copper paint AF23 preceding inactivation of antifouling action by coupling to galvanized iron.

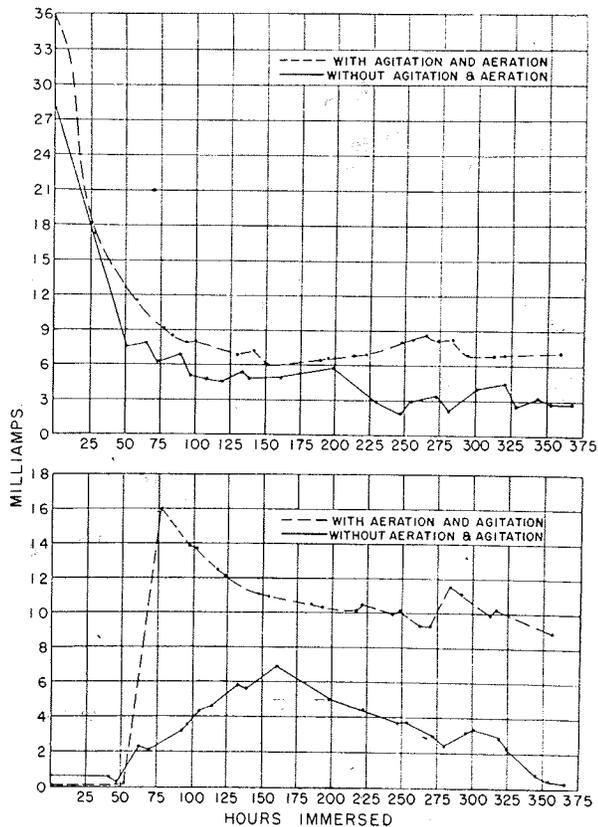


FIGURE 10. Galvanic current from copper-steel couple (above) and from metallic copper paint-steel couple (below). From Alexander and Benemelis (1).

current developed which increased markedly after an initial period when little or no current flowed. Figure 10 shows the current produced by such a couple during immersion, and also that produced by a similar couple of copper and steel. At the time of its maximum development the current produced by the paint-steel couple is as great or greater than that of the copper-steel couple. The resistance of the paint films was also shown to decrease during coupling to values characteristic of good conductors. This change in resistance did not occur if the paint films were soaked without being coupled to steel, and is evidently the result of some change produced in the paint as the result of coupling. These phenomena did not occur in films having a pigment-volume ratio of 25 per cent or less, which is close to the limit mentioned on a previous page below which inactivation of antifouling action does not occur.

Alexander and Benemelis conclude that, when placed in the role of a cathode, the copper particles of a metallic copper paint undergo some change in their position relative to each other, either because a breakdown occurs in the resistance of intervening barrier insulators formed by envelopes of the matrix, or because copper passes into solution and redeposits according to the theory of Young, Seagren and Zehner (19). Below

a critical value of the pigment-volume ratio, the distance between the majority of the pigment particles is so great that the insulating properties of the organic matrix are not disturbed by the applied potential, and no significant change occurs in the resistance of the film. Above this critical value, when the paint is coupled with steel, nullification of the antifouling properties and an acceleration of the rate of corrosion of the steel should follow.

Whatever the nature of the change in the paint film may be which results from coupling a metallic copper paint with steel, it is very difficult to believe that the phenomenon of inactivation described above can depend on any mechanism other than an electrochemical one. When the phenomena relative to corrosion and inactivation are considered together, it seems quite clear that the severe corrosive reactions which result when metallic copper paints are in direct contact with steel are also the result of the formation of bimetallic galvanic couples.

EFFECT OF CORROSION ON THE FOULING RESISTANCE OF CUPROUS OXIDE PAINTS

A report of the British Corrosion Committee (8) concludes that the behavior of an antifouling composition is indissolubly connected with that of the protective paint beneath it, and can only be fully satisfactory when the latter prevents any rusting of the steel. This is in accord with the experience of all those who have conducted extensive panel tests with antifouling paints. Young and Seagren (9) state that antifouling efficiency over unprimed steel is almost always poor, and that over nonmetallic surfaces antifouling action is nearly always better than over corrodable metal surfaces, even though these are primed in the conventional manner.

It is not easy to determine whether the fouling which accompanies the corrosion of a badly protected steel surface results merely from the opportunities which are afforded by the interruption of the antifouling coating when the underlying metal corrodes away, or whether the corrosion products have some direct action in inhibiting the antifouling action of the toxics in the paint.

Where metallic copper paints are involved, it is reasonable to believe that bimetallic galvanic cells are formed between the steel and the metallic copper pigment if the undercoating is absent or inadequate. These depress the solution of the copper and lead to fouling. This effect is il-

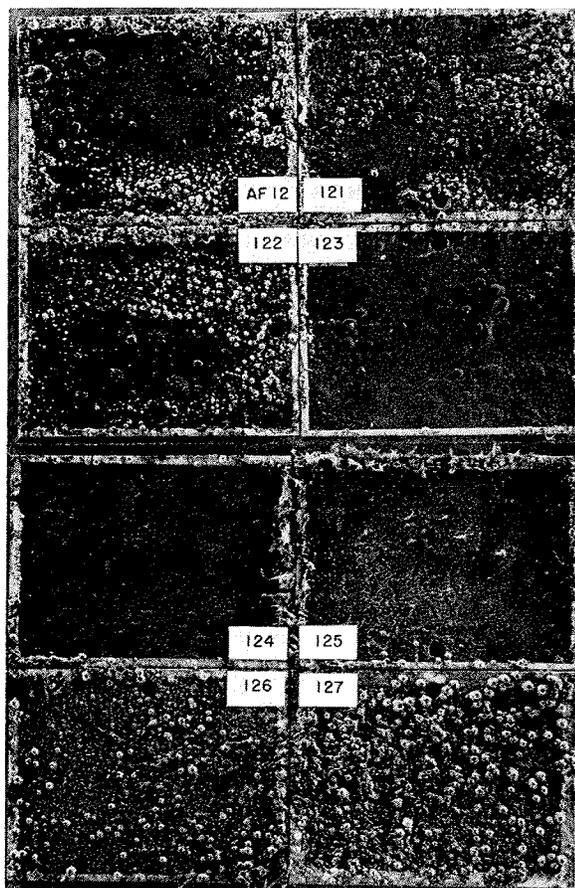


FIGURE 11. Fouling of a series of dilutions of metallic copper paint, AF12, applied to steel over a single coat of P8 primer. Exposure 30 days. Note that the more heavily loaded samples, AF12 to AF122, are inactivated. Compare Figure 4 for controls on wood panels.

lustrated in Figure 11, which shows the fouling of a series of dilutions of AF12, applied to steel over a single coat of P8 primer, after one month's exposure at Miami. The copper contents of these paints are recorded in Table 7, and their fouling when applied to wood, coupled or uncoupled, is illustrated in Figure 4. The more heavily loaded coatings AF12, 121, 122, have fouled heavily, just as they did when applied to wood and coupled to steel. The less heavily loaded coatings AF123 and 124 have retained some fouling resistance. The most dilute coatings, AF125, 126, 127, fouled from inadequate toxicity, as they did when applied to wood without coupling. The result of this experiment parallels that of the coupled wood application so closely as to leave little doubt that the failure of the heavily loaded coatings is attributable to galvanic action.

Where cuprous oxide paints are involved, this simple explanation will not hold. It is conceivable that if dissolved copper plates out under the paint film, as discussed on page 368 above, localized

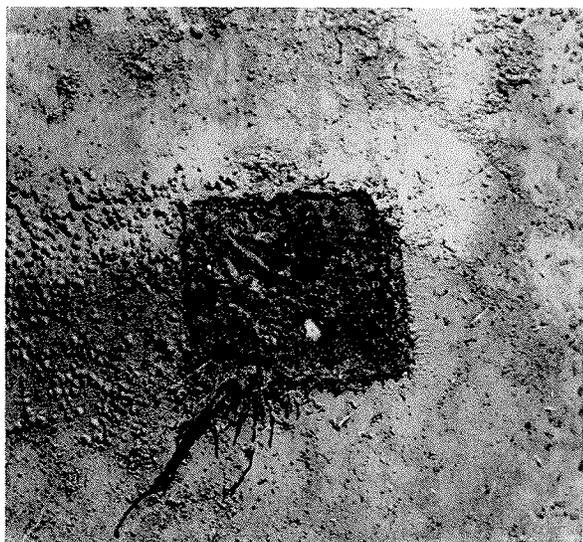


FIGURE 12. Fouling on rust deposit which formed downstream from a holiday in antifouling paint. Exposure 5 months. Reproduced by courtesy of F. L. LaQue, International Nickel Company.

electric fields may be set up sufficiently strong to prevent copper ions, dissolved from the cuprous oxide, from leaving the paint surface. Localized suppression of the leaching rate would then offer an opportunity for fouling.

Experiments indicate that the leaching rate of cuprous oxide paints applied without primers to steel panels is depressed after corrosion has set in. However, it is not clear whether less copper has left the panel or whether some dissolved copper has been picked up by the corrosion products and as a result is not measured by the procedure.

Young and Seagren (9, 18) call attention to the fact, which has doubtless been observed by others, that when heavy localized corrosion of iron occurs in proximity to a painted surface, iron corrosion products tend to spread over the neighboring paint, with the result that the antifouling action is interfered with. Figure 12 illustrates fouling on antifouling paint adjacent to a corroding holiday which was distributed in the direction in which corrosion products were carried by the movement of the sea water.

Young and Seagren (18) suggest that a soluble iron complex arises from the corroding iron which is washed along and through the slimy interface region at the surface of the paint, where it reacts with and precipitates the dissolved copper arising from the coating. The result is an inactivation of the antifouling paint. Harris (4) questions this explanation on two grounds: that it is doubtful that conditions are such as to encourage the formation of such complexes; and that similar inactiva-

tion may be observed in paints which rely largely or entirely on organic poisons. He suggests that ferrous ions passing into solution at anodic regions of the bare steel are oxidized and deposited as $\text{Fe}(\text{OH})_3$ near the cathodic alkaline regions of the paint, forming an anodic rust coating. This affects the antifouling properties in two ways: in the presence of alkali in the cathodic regions, copper will be rendered less soluble and rust will be deposited in the pores of the paint surface, preventing the normal loss of copper from the surface.

PRACTICAL CONSIDERATIONS

It seems clear from the foregoing discussion that, on steel construction, accelerated corrosion may be expected if paints containing either copper metal or cuprous oxide are applied unless adequate barrier coats are employed. If the coating contains metallic copper as a pigment, and the barrier coat is inadequate, more serious pitting may result at holidays or breaks in the paint surface. The protection afforded by the paint against fouling will be decreased whenever the conditions lead to increased corrosion, and this may, in fact, be a more serious consequence than the damage to the steel or the destruction of the paint film by corrosive action.

The theoretical discussion has brought out the probability that the corrosive action is dependent upon the formation of either gross or localized galvanic couples. The gross couples depend upon contact between particles in the paint and with the underlying steel, and are limited to highly loaded metallic paints. More generally, the effects appear to be explained by the diffusion of dissolved copper through the barrier coat where it is deposited to form local galvanic couples.

The logical method of overcoming corrosive effects of the latter sort appears to lie in the use of barrier coats which, through their impermeability and electrical insulating properties, will interfere with the formation and operation of localized galvanic couples beneath the paint. On the one hand, they should prevent dissolved copper from reaching the metallic surface, and on the other, should insulate the surface from sea water so as to prevent the completion of local circuits through that medium. Young, Seagren, Schneider, and Zehner (17) have pointed out that these findings confirm best shipyard practice, namely, the use of multiple barrier coats or of very heavy undercoats, beneath antifouling paints. They further suggest that relatively impermeable barrier coats, topped by medium coats of antifouling paints, should give

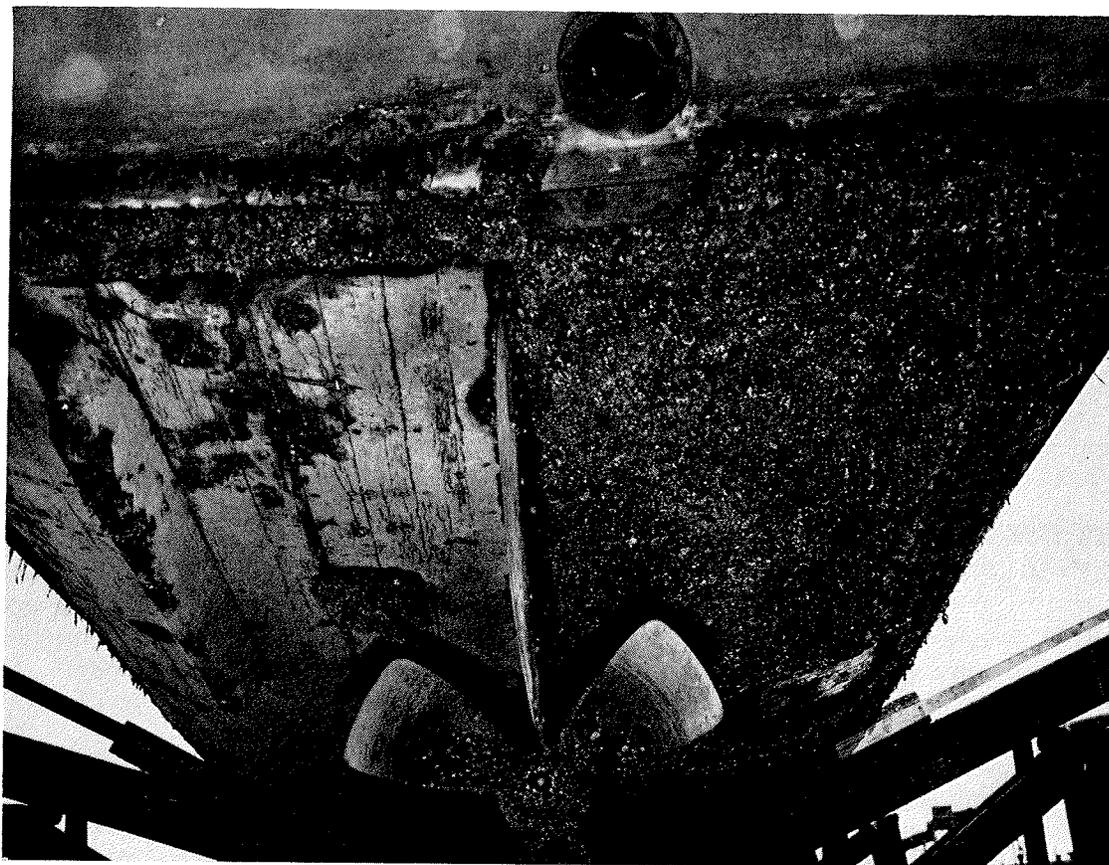


FIGURE 13. Fouling of metallic copper paint AF23 induced by a galvanize.iron patch which may be seen to right of propeller. The cuprous oxide paint AF22 coating the port quarter has not been inactivated. The uncoupled AF23 on the port bow quarter was also unfouled.

better corrosion protection, combined with efficient antifouling action, than can be had with light priming coats and a heavy antifouling layer.

The possibility of decreasing corrosive attack by proper formulation of the antifouling composition itself should not be overlooked. The evidence given in Chapter 16 indicates that the plastic paints currently used by the Navy are attacked by sea water largely at the outer surface, and that relatively little solution of cuprous oxide takes place in the deeper layers of the paint. That such an impermeable paint does, indeed, cause less severe corrosive attack at holidays is indicated by an experiment of the Mellon Institute investigators with Navy formulation 143, the results of which are given in Table 3.

It is also probable that by correct formulation the corrosive effects of metallic copper paints may be reduced and perhaps kept as small as those of cuprous oxide paints. It is not clear that this can be done and still retain the advantage of an ample reserve toxicity. Only two of the commercial metallic copper paints examined at Woods Hole have

shown no excessive corrosive tendencies, and these are not very satisfactory antifouling paints when compared to the best Navy coatings now available. On the whole, in view of the demonstrated tendency of metallic copper paints to form gross galvanic couples with steel, and of the attendant corrosion and loss of protection against fouling, their use on steel construction should not be encouraged until compensating advantages have been demonstrated.

On wood construction, the danger of corrosion and inactivation are much less serious. Young and Seagren (18) suggest that accidental contact of chain, rudder posts, and similar ironware with the antifouling paint on a wood hull would have very little deteriorating effect on antifouling efficiency, unless the contact area be large. However, experiments show that heavily loaded metallic copper paints of the type recently developed may result in severe corrosion of galvanized iron fittings and fastenings which they contact. Fouling of the paint in the neighborhood of metallic contacts may also result. This is illustrated by Figure 13, which

shows an area of the hull of a torpedo retriever which had been painted with AF23. The painted surface of the wood planking has fouled over the entire quarter of the bottom to which a galvanized iron plate had been applied to repair damage to the planking.

If the fittings and fastenings are of bronze or brass, or if they are protected by a coat of cuprous oxide paint applied so that contact between the fitting and the metallic paint is avoided, these effects will not take place. The disadvantages of attempting such protection must be weighed against the supposed advantage of using the metallic pigment.

THE USE OF PAINT TO PROTECT GALVANICALLY COUPLED METALS

When it is necessary to expose dissimilar metals in contact under sea water, the corrosive effects of the resulting galvanic couples may be reduced by the use of protective coatings. LaQue (6, 7) has recorded the effect of painting either or both members of a couple consisting of steel and copper. The following was found to be the order of preference in the application of the paint:

- 1st choice—Paint both the copper and the steel.
- 2nd choice—Paint the copper and leave the steel bare.
- 3rd choice—Leave both metals bare.
- 4th choice—Paint the steel and leave the copper bare.

The reason for not painting the steel, if the copper is not painted, is that imperfections in the paint coating may lead to severe localized attack which, on the whole, is more harmful than the uniformly distributed corrosion which occurs on bare steel.

In additional experiments, it was found that if the steel member of a copper/steel couple was painted with an adequate anticorrosive system, the antifouling action of the copper was no longer inactivated, and the copper remained free of fouling. It was also possible to prevent fouling on the copper member of a couple by painting it with an adequate barrier coat topped off with a metallic copper paint. That is to say, the inactivating action of the steel on the copper member did not extend through the barrier coat to influence the overlying metallic copper paint. The practice of painting Muntz metal sheathing with antifouling paint may have justification in this principle.

BLISTERING OF PAINT FILMS BY ELECTROLYTIC REACTIONS

The discussion of the acceleration of corrosion has emphasized the importance of local electrolytic processes resulting from interaction between copper paints and the underlying steel when adequate barrier coats are not present. A report from the Bakelite Corporation (3) points out that blistering can be induced by coupling a painted steel panel with either copper or zinc. With a zinc coupling, the steel is cathodic and becomes the site of hydrogen liberation accompanied by increased hydroxyl ion concentration. The steel beneath the blisters is found to be bright and clean. With a copper coupling, the steel is anodic and severe corrosion occurs in isolated imperfections in the paint film. Blisters are not formed as readily, but when present they are filled with rust. On several uncoupled panels, both types of blisters were observed to be present as little as $\frac{1}{8}$ inch apart. This illustrates the effects produced by local electrolytic cells, and shows that greater activity may exist at small, isolated points.

Since blistering, arising from electrolytic processes, is thought to be a frequent cause of paint failure, especial attention should be given to developing anticorrosive coatings which discourage such effects. The Bakelite report (3) recommends the use of steel panels to which small pieces of zinc or copper are coupled to test the resistance of barrier coats to conditions which produce electrolytic blistering.

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