

CHAPTER 21

The Fouling of Metallic Surfaces

Sheathing with copper appears to have been the first adequate method of preventing the fouling of ships' bottoms, and was also the most successful technique employed for this purpose. The use of lead sheathing by the ancients, which was also current at the time copper sheathing was introduced, was doubtless intended as a protection against borers or for other purposes, since lead gives practically no antifouling protection.

The first record of the use of copper sheathing is found in the Navy Board's report to the Admiralty on His Majesty's Ship *Alarm*, which, in 1761, returned from a twenty month's voyage to the West Indies (21). This report, which is reprinted in the Appendix to Chapter 11, showed that the ship's bottom had remained clean during this period. It was noted that the copper covering the rudder had fouled with barnacles, which was accounted for by the fact that the plates there had been fastened with iron nails "to vary the experiment," and it was thought that the rust from these nails had drained down and spread over the surface so as to occasion the fouling. The effect which the copper had upon the iron where the two metals touched was also noted with surprise, for it was found that the rudder iron, the fastenings of the false keel, the pintles, etc., were corroded and eaten. Thus, in the earliest extant account of a copper-sheathed ship we find recorded two great limitations of copper sheathing, namely, the corrosion of adjacent iron parts and the inactivation of the copper as a nonfouling surface under this association.

The sheathing on the bows of the *Alarm* was wasted away by the erosive action of the sea so that only the edges and fastenings remained as first put on. The life of the copper sheathing of sailing vessels was, in general, about four or five years, so that the upkeep of the bottom was a considerable expense. In spite of this difficulty, copper remained the approved method of treating ships' bottoms until the use of iron in the construction of ships became prevalent, when the galvanic corrosion of iron induced by the copper plating led to great difficulties. It was necessary to insulate the hull from the sheathing by means of a wood backing or in some other way. The procedure was expensive and, though done with great care, the insulation was never perfect. Danger al-

ways existed that damage to the insulation would expose a small area of the ship's plating to very severe corrosion. In spite of this difficulty, United States battleships and many cruisers of foreign powers were sheathed with wood and copper as late as 1900, the antifouling virtues of the method having been amply demonstrated during the Spanish-American war (1).

The expense and difficulty of insulating copper sheathing stimulated the development of antifouling paints. As these became effective, the economy and ease of application of such coatings gradually caused the disuse of copper sheathing even on small wooden vessels. Now the employment of metallic sheathing is usually restricted to the protection of wood hulls from the abrasive action of ice and the like, or to situations where the superior protection against the worm warrants the initial expense.

It is reported that in The Netherlands Navy, where copper sheathing is used as a protection against worms in East Indian waters, 50 per cent of the sheathing must be replaced annually. Sheathing is not only damaged by grounding but is torn away by the seas and by high speed operation. Consequently, it is not recommended for speeds over 15 knots, and is unsuited to modern high-speed vessels.

At the time of the introduction of iron into the construction of ships' hulls, zinc sheathing was seriously suggested as a substitute for copper (4). Zinc sheets were tried on several ships, notably the Italian battleship *Italia* (1), but did not prove a great success. While its use may have served to protect the iron hull from corrosion, it can have had little value as an antifouling surface. This fact, coupled with the difficulty and expense of attaching the zinc plates to the steel hull, evidently led to its early abandonment.¹

Alloys of copper, particularly Muntz or yellow metal, have been employed as substitutes for copper in sheathing wood bottoms because of economy and the greater resistance of these alloys to erosion. Muntz metal is not a very effective antifouling surface, and it is found to be an advantage to use antifouling paint over the sheathing.

¹ Zinc coatings, applied directly by galvanizing, are currently used in the construction of light Naval vessels to reduce corrosion within the bilges. Antifouling paints are applied over the outer galvanized surface of the ships' plates.

Recently, copper-nickel sheathing (copper 70 per cent, nickel 30 per cent) has been employed by the United States Coast Guard as a sheathing for motor lifeboats which are exposed to ice abrasion as well as to fouling (12).

Although the use of metallic sheathing has been largely abandoned, the fouling of copper alloys has a practical application in connection with localized structures, such as the propellers, propeller struts, the salt water piping systems of vessels, and specialized underwater equipments including sound gear, and the like. Special aspects of these problems are discussed in Chapter 1. The general principles involved in the use of metals for structures which should remain free of fouling when exposed in sea water are reviewed below.

RESISTANCE OF METALLIC SURFACES TO FOULING

The relative tendency of metallic surfaces to foul was studied by Parker, who rated the fouling which accumulated on panels submerged for 53 days in mid-summer in the Eel Pond, Woods Hole, Massachusetts, as follows (23):

Aluminum—10 Iron—10 Lead—10 Tin—6
Zinc—0.2 Copper—0

Similar results from exposure in Hawaii are reported by Edmondson and Ingram, who add to the list German silver, an alloy of copper, zinc and nickel, as superior to zinc in resistance to fouling (8).

Tests at Point Reyes, California, have shown

TABLE I
Group I—Metals and Alloys Least Likely to Foul

Admiralty Brass	Cu 70	Zn 29	Sn 1		
with As	Cu 70	Zn 29	Sn 1	As 0.05	
with Sb	Cu 70	Zn 29	Sn 1	Sb 0.05	
with P	Cu 70	Zn 29	Sn 1	P 0.02	
Admic	Cu 70	Sn 1	Ni 29		
Ambrac	Cu 75	Zn 5	Ni 20		
Arsenical Copper	Cu 99.5	As 0.3			
Beryllium Copper	Cu 97.4	Ni 0.25	Be 2.3		
Brass, Leaded Free Cutting	Cu >65	Pb 1.5	Zn balance		
Brasses, more than 65% Copper	Cu >65	Zn <35			
Brasses—Tin with more than 80% Cu	Cu >80	Sn 1-2.5	Zn balance		
Bronzes—Tin	Cu >80	Sn <10			
Bronze—Comp. G	Cu 88	Zn 2	Sn 10		
Bronze—Comp. M	Cu 88	Zn 3	Sn 6.5	Pb 1.5	
Bronze—Nickel	Cu >80	Ni 1-10			
Cartridge Brass	Cu 70	Zn 30			
Chain Bronze	Cu 95	Sn 5			
Commercial Bronze	Cu 90	Zn 10			
Copper	Cu 99+				
Copper Nickel Alloys less than 30% Ni & less than 0.15% Fe	Cu >70	Ni <30	Fe < .15		
Duronze	Cu 97	Sn 2	Si 1		
Everdur	Cu 96	Si 3			
German Silver (Nickel Silver)	Cu 64	Zn 18	Ni 18		
Gilding Metal	Cu 96	Zn 4			
Government Bronze	Cu 88	Zn 2	Sn 10		
Gun Metal	Cu 88	Zn 2	Sn 10		
Hardware Bronze	Cu 89	Zn 9	Pb 2		
Herculoy	Cu 96	Sn 0.5	Si 3.25		
Low Brass	Cu 80	Zn 20			
Olympic Bronze	Cu 96.5	Zn 1	Si 2.75		
Ounce Metal	Cu 85	Zn 5	Sn 5	Pb 5	
Phosphor Bronze	Sn 4-10	Cu balance			
Rich Low Brass	Cu 85	Zn 15			
Silicon Bronze	Cu 97	Si 3			
P.M.G. Bronze	Cu 95.5	Fe 1.5	Si 3		
Red Brass, Cast	Cu 85	Zn 5	Sn 5	Pb 5	
Red Brass, Wrought	Cu 85	Zn 15			

Group II—Metals and Alloys Variable in Fouling Tendency

Brasses with less than 65% Copper	Cu <65	Zn balance			
Common Brass	Cu 65	Zn 35			
Copper Nickel Alloys, less than 30% Ni & more than 0.15% Fe	Cu >70	Ni <30	Fe > .15		
Copper Nickel Alloys 30 to 40% Ni	Cu 60-70	Ni 30-40			
High Brass (Yellow brass)	Cu 65	Zn 35			
Leaded High Brass	Cu 65	Zn 34	Pb 1		
Manganese Bronze	Cu 58	Zn 40	Mn 2		
Muntz Metal	Cu 60	Zn 40			
Naval Brass (Tobin Bronze)	Cu 60	Zn 39	Sn 1		
Silver					
Sterling Silver	Cu 7.5	Ag 92.5			
Zinc	Zn 99+				

TABLE 1 (continued)
Group III—Metals and Alloys Likely to Foul

Aluminum								
Aluminum Alloys								
Aluminum Brass with or without dezincification inhibitors	Cu	76	Zn	22	Al	2		
Aluminum Bronze	Cu	90	Al	10				
Antimonial Lead								
Antimony								
Armco Iron	Fe	99+						
Babbitt	Cu	35	Sn	89	Sb	7.5		
Cadmium Plate								
Cast Iron								
Cast Steel								
Chemical Lead								
Chromium Plate								
Cobalt								
Constanten	Cu	55	Ni	45				
Copper Steel	Cu	.25	Fe	99+				
Copper Nickel Alloys more than 40% Ni	Cu	<60	Ni	>40				
Dowmetal (Magnesium alloys)								
Duralumin								
Duriron	Fe	82	Si	14.5				
Galvanized Steel								
Gold								
Hastelloy A	Fe	22	Mo	22	Ni	balance		
Hastelloy B	Fe	6	Mo	32	Ni	balance		
Hastelloy C	Cr	17	Fe	6	Mo	19	W	5 Ni balance
Hastelloy D	Cu	3	Si	10	Ni	balance		
Inconel	Cr	13	Fe	6.5	Ni	balance		
Ingot Iron								
Invar	Ni	36	Fe	64				
Iron								
K-Monel	Cu	29	Ni	66	Fe	0.9	Al	2.75
Lead								
Lead Tin Alloys								
Magnesium								
Magnesium Alloys								
Manganese Steel	Mn	11-15	Fe	balance				
Monel	Cu	30	Ni	67	Fe	1.4		
Nichrome	Ni	62	Cr	15	Fe	balance		
Nickel								
Nickel Alumin Bronze	Cu	92	Ni	4	Al	4		
Nickel Chromium Alloys								
Nickel Chromium Iron Alloys								
Ni-Resist	Cu	5-7	Ni	12-15	Fe	balance		
Nitrided Steel								
Palladium								
Pewter	Sn	85-90	Pb	balance				
Platinum								
S-Monel	Cu	30	Ni	63	Fe	2	Si	4
Silver Solder	Cu	16	Zn	17	Ag	50		
Soft Solder	Sn	50	Pb	50				
Stainless Steels								
Stellite								
Tin								
Tin Lead Alloys								
Wiping Solder	Sn	40	Pb	60				
Worthite	Ni	24	Cr	19	Mo	3	Fe	balance
Wrought Iron								

that copper panels remained free of gross fouling for at least twelve months, but that brass and an alloy of copper and nickel (Cu 70 Ni 30) fouled lightly, and galvanized iron fouled heavily after the first four months (19).

Friend (9) had previously reported that of a large number of ferrous and nonferrous metals and alloys exposed for three years at Southampton Dock, "the shell fauna did not collect in any appreciable numbers on the copper or alloys rich in copper, although all the other bars were covered, even the lead . . . and zinc bars."

The fouling of a large number of materials, exposed for three months at Miami, has been discussed in Chapter 13 and the results presented in Table 2 of that chapter. Among the metals the intensity of fouling with barnacles was as follows:

Number of Barnacles Per Square Foot (24)	
Lead	396
Nickel	126
Steel	88
Galv. Iron Pipe	27
Galv. Iron	6
Monel	6
Zinc	0
Copper	0

TABLE 2. Relative Merit of Copper Alloys in Resisting Fouling During One Year's Exposure at Miami

Alloy	Composition—per cent								Months to foul > ¼ surface	Area fouled after 1 year per cent	LaQue Rating
	Cu	P	Si	Zn	Fe	Mn	Pb	As			
Copper	Cu 99.9								>12	<25	I
Copper, deoxidized	Cu 99.96	P 0.02							>12	<25	—
Everdur	Cu 95.61	Si 3.14	Zn 0.15	Fe 0.12	Mn 0.92				>12	<25	I
Aluminum Bronze	Cu 99.88	Al 0.12							>12	<25	—
Aluminum Bronze	Cu 99.82	Al 0.18							>12	traces	—
Aluminum Bronze	Cu 99.47	Al 0.53							>12	<25	—
Commercial Bronze	Cu 90.01	Zn 9.97	Pb 0.01	Fe 0.01					>12	<25	I
Silicon Brass	Cu 81.00	Zn 15.5	Si 3.5						>12	<25	—
Admiralty	Cu 70.58	Zn 28.33	Sn 1.06	Fe 0.01	Pb 0.02	As 0.004			12	<25	I
Everdur	Cu 98.32	Si 1.21	Fe 0.13	Mn 0.22					12	25-50	—
Phosphor Bronze	Cu 94.39	Sn 5.42	Pb 0.01	Fe 0.01	P 0.17				12	25-50	I
Red Brass	Cu 85.22	Zn 14.76	Pb 0.005	Fe 0.01					12	25-50	I
Arsenical Admiralty	Cu 71.11	Zn 27.87	Sn 0.98	Fe 0.01	Pb 0.01	As 0.02			12	25-50	—
Copper, arsenical deox.	Cu 99.64	As 0.29							11	25-50	—
Aluminum Bronze	Cu 98.96	Al 1.04							11	25-50	—
Cupro-nickel	Cu 94.18	Ni 5.42	Mn 0.27						11	<25	I
Super-nickel	Cu 69.05	Ni 30.26	Zn 0.15	Fe 0.06	Pb 0.002	Mn 0.48			11	50-75	I
Naval brass	Cu 60.50	Zn 38.65	Sn 0.85						11	25-50	II
Copper, tough pitch	Cu 99.96								10	50-75	I
Copper, silver bearing	Cu 99.86	Ag 0.093	As 0.004						10	50-75	—
Cupro-nickel	Cu 89.26	Ni 10.13	Mn 0.41						10	50-75	I
Cupro-nickel	Cu 92.56	Ni 5.34	Fe 1.15						10	25-50	II
Tobin Bronze	Cu 60.09	Zn 39.20	Sn 0.65	Fe 0.02	Pb 0.04				10	50-75	II
Brass, 70-30	Cu 70.61	Zn 29.33	Fe 0.02	Pb 0.04					9	50-75	I
Hitensiloy	Cu 57.25	Zn 39.90	Ni 1.75	Pb 1.1					9	>75	—
Ti-nic-o-sil #10	Cu 47.10	Zn 37.80	Ni 10.50	Fe 1.0	Pb 1.6	Mn 1.0			9	>75	—
Ti-nic-o-sil #14	Cu 42.00	Zn 43.00	Ni 15.00						9	25-50	—
Cupro-nickel	Cu 83.89	Ni 15.37	Mn 0.46						8	>75	I
Aluminum Bronze	Cu 97.94	Al 2.06							7	>75	—
Nickel Silver	Cu 64.23	Zn 17.10	Ni 18.30	Fe 0.07	Pb 0.01	Mn 0.29			7	>75	I
Ti-nic-o-sil #54	Cu 46.75	Zn 38.5	Ni 10.50	Pb 2.25	Mn 2.0				7	50-75	—
Cupro-nickel	Cu 79.54	Ni 19.76	Mn 0.46						6	>75	I
Cupro-nickel	Cu 68.09	Ni 29.88	Fe 0.49						4	>75	II
Ambrac B	Cu 64.63	Zn 5.46	Ni 29.37	Mn 0.54					4	>75	—
Nickel Silver	Cu 68.08	Zn 21.55	Ni 10.37						4	>75	—
Super-nickel	Cu 68.90	Ni 30.07	Zn 0.15	Fe 0.41	Mn 0.46				3	>75	II
Muntz Metal	Cu 61.00	Zn 38.94	Sn 0.02	Fe 0.01	Pb 0.025				3	>75	II
Cupro-nickel	Cu 88.43	Ni 10.06	Fe 0.79						2	50-75	II
Phosphor Bronze	Cu 89.99	Sn 9.76	Zn 0.10	Pb 0.02	Fe 0.01	P 0.12			2	>75	I
Cupro-nickel	Cu 66.88	Ni 32.52	Fe 0.02	Mn 0.45					2	>75	II
Cupro-nickel	Cu 59.26	Ni 40.30	Mn 0.35						2	>75	II
Cupro-nickel	Cu 53.54	Ni 44.71	Fe 0.12	Mn 1.02					2	>75	III
Cupro-nickel	Cu 83.57	Ni 15.39	Fe 0.62						2	>75	II
Cupro-nickel	Cu 79.81	Ni 19.88	Fe 0.58						2	>75	II
Ambrac A	Cu 73.39	Zn 6.08	Ni 19.89	Fe 0.07	Pb 0.01	Mn 0.56			2	>75	I
Ambraloy	Cu 94.94	Al 4.85	Zn 0.10	Ni 0.05	Fe 0.06				2	>75	—
Ambraloy	Cu 76.51	Al 2.12	Zn 21.30	Fe 0.04	As 0.017	Pb 0.005			2	>75	III
Aluminum Bronze	Cu 94.45	Al 5.05							1	>75	—
Aluminum Bronze	Cu 90.19	Al 9.81							1	>75	III
Aluminum Brass	Cu 68.00	Al 2.00	Zn 30.00						1	>75	III
Resistaloy	Cu 59.25	Al 2.00	Zn 37.65	Ni 1.1					1	>75	III
Monel	Cu 31.18	Ni 66.03	Fe 1.68	Si 0.05	Mn 1.68				1	>75	III
Monel, CIF-349	Cu 16.94	Ni 81.58	Fe 0.41	Si 0.05	Mn 0.41				1	>75	III
Nickel	Ni 100								1	>75	III

On the basis of very extensive observations, made in the course of corrosion tests, LaQue (15) has arranged the common metals and alloys in three groups depending on the probability that they will foul when exposed in the sea. The lists are given in Table 1. Of the many metals which have been tested, only copper (and its alloys), silver, and zinc appear to resist fouling to a degree greater than that of other hard smooth surfaces. The metals listed by LaQue as least likely to foul all contain copper in excess of 64 per cent. Among those with a variable tendency to foul the only pure metals are zinc and silver.

Zinc appears to resist fouling only temporarily. Thus British observers (20) have noted that zinc-coated specimens of steel may remain relatively free of fouling for six months under conditions when control surfaces foul heavily. The protective action of galvanizing, however, is usually lost as the surface becomes coated with corrosion products.

Pure silver also appears to have limited resistance to fouling. In tests conducted at Miami it was found that pure silver commenced to foul during the first month or two of exposure and became heavily fouled by the fourth month. In contrast,

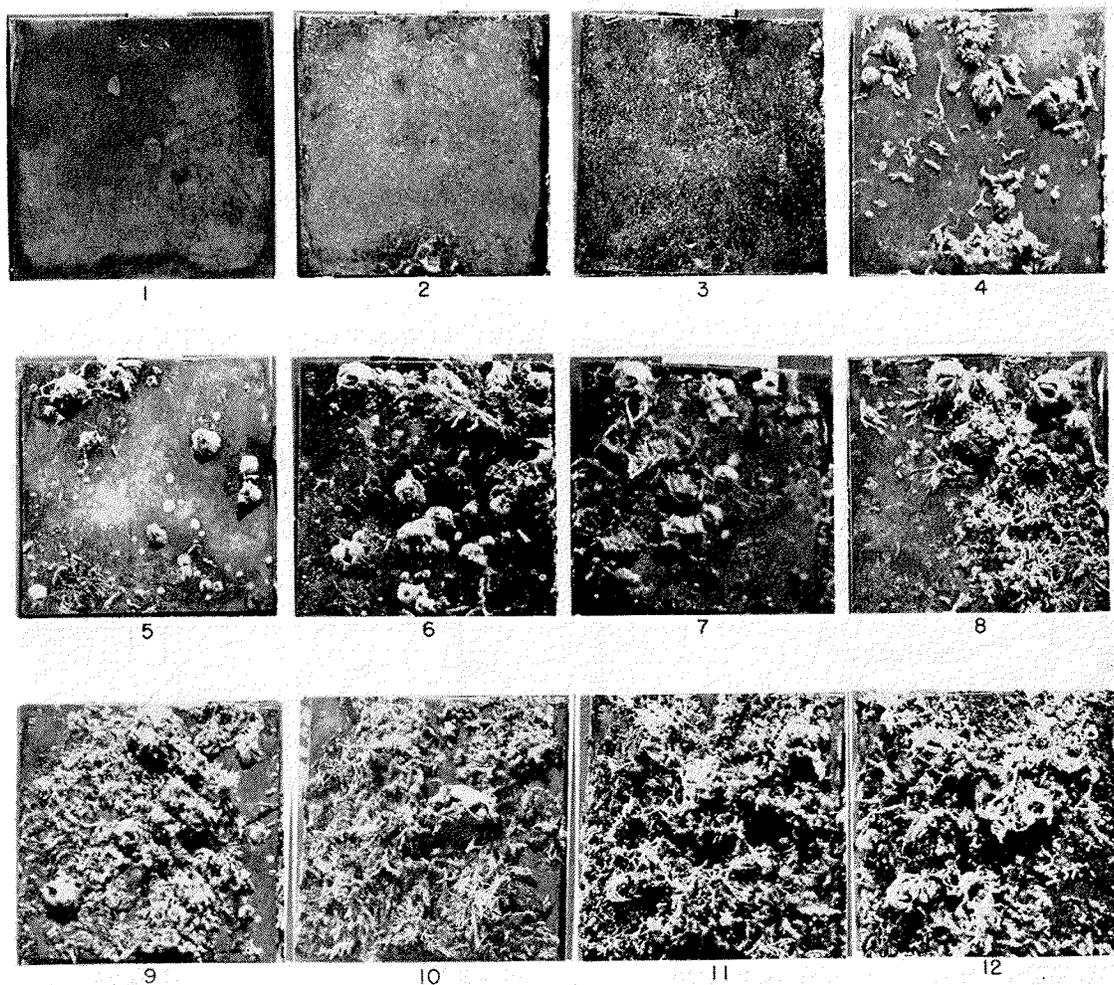


FIGURE 1. The development of fouling on a specimen of copper-nickel (30 Cu:20 Ni). The numbers indicate the months of exposure.

coin silver, which contains 10 per cent of copper, remained free of fouling for twelve months (26).

The alloys of copper are extensively used for underwater construction because of their resistance to corrosion and other appropriate physical properties. Their selection is commonly made without regard for their antifouling properties, which are variable. No attempt appears to have been made to develop alloys combining particularly good resistance to marine growth with other desirable qualities. Extensive tests have recently been made at Miami to compare the resistance of a large variety of copper alloys to fouling (25).

The fouling of the alloys, excepting those which become covered completely in the first month or two, is a gradual process. The growth is localized at first, the intervening areas being quite clean. Only gradually does the growth encroach on the unfouled areas to cover the entire surface. Figure 1 illustrates this characteristic in the case of a

copper-nickel alloy. It is not possible to separate the alloys into those which do or do not foul; rather, they must be rated in accordance with the time of exposure required to develop some standard degree of fouling, such as the time at which one-half the surface is covered.

The results of these tests during one year of exposure are given in Table 2, in which the metals are arranged in accordance with the time required for one-quarter of the surface to become covered with fouling. With some exceptions the ratings assigned on this basis agree with those of LaQue, but it is possible to draw finer distinctions within the group designated by him as least likely to foul. None of the metals remained completely free of fouling for the entire year.

Alloys containing small quantities of silver, tin, silicon, and zinc can not be distinguished with assurance from pure copper by their resistance to fouling. Additions of aluminum of 0.5 per cent or

less appear to postpone the onset of fouling. Additions of larger amounts of aluminum, tin, nickel, and zinc shorten the time required for fouling to a degree which increases as the percentage of copper in the alloy decreases. The effect of a given proportion of these alloying ingredients is to decrease the time in the following order

Aluminum Tin Nickel Zinc

as shown in Figure 2.

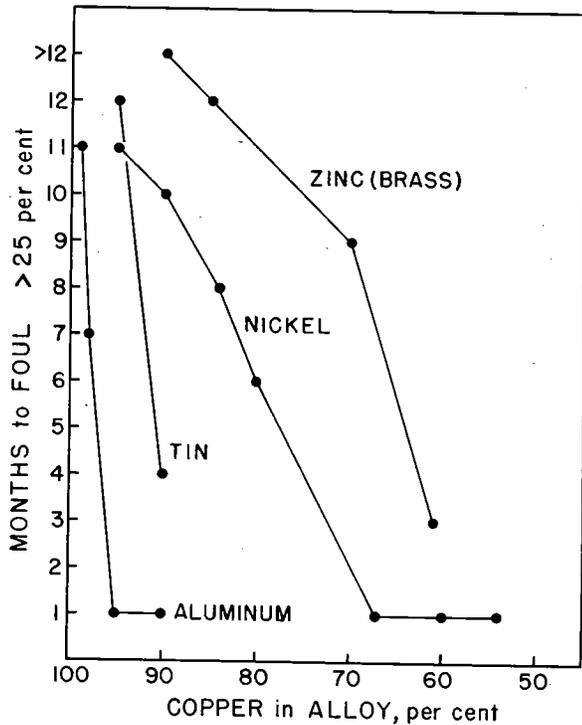


FIGURE 2. Relation of copper content to time required for alloys of copper with aluminum, tin, nickel, and zinc to develop fouling covering more than 25 per cent of surface.

Additions of a third component to an alloy sometimes increased and sometimes decreased the tendency to foul. Small additions of iron invariably shorten the time required for copper-nickel alloys to foul. Similarly, additions of aluminum to brasses cause these copper-zinc alloys to foul quickly. Small quantities of tin, on the other hand, when present in copper-zinc alloys as in Admiralty, Naval, and Tobin bronze, prolong the time of fouling when compared to simple brasses of the same copper content. (See Figure 3.)

The nickel-silvers are alloys of copper, zinc, and nickel which are combined in various proportions. Some of the resultant alloys resisted fouling very much longer than was to be expected from their copper content. Thus Ti-nic-o-sil #10 and Ti-nic-o-sil #14 containing 47 and 42 per cent copper,

respectively, compared favorably with brass containing 70 per cent copper in the time required for half the surface to become fouled. None of the nickel silver, however, had outstanding fouling resistance.

THE THEORY OF ANTIFOULING ACTION OF METALLIC SURFACES

There has been much discussion about whether metals prevent fouling because they dissolve or exfoliate too rapidly, or whether the action is a toxic one.

Exfoliation

Gross exfoliation was put forward by Sir John Hay in 1860 as the reason for the failure of copper to foul. He wrote (1),

"We find that copper oxidizes in parallel layers

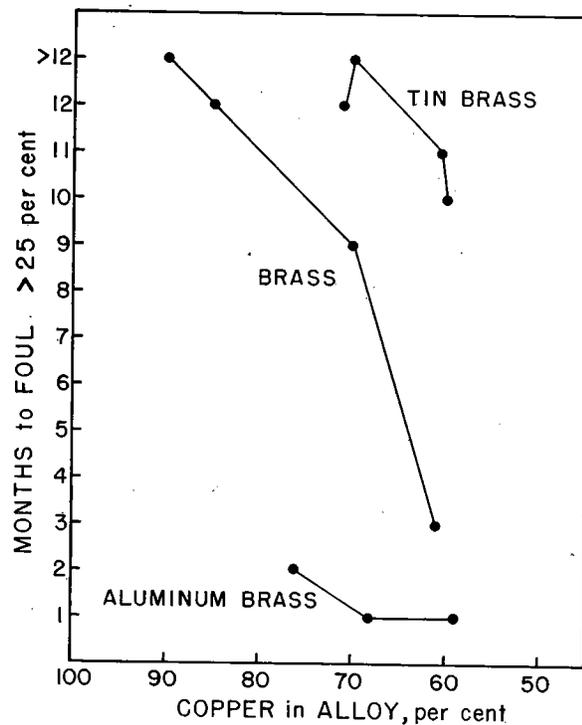


FIGURE 3. Effect of additions of tin and aluminum on the time required for brass (alloys of copper and zinc) to develop fouling covering more than 25 per cent of surface.

and that it shreds off in very thin layers, so that the substances which cause the fouling of the ship lose their hold and are detached by the continual exfoliation of the copper."

A somewhat more subtle form of exfoliation theory was proposed by Van Meerten (1), who suggested that a slightly soluble oxide of copper is formed between the scales of the barnacles and

the metal, which through its solubility is washed away, preventing the barnacles from adhering firmly to the metallic copper. It is difficult to see how this view differs from gross mechanical exfoliation in principle, since both theories depend on the sloughing off of the fouling as the result of corrosive processes at the surface of the metal.

There can be little doubt that iron and zinc remain free of fouling because of exfoliation when corrosion is accelerated by galvanic effects due to contact with more noble metals. The same is probably true of cadmium, aluminum, and mag-

Parker (23) also associated antifouling action with the solution rate. He concluded that marine animals will grow upon any heavy metal, provided that metal does not liberate ions or soluble compounds.

There can be no doubt that while solubility may be a prerequisite for antifouling action, it is not a sufficient cause unless the rate is inordinately high. The copper alloys exert a specific action which must be due to the chemical properties of that element, that is, to a true toxic effect. As evidence for this, the following facts may be cited:

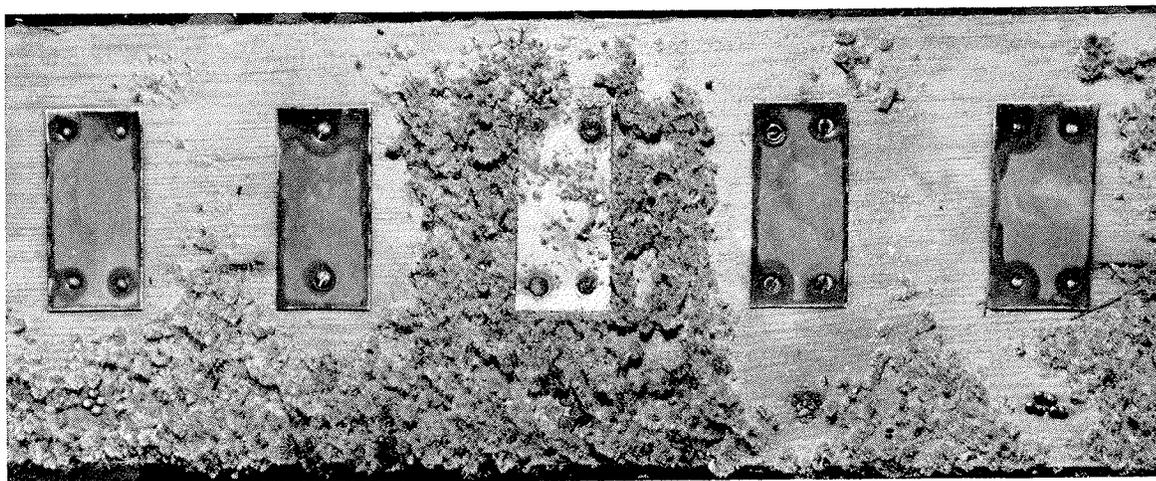


FIGURE 4. Prevention of fouling on wood surface adjacent to metallic copper. The central coupon was fastened with galvanized iron nails, which have sup-

pressed the solution of copper by galvanic action, and have permitted fouling to grow close to the metallic copper.

nesium. It has been pointed out in Chapter 13 that the critical rate of corrosion required to prevent the fouling of iron is between 4 and 9 mg./cm.²/day. This is well in excess of the normal corrosion rate of iron, which is about 0.25 mg./cm.²/day. On the other hand, copper alloys do not foul when corroding at a rate as low as 0.05 mg./cm.²/day, and it seems very unlikely that such a rate of exfoliation is sufficient to account for the effect.

Toxic Action

Antifouling action has been associated with the rate of solution or corrosion of the metal since the days of Sir Humphry Davy. He observed that when copper is coupled to iron or zinc it is likely to foul, and he realized that under these conditions the solution of the copper is prevented. Consequently, he drew the conclusion (*6*):

"There is nothing in the poisonous nature of the metal which prevents these adhesions. It is the *solution* by which they are prevented—the wear of surface."

1. Copper occurs in proportions greater than 64 per cent in all the metals which are listed in Table 1 as least likely to foul.

2. Copper prevents the fouling of neutral surfaces at a short distance. This can only be interpreted as action of a toxic nature by dissolved copper. The effect is illustrated in Figure 4, which shows several pieces of sheet copper nailed to a wooden board. Only in the case of the piece fastened with galvanized nails which have suppressed the solution of the copper, has the fouling occurred close to the copper.

3. The evidence discussed in Chapter 14 makes it clear that specific differences occur in the toxicity of metallic ions. Of the metals suitable for structural purposes, copper and silver are much the most toxic. The liability of silver to foul is presumably due to its low solubility in sea water.

Rate of Corrosion and Leaching

LaQue has attempted to determine the rate of corrosion required to free enough copper to prevent fouling in copper-nickel alloys. In a series of alloys

exposed at Barnegat Bay, New Jersey, and at Kill van Kull, New York Harbor, all specimens containing 50 per cent copper or less fouled heavily. From the weight loss of the specimens, LaQue estimated that a rate of solution of 7 to 10 milligrams of copper per square decimeter per day was sufficient to prevent the growth of fouling organisms (12). Subsequent experiments at Wilmington, North Carolina, indicated that the critical rate

rate, or to a difference in the mechanism of dissolution of a metallic surface as compared to that of a paint.

To check these alternatives, measurements were made of the weight loss due to corrosion and of the leaching rates of the series of copper alloys, whose fouling characteristics are recorded in Table 2. It was found that the losses of copper as measured by weighing did not agree well with the average

TABLE 3. Corrosion and Fouling of Copper Base Alloys Exposed to Sea Water 8 Months at Kure Beach, North Carolina¹

		Composition—per cent				Corrosion Rate mg./dm. ² /day		Fouling ³ per cent
						Total	Copper Loss ²	
Cu 99.9	O	0.04				9.8	9.8	4
Cu 99.9	P	0.01				9.4	9.4	6
Cu 99.9	P	0.02	As	0.33		10.8	10.8	2
Cu 98.0	Sn	2				9.6	9.6	2
Cu 97.5	Sn	1.5	Si	1.0		9.4	9.2	2
Cu 97	Si	3	Fe	0.10		10.2	9.9	2
Cu 95	Sn	5	P	0.1		7.6	7.2	8
Cu 95	Al	5				10.6	10.0	66
Cu 95	Al	5	As	0.25		6.5	6.2	82
Cu 91	Al	7	Si	2		6.8	6.2	64
Cu 90	Zn	10				10.8	9.6	4
Cu 85	Zn	15				10.2	8.8	8
Cu 80	Zn	20				11.0	8.8	16
Cu 76	Zn	22	Al	2	As	0.02	4.5	92
Cu 75	Zn	25				10.8	8.2	8
Cu 70	Zn	30				12.0	8.4	2
Cu 70	Zn	29	Sn	1		10.1	7.0	2
Cu 70	Zn	29	Sn	1	As	0.04	9.0	1
Cu 70	Ni	30	Fe	0.42		2.2	1.6	62
Cu 70	Ni	30	Fe	0.03	C	0.08	10.4	12
Cu 70	Ni	30	Fe	0.02	C	0.04	13.5	20
Cu 66	Zn	34				9.8	6.4	8
Cu 63	Zn	37	As	0.10		12.8	8.1	32
Cu 62	Zn	37	Sn	0.75		10.0	6.2	5
Cu 61	Zn	38	As	0.21	Pb	0.30	9.2	45
Cu 60	Zn	40				12.6	7.6	48
Cu 60	Zn	39	Sn	0.75	As	0.07	10.8	4
Cu 59	Zn	39	Sn	0.75	Fe	1.0	11.6	8

¹ This table is based on graphs kindly supplied by C. L. Bulow, Bridgeport Brass Company.

² Copper loss is estimated on the assumption that the material lost by corrosion contains copper in the proportion in which it is present in the alloy.

³ Fouling is estimated as per cent of surface covered by macro-organisms.

of solution required to prevent fouling with copper-nickel alloys is between 4.5 and 7 mg. per square decimeter per day (14).

The rate of corrosion and fouling of a large series of copper base alloys has been determined by Bulow, and is summarized in Table 3. Most of the alloys lost copper by corrosion at rates of 6 to 10 mg. per dm.² per day, and fouled only lightly. Others, corroding at comparable rates, fouled heavily. Heavy fouling occurred on all those alloys which lost less than 6 mg. per dm.² per day.

It is evident that fouling on copper alloys may occur at corrosion rates which indicate a loss of copper much greater than the leaching rate of 1.0 mg./dm.²/day which is known to prevent fouling on paints pigmented with metallic copper or cuprous oxide. This difference might be due to some difference between the method of measurement of copper loss by corrosion and by leaching

leaching rates as measured by the standard method used in testing antifouling paints. The weight loss method gave results which averaged 0.4 to 0.3 the leaching rate value. This difference can not explain the discrepancy in the critical rates of solution required to prevent fouling in the case of paints and copper alloys, since it is in the wrong direction. The experiments indicated that the resistance of copper alloys to fouling correlated with the leaching rate, and confirm the view that copper must be given off at much greater rates to prevent fouling than in the case of paints.

When freshly exposed in the sea, copper dissolves at a rate which is relatively great. During prolonged exposure, the rate of solution declines regularly for about six months, after which it becomes almost constant at a value about one-tenth the initial rate. (See Figure 5.) The alloys of copper behave similarly, but with initial and

final rates of solution which are characteristic of the kind and quantity of alloying metal. In general it was found that the metals did not foul until the leaching rates had fallen from their initial high values. Those which fouled heavily in the first month or two were characterized by relatively low initial leaching rates. Within each group of similar alloys the tendency to foul increased and the leaching rate decreased as the proportion of copper in the alloy was less.

In the case of the copper-zinc alloys it was possible to show a close statistical correlation between the fouling at any time and the leaching rate of the alloy after a corresponding period of exposure. This correlation is presented in Table 4,

TABLE 4. Correlation of Fouling (at Miami) and Copper Leaching Rate (at Woods Hole) of Specimens of Copper-Zinc Alloys After Corresponding Periods from One to Twelve Months of Exposure in the Sea. The Numbers Indicate the Number of Cases in Each Class

Leaching Rate mg./dm. ² /day	Fouling Rating					
	0	1/2	1	2	3	4
0-0.9					1	4
1-1.9					1	2
2-2.9	1		4	2	2	
3-3.9	3		7	1	1	
4-4.9	1	1	5	1		
5-5.9	5	2				
6-6.9	4	1				
7-7.9	1					
8-8.9	1					
9-9.9	1					
>10	7					

Fouling Rating 0=no fouling
 1/2=incipient fouling
 1=<25 per cent surface covered
 2=25-50 per cent surface covered
 3=50-75 per cent surface covered
 4=>75 per cent surface covered

which shows that fouling may be expected to begin when the leaching rate falls to about 6 mg./dm.²/day and will be complete with leaching rates of 2 mg./dm.²/day. A very similar correlation was obtained in the case of a selected group of alloys by comparing the average copper leaching rate after prolonged exposure with the fouling at that time. This relation is shown in Figure 6, and applies to the data for the specimens of aluminum bronze, silicon bronze, brass, and tin bronze. With pure copper, tin bronze, and the alloys of nickel, leaching and fouling are less closely correlated, and in general fouling may occur at higher leaching rates (25).

LaQue suggests (16) that the copper alloys which do not dezincify may be divided into at least two broad classes which corrode in sea water in quite different ways, and which show in consequence quite different behavior when solution rates are related to the tendency to foul.

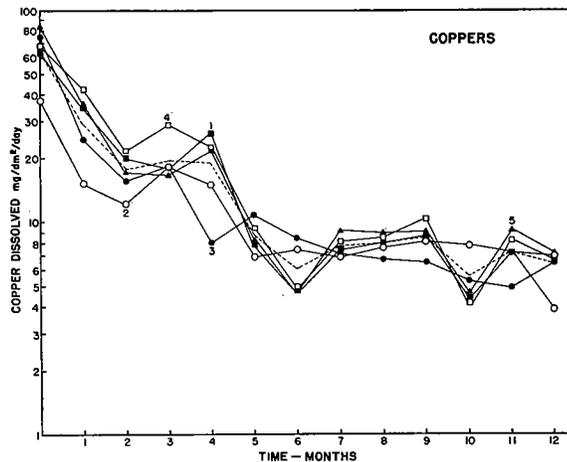


FIGURE 5. Copper leaching rates of four specimens of metallic copper during prolonged exposure in the sea at Woods Hole.

The first class includes copper, copper-silicon alloys, copper-nickel alloys of low iron content containing less than 30 per cent nickel, copper-nickel-zinc alloys (nickel silvers), brasses containing less than 15 per cent zinc, and true tin bronzes. These are characterized by uniform corrosion of the whole surface.

The second class includes copper-nickel alloys containing more than 40 per cent nickel (or a lesser amount of nickel when small percentages of iron or aluminum are present) and aluminum bronzes.

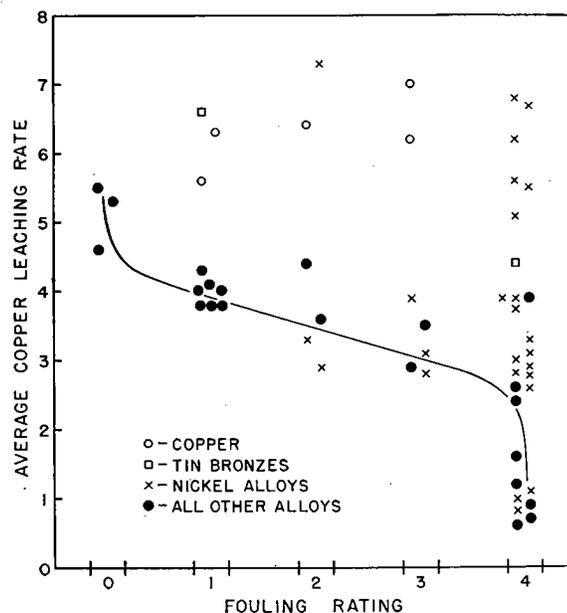


FIGURE 6. Correlation between fouling and the copper leaching rate of copper and its alloys. Ordinate: average leaching rate of specimens after 10, 11, and 12 months' exposure at Woods Hole. Abscissa: Fouling rating after 11 months' exposure at Miami. Fouling Rating 0=no fouling
 1=<25 per cent covered
 2=25-50 per cent covered
 3=50-75 per cent covered
 4=>75 per cent covered

These alloys are characterized by non-uniform corrosion. The attack is confined chiefly to well defined areas, while the rest of the surface is attacked only slightly or not at all. Fouling can occur readily on the unattacked areas, even though copper may dissolve at high rates from the attacked areas.

It is probable that inequalities in the leaching rate of different parts of the surface of metals of the second class are responsible for the anomalous fouling characteristics of copper base alloys. The distinction between the types of corrosion on which the classes depend is not rigid. Presumably, it depends on characteristics of the corrosion films which passivate the surface. In metals of the first class these are relatively uniform and stable. In those of the second class, they are less stable and tend to break down locally, forming anodic areas which corrode, and at the same time protect the remainder of the surface, which becomes cathodic, against corrosion.

MODIFICATIONS IN TOXICITY OF METALLIC SURFACES

Corrosion Products

When fresh surfaces of zinc or galvanized iron are exposed in the sea, fouling is retarded for some time, but ultimately the surface may become completely covered with a dense growth of organisms. Orton observed that zinc fouled after about 3 months' exposure at Plymouth (22). Copper sheathing also appears to lose its antifouling properties at times, but the testimony is somewhat conflicting, indicating that the phenomena may vary greatly depending on unknown circumstances. The sheathing on the *Alarm* apparently prevented fouling during a period of 20 months. It is stated, on the other hand, by Young (29) that the ships of the British Navy commonly had to be cleaned after 10 months' service.

While there can be little doubt that copper sheathing frequently fails to protect ships after some time, it is far from clear that this is a regular happening, or what the circumstances are which lead to its occurrence. Van Meerten, who was Chief Constructor of the Dutch Navy, has reported (1), "From time to time I have docked copper-sheathed ships badly fouled, without having discovered any apparent reason for this fouling. And, curiously enough, copper which has lost its antifouling properties seems not to be able to recover them. Copper once fouled, either by electro-negating it with zinc, or through other unknown reasons, however well cleaned in

dock, soon becomes again fouled. Some permanent setting of the molecules must be the cause of this strange circumstance."

Observations by Edmondson and Ingram (8) may have some bearing on this experience. They state that copper and brass panels which are relatively effective in preventing fouling apparently no longer possess this efficiency upon re-exposure after short-time removal from the water. Copper plates free from organisms after one month in the sea were exposed to the air for 30 days, after which they were replaced in water. In 26 days they had fouled heavily with serpulid worms, *Bugula*, and a few barnacles, which from their size were judged to have made attachment immediately following resubmergence. Unfortunately, no control is recorded to show that a similar plate would not have fouled had it not been exposed to the air.

LaQue (16) has observed that corrosion products formed by exposure to the atmosphere may have a temporary effect on the resistance of copper to fouling. Some specimens which had been previously exposed in the sea were cleaned to remove salt water corrosion products, and were stored for a year or more. When re-exposed in the sea these specimens fouled. After two to three months, however, the fouling disappeared and the specimens became indistinguishable from controls which had been sand blasted and had remained free of fouling at all times.

In order to test the effect of exposure to air on the fouling of copper, two panels were exposed at Miami respectively to corrosion in the sea and in a moist situation in the air. After 172 days both had become covered with a green deposit. The panel which had been in the air was then immersed in the sea, whereupon it fouled lightly. This seems to support the idea that corrosion in the air favors the attachment of fouling to copper. On the other hand, a third panel which had been corroded in the sea was exposed to the air for 7 days. On returning the panel to the sea, it remained free of fouling. In other experiments copper panels were allowed to corrode in the sea for 1 month, and others for 8 months, and were then allowed to dry in the air for periods ranging from 1 to 6 weeks before being reimmersed in the sea. Fouling was limited to a few colonies of a bryozoan, *Wateripora cucullata*, which is exceptionally resistant to copper poisoning, and to an occasional small barnacle. No relation between the duration of drying and the tendency to foul was evident.

It is natural to attribute changes in the fouling resistance of exposed metallic surfaces to the accumulation of corrosion products on the metal surface.² These deposits were described in some detail by Sir Humphry Davy (7) who wrote, "When copper has been applied to the bottom of a ship for a certain time, a green coating or rust consisting of oxide submuriate and carbonate of copper, and carbonate of magnesia, forms upon it to which weeds and shellfish adhere.

"As long as the whole surface of the copper changes or corrodes, no such adhesions can occur."

While Davy considered that the corrosion products favored the adhesion of fouling, Holtzapfel (10) attributed the antifouling action of copper to the toxic nature of this material. This view has its modern counterpart in the suggestion that deposits of basic cupric carbonate are an indication of good antifouling action in paints (see Chapter 14). In favor of Holtzapfel's view, as against Davy's, it may be pointed out that the copper surfaces which remain free of fouling after long exposure to sea water are invariably covered with a green deposit.

A consideration of the leaching behavior of copper and its alloys throws light on the relationship of corrosion products to fouling. As the data illustrated in Figure 5 show, the rate of solution of copper is greatly depressed as time permits the corrosion products to accumulate. It is difficult and perhaps meaningless to state whether the toxicity of the surface is due to copper ions derived from the solution of the original copper or from the deposit. The important point is that the overall solution rate on which antifouling action depends is reduced with the accumulation of the deposit, and may be reduced to levels which permit fouling.

There is some evidence that over long periods of immersion the protection afforded by corrosion products increases. Thus, in Figure 5, the leaching rate of copper shows a progressive decline, at least for a while. Studies of the corrosion rate of copper exposed at half-tide level by Tracy, Thompson, and Freeman (27), indicate that the weight loss declines with time during the first and second year of exposure. From their data the following average daily solution rates may be calculated.

During first ½ year	90 mg./dm. ² /day
During second ½ year	26 mg./dm. ² /day
During second year	21 mg./dm. ² /day

² The chemical character of the corrosion products which result from interaction of copper and sea water are discussed in Chapter 15.

LaQue and Clapp (17) show that the corrosion rates of copper and copper-nickel alloys of high copper content decrease with time of exposure to sea water. In the case of copper, the weight loss is at a rate of 37 mg. per dm.² per day in the first 10 days. After prolonged exposure the rate is reduced to about 10 mg. per dm.² per day (16). These observations may be associated with the fact mentioned in Chapter 15 that basic cupric carbonate becomes less soluble on ageing in sea water.

Galvanic Action

The occasional or ultimate fouling of copper sheathing has been attributed by Kühl (11) to the presence of impurities giving rise to electrolytic effects. There can be little doubt that in many cases the failure of copper to protect is due to the presence of dissimilar metals in contact with the copper sheathing. It will be recalled that on the *Alarm* fouling was noted on the rudder where iron nails had been used to attach the copper plates. Sir Humphry Davy observed (7), "In general in ships in the Navy, the first effect of the adhesion of weeds is perceived upon the heads of the mixed metal nails which consist of copper alloyed by a small quantity of tin."

A ship's boat was recently exhibited at the Mare Island Navy Yard in which the sheathing was heavily fouled along the edges of the plates over the fastenings. A yacht examined at Miami was found to have a large copper plate attached to the bottom with Everdur screws. This plate had fouled over the screw heads.

A striking example of the inactivation of the copper sheathing of a wooden vessel is shown in Figure 7. Heavy fouling has occurred over an area of 100 square feet about the propeller struts and rudders on which zincs were mounted. Resistance measurements showed in this case that the zincs were not properly insulated from the copper sheathing of the hull. Extending forward from the inactivated area, a heavy slimy fouling occurred for a distance of five or six feet. The remainder of the underbody was unfouled except that each seam overlap of the copper plates and each nail head were lined or coated with heavy slime which may be seen in the figure hanging down.

Although the action of the base metals in inactivating the antifouling property of copper sheathing was noted in the report on the *Alarm*, the first to explain the nature of this action was Sir Humphry Davy, who had been asked by the Admiralty to consider methods of reducing the rapid erosion of copper sheathing employed on

men-of-war. Davy was aware that, when two metals were brought in contact with one another and with sea water, an electro-chemical couple is set up, with the result that the baser metal dissolves and the solution of the nobler metal is inhibited (5). He consequently proposed that the dissolution of the copper plates on ships could be suppressed by placing bars of base metal, such as zinc or iron, in contact with the ship's plating.

copper by the galvanic couple formed with the iron or zinc. Davy's experiment, showing that copper will foul when coupled with a baser metal, has been repeated by Parker (23), who found, in addition, that zinc also loses its somewhat mild antifouling action when coupled with aluminum. Davy's experiment has also been confirmed by Copenhagen (3), Kühl (11), LaQue (12), and doubtless many others.

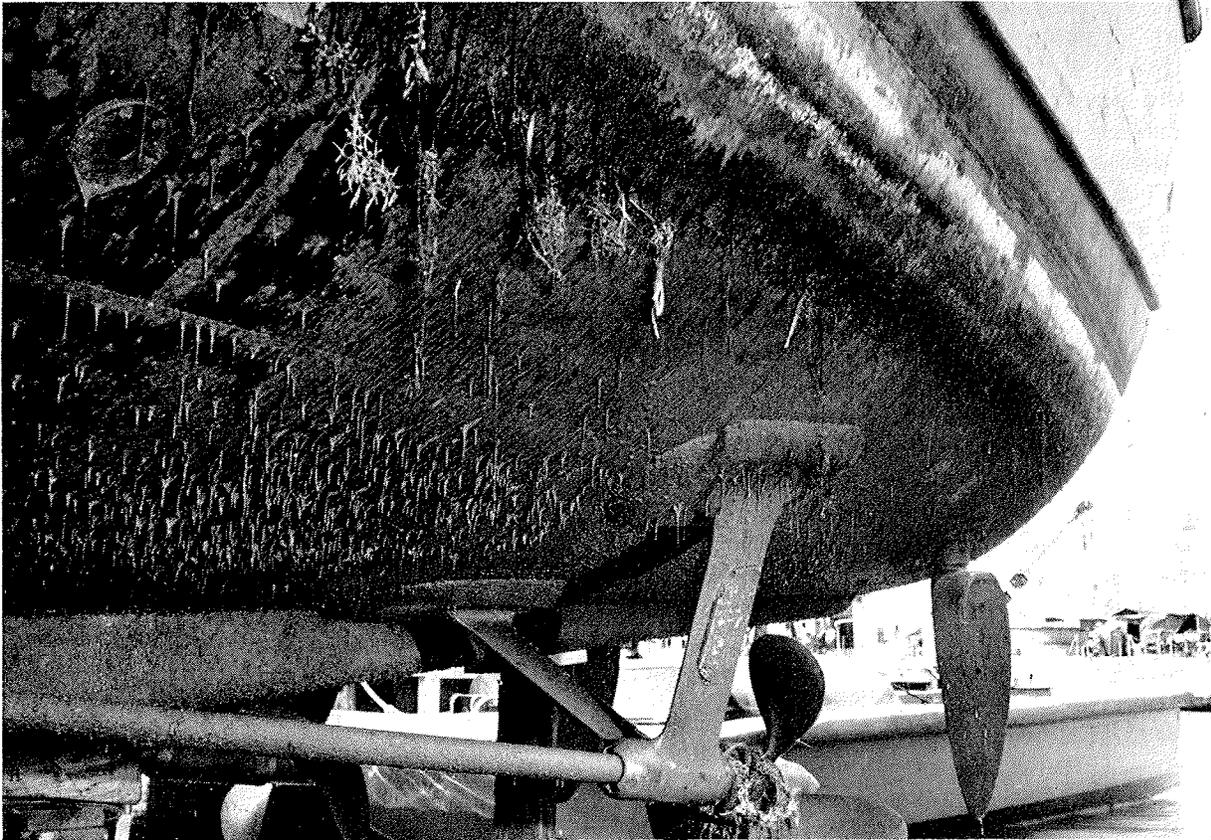


FIGURE 7. Fouling of copper sheathing in the neighborhood of propeller struts on which zincs were mounted. The areas of the hull in the upper left hand corner, which appear dark, are unfouled except over the nail heads and along the seams.

His experiments showed that extremely small surfaces of iron or zinc would serve to protect areas of copper more than 150 times as great from corrosion. When protective bars of iron were attached to the plates on the bows of a swift ship, the wearing away of the copper plates was reduced to less than one-third the value observed when the plates were unprotected (6). The use of protectors introduced by Davy still finds its counterpart in the zincs which are applied to modern vessels to minimize corrosion.

Unfortunately, Davy's protectors also protected the fouling organisms from the toxic action of the copper surface, an effect which he correctly attributed to the suppression of the solubility of the

The fundamental observations required for predicting galvanic effects were first made by Volta. He showed that the metals could be arranged in a series so that, when two metals were coupled by a salt solution, the metals higher in the series were electronegative to the lower ones. The work of physical chemists at the end of the last century led to the view that when a metal is immersed in an aqueous solution, positive metal ions dissolve from the surface, leaving the metal negatively charged. This reaction continues until the resulting polarization at the metallic surface checks further solution. When this condition is reached, the metal is found to have a potential, relative to the liquid, which is characteristic of the kind of metal.

The order of these potentials agrees with the position of the metal in the galvanic series, and it may be assumed as a first approximation that the strength of a galvanic couple will be equal to the difference in potential of the two metals which form the couple.

It is undoubtedly true that the couples which exist on ships' bottoms, due to the juxtaposition of copper sheathing and nails and other hardware, depart rather widely from these ideal conditions, since equilibrium is doubtless rarely reached between the metal and the sea water. Otherwise, the metal would not continue to corrode. Also, the reaction products formed at the surface between sea water constituents and metals modify the conditions at the surface greatly.

TABLE 5. Galvanic Series in Sea Water After LaQue and Cox (18)

- Magnesium, magnesium alloys
- Zinc, galvanized steel, galvanized wrought iron
- Aluminum 52SH, 4S, 3S, 2S, 53S-T, alclad
- Cadmium
- Aluminum Al7S-T, 17S-T, 24S-T
- Mild steel, wrought iron, cast iron
- Ni-Resist
- 13% chromium stainless steel type 410 (active)
- Lead tin solder 50-50
- Stainless steel 18-8 type 304, 18-8-3 type 316 (active)
- Lead, tin
- Muntz metal, manganese bronze, Naval brass
- Nickel (active), inonel (active)
- Yellow brass, Admiralty brass, aluminum bronze, red brass, copper, silicon bronze, ambrac, copper nickel 70-30, comp. G-bronze, comp. M-bronze
- Nickel (passive), inonel (passive)
- Monel
- Stainless steel 18-8 type 304, 18-8-3 type 316 (passive)

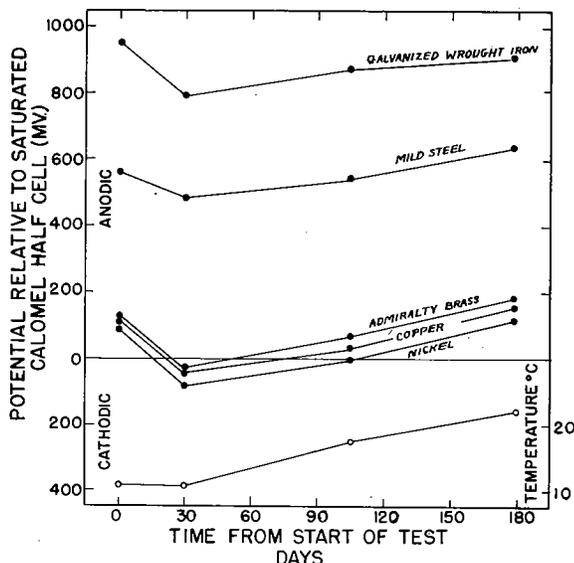


FIGURE 8. Potentials of metals in flowing sea water. Selected curves modified after LaQue (12).

From these results it may be seen that the various alloys of copper do not differ greatly in the ranges of their potentials, and it is probable that these alloys may be coupled without inducing serious corrosion. This fact is commonly taken into account in the construction of vessels and equipment to be exposed to salt water. On the other hand, it is quite evident that small differences in potential can exist between these metals, provided the state of activity of the coupled members does not vary in the same way. At present there appear to be no measurements to show the potentials which actually exist with such permanent couples in sea water.

Experiments have been conducted in Miami with a view to determining whether the coupling of metals which differ only slightly in position in

LaQue and Cox (18) have made a careful study of the potentials existing between a variety of metals and flowing sea water. Their results show that in a general way the potentials observed under this condition follow the same order as the potentials of metals in equilibrium with solutions of their own salts. The values of the potentials observed, however, were somewhat different and showed a striking change with time. In general, the potentials became more positive during the first month and then returned to their original values, and in some cases became even more negative. Different metals varied in the intensity and regularity of these effects, as is shown in Figure 8. In spite of this difficulty, LaQue and Cox have grouped the commoner metals in a series of increasing potentials as shown in Table 5. Within each group the members may change places depending on conditions of exposure. The range of variation in potential as commonly observed is shown in Figure 9.

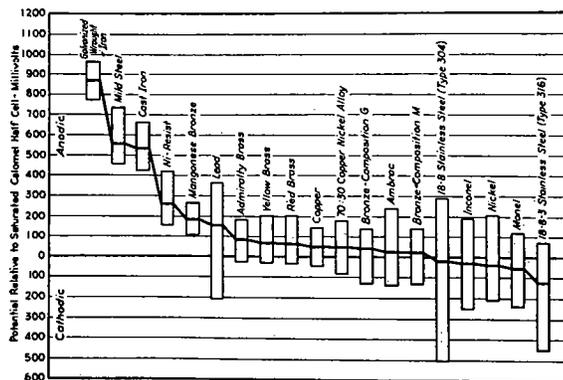


FIGURE 9. Potentials of metals and alloys in flowing sea water. From LaQue and Cox (18).

the galvanic series, would lead to the inactivation of the antifouling properties of copper and its alloys. This experiment was arranged so that 6 by 18-inch plates of Muntz metal, soft copper, brass, and nickel-silver were coupled each with 6 by 6-inch plates of one of a number of metals chosen so as to cover a wide range of potentials. These plates were exposed to the sea at Miami for 12 months. Zinc, galvanized iron, and aluminum completely inactivated the various copper alloys, as was to be expected. These metals differ in potential from the copper alloys by more than 200 millivolts. Lead did not produce or increase fouling of any of the copper alloys.

Stainless steel, Monel, and brass appeared to increase the fouling which occurred on Muntz metal and nickel-silver. There was no clear evidence that the smaller pieces of inconel, nickel, nickel-silver, or Muntz metal influenced the antifouling action of the larger pieces of any of the metals. However, when the influence of the larger pieces on the fouling of the smaller was examined, it was found that Muntz metal caused light fouling on copper and increased the fouling on nickel-silver. There was some evidence that Muntz metal and nickel-silver inactivated the brass.

The experiment also brought out the interesting fact that the resistance to fouling of small pieces of Muntz metal was improved when coupled to larger pieces of nickel-silver or brass. The same effect was observed with a small piece of nickel-silver when coupled with larger pieces of copper. Neither of these fouled in twelve months, though uncoupled specimens fouled after the first few months of exposure.

While the results of this experiment were not sufficiently clear cut to permit arranging the several alloys in a series which would enable predictions to be made as to which metal would influence another, they indicate that metals closely associated in the electro-chemical grouping shown in Table 5 may, nevertheless, influence the fouling resistance of one another when coupled. Three factors may be discerned which appear to determine whether one metal inactivates another. These are:

1. electro-chemical potential
2. relative size of the two coupled surfaces
3. inherent solution rate

The influence of electro-chemical potential is evident in the action of zinc, iron, and aluminum. The observations that Muntz metal influenced or

was influenced by other copper alloys may be associated in part with the fact that it is slightly more electronegative than the others. The increased antifouling action produced by coupling Muntz metal with copper is particularly interesting since it indicates that galvanic action has increased the solution rate of Muntz metal, as it should on electro-chemical grounds.

The influence of the relative area of the coupled members is in agreement with the well established facts of corrosion. It is known that the corrosion of iron when coupled to copper is proportional to the ratio of the area of copper to that of iron (13).

The influence of the inherent solution rate of the metal is particularly important in the inactivation of antifouling surfaces, since a fairly definite solution rate determines whether the fouling does or does not occur. It is noteworthy that the metals which were most definitely influenced by coupling to other alloys are Muntz metal and nickel-silver, both of which fouled lightly when coupled with themselves. Apparently, these metals give off copper nearly at the critical rate. Obviously, the lower the natural rate of solution from the metallic surface, the less potential difference is required to suppress solution to below the critical level. This matter can be formulated in a quantitative manner.

Theoretically, the rate of solution of an anodal surface is proportional to the current density across the surface. Copper dissolves at a rate of 28.4 mg. per day per milliamper, assuming the product is Cu^{++} (or 56.8 mg. per day per milliamper, assuming Cu^+ to be the product). Presumably, the solution rate is decreased in the same ratio at the cathode. It is not clear whether the product is Cu^{++} or Cu^+ , or on what conditions their ratio depend. However, some rather rough experiments with copper/iron couples in sea water, made by G. T. Scott, have indicated that applied potentials increase the rate of solution of the copper by about 35 mg. per cm^2 per day for each milliamper per cm^2 when the copper is the anode. When the current flowing through a couple as the result of its inherent electromotive force was decreased by introducing resistance between the electrodes, it was found that the solution rate of the copper cathode increased about 35 mg. per dm^2 per day for each milliamper per cm^2 drop in the galvanic current.

This result is of interest because it indicates what very small current densities are required to suppress the solution of copper from a surface. Copper has a solution rate of about 0.07 mg. per

cm.² per day after a few months' exposure to the sea, as shown in Figure 5. Solution of copper would be entirely suppressed by a current density of 0.002 milliampere per cm.² A potential difference due to galvanic coupling of 1 millivolt would yield this current density, provided the conductance of the system exceeded 0.002 mho. per square centimeter of surface.

There is every reason to believe that propellers as commonly mounted form effective galvanic couples with the iron or steel structures of the ship. In large vessels the propeller shaft is frequently composed of steel. In small boats it is more

is proposed that the damage caused by the field in promoting corrosion of the steel hull, and in suppressing the antifouling properties of the bronze propellers, may be remedied by placing a nonconducting insulation between the propeller shaft and the propeller, since this would serve to break the galvanic couple.

METALLIC COATINGS

Various attempts have been made from time to time to apply coatings of copper directly to the steel plates of ships or to wood. For this purpose, copper has been deposited on the metal by elec-

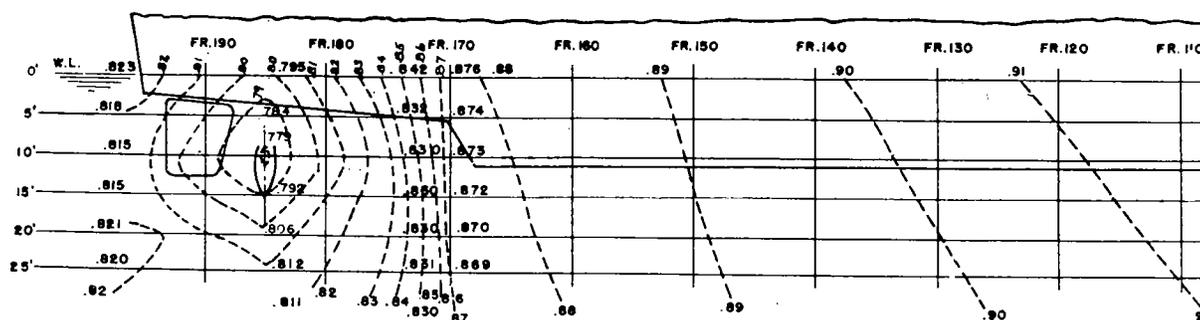


FIGURE 10. Electric field surrounding U.S.S. *Farenholt* (D.D. 491). Potentials in volts relative to calomel electrode. From Reference 2.

commonly made of bronze, so that the entire assembly exposed to the sea water appears to be composed of the same metal. However, inside the vessel the propeller shaft is coupled to the iron of the engine, which in turn makes contact with sea water through the circulation of cooling water. It is, consequently, not at all surprising that propellers are generally inactivated and frequently foul before other parts of the under water surface.

Extensive measurements have been made of the potential field surrounding the propellers of Naval vessels (2). It has been found that when a submarine is launched and before the propeller shafts have been connected with the machinery, a current of about $2\frac{1}{2}$ amperes may flow through an ammeter connecting the shaft to the hull. The shaft bearings on the strut and on the stern are of lignum vitae or Bakelite, which serve as an insulation. It was estimated that the current density entering the propeller surface is about 25 milliamperes per square foot. This is sufficient to suppress a natural solution rate of 95 mg. per dm.² per day, which is 13 times the probable leaching rate of the propeller. The potential field surrounding the propeller is illustrated in Figure 10. Similar fields are found to surround the bronze structures at the mouths of torpedo tubes of submarines. It

trolysis, by spraying, or by suspending it in a matrix in powder form as in a "bronze" paint.

Atherton (1) has described several early attempts to coat the steel plates of vessels electrolytically. Cofferdams were constructed to fit various sections of the ship and were filled with the electrolyte, so that the entire bottom could be covered with a deposit of copper. A tug which was treated in this way was found to be so badly damaged after two years, owing to galvanic action, that the treatment was abandoned. In the United States a method known as Crane's System for copper plating the entire hull of a ship was favorably reported on to the Government after trials lasting four years. The method does not seem to have come into general use.

Experiments to determine the practicability of spraying wooden boat bottoms with copper have been conducted by the U.S. Naval Engineering Experiment Station (28). Copper sprayed on the planks of the bottom of a wooden boat were found to be superior in condition to copper-painted surfaces after 311 days. Although the coating had been dislodged over a number of small areas, these areas showed no appreciable fouling. This method of treatment does not yet appear to have received any general use.

The application of metallic copper in powder or flake form as a paint has been considered in the chapters dealing with paints. The tendency of such coatings to accelerate corrosion, and to become inactivated by galvanic action, will be discussed in the following chapter.

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