Marine Fouling and Its Prevention,
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CHAPTER 11

The History of the Prevention of Fouling

The effects of fouling have only recently been subject to systematic scientific inquiry. Its seriousness, however, has been recognized from very ancient times. Although written records of the treatment of ship bottoms as early as the 5th century B. C. have been found, the search for an antifouling surface undoubtedly began with even earlier ships about which we have little information.

Historically, the development of these surfaces falls readily into three parts: (1) the repeated introduction and use of metallic sheathing, culminating in the discovery of copper sheathing as an effective antifouling surface; (2) the invalidation of the use of metallic copper on iron hulls because of galvanic effects, which followed the development of iron ships; and (3) the eventually successful efforts to devise antifouling paints that, in the case of iron or steel hulls, could be applied over an anticorrosive coating.

Numerous other antifouling devices were continually being tried or suggested. In periods of peace, the tendency has been to use the current antifouling system regardless of its efficiency. Periods of war have always intensified experimental investigation.

EARLY SHIPBOTTOM SURFACES

The history of both ships and sea power is older than written records, some of the great maritime nations of the ancient world being known to us only through the records of a later period. But even the earliest records, although they say little or nothing about shipbottom treatment, tell of large fleets and big ships, of long voyages and naval battles. We can assume, therefore, that fouling was a problem to ancient ships even though we do not know what measures were taken against it.

The early ships and fleets were larger, and the voyages longer, than is generally realized. Ancient Egyptian ships were sometimes 160 feet long (*23*) and traded as far as the land of Punt (Somaliland) (*22, 77*). The Phoenicians in 1000 B. C. were reputed to have circumnavigated Africa, voyaged to Cornwall in Britain for tin, and as early as the 6th century B. C. explored the west coast of Europe (*60, 73*). Early sea fights involved fleets of hundreds, and sometimes thousands, of ships (*52, 85, 93*). While the warships of the ancient world were often intended to be beached, or even transported overland, the merchant ships were not and were correspondingly larger (*22, 93*). An Egyptian corn ship at Piraeus in Roman times was described by Lucian (*66*) as "180 feet long, over a quarter of that in width, and 44 feet from deck to keel;[1] with a crew like a small army, and carrying as much corn as would feed every soul in Attica for a year".

The earliest mention of fouling that we have found is a casual reference to it in connection with the Echeneis or Remora; the fabled "ship-stopper". This comparatively small fish, mentioned by Aristotle as early as the 4th century B. C., is credited by both ancient and modern writers with being able to slow down ships going at full speed, or even to stop them entirely as if they were tied to one spot in the ocean. In commenting on this belief, Plutarch (*82*) pointed out that fouling rather than the Echeneis might be responsible. He stated that it was usual to scrape the weeds, ooze, and filth from the ships' sides to make them go more easily through the water. In 1559 Laevinus Lemnius (*64*) wrote "shell-fish and a little fish called Echeneis stick so fast that they will stop ships, and hinder their courses, therefore our men use to rub them off with sharp brushes, and scrape them away with irons that are crooked for the purpose, that the ship being tallowed and careened well and smoothly may sail the faster".[2]

The ancient Phoenicians and Carthaginians were said to have used pitch and possibly copper sheathing on their ships' bottoms (*69*). Wax, tar, and asphaltum also have been used from very early times (*21, 55, 77, 95*). We can not be certain of the purpose of these surfaces even in later times when written records exist. While it is probable that some of them were at least in part an attempt to prevent fouling, they may also have been applied for water-tightness, to achieve a smooth surface, for structural strength, or, particularly in the case of metallic sheathing, as protection against ship worms.

There is a record of the use of arsenic and sulfur mixed with oil in 412 B. C. (*27*). The Greeks are known to have used tar or wax, and, at least as

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[1] This ship, the *Goddess Isis*, was not unusually large (*23*); other Roman corn ships were up to 200 feet long (*53*). As a comparison, the U.S.S. *Constitution* was 174 feet 10 inches on the main deck (*43*).

[2] See Gudger (*46*) for a full discussion of this subject.

early as the 3rd century B. C., lead sheathing (*77, 95*). The wax was applied hot and was burnt into the hull with hot irons, a process that became known as "encaustic" or as "ship-painting". According to Pliny, coatings of this nature applied to vessels "will never spoil from the action of the sun, winds, or salt water" (*81*). When lead sheathing was used, it was attached to the ship's hull with copper or gilt nails, usually over an insulating layer of paper or cloth (*4, 21, 77*). According to Chatterton (*22*), this suggests strongly that the corrosive effect of lead on iron, which finally forced the discontinuance of lead sheathing altogether, was recognized even then.

In spite of its corrosive action, lead sheathing was perhaps the material most frequently tried for the protection of ship bottoms prior to the 18th century. Repeated attempts to use it had been made from the time of the ancient Greeks. The ships of Archimedes of Syracuse (287–212 B. C.), for example, were sheathed with lead and fastened with heavy copper bolts (*9, 95*). The Romans also used lead sheathing (*54*), and several of their ships, with the lead sheathing intact, have been recovered within comparatively modern times (*11, 104*).

Although forgotten for several centuries, lead was used in 15th century England. In the reign of Henry VI (1421–1471), a report of a ship sent on a voyage of discovery records as an "invention" that "they cover a piece of the Keeles of the Shippe with their sheets of Leade, for they have heard that in certain partes of the ocean a kind of wormes is bredde which many times pearseth and eateth through the strongest oake that is". While lead sheathing is a poor antifouling surface, it would be, as this 15th century report suggests, a good protection against ship worms. This report suggests, also, that in England lead sheathing was not usually used at that time. Its use was said to be copied from contemporary Spanish ships (*22*).

Leonardo da Vinci designed a rolling mill in 1500 for making sheet lead (*51*). Early in the 16th century, Spain officially (*34*) adopted lead sheathing, and its use spread to France and England (*14*). In the reign of Charles the Second (1660–1685), a monopoly was granted to Howard and Watson for the use of milled lead for sheathing; and it was ordered that no other sheathing be used on His Majesty's ships (*38, 49*). Accordingly, the *Phoenix* and some twenty other ships were sheathed with lead fastened with copper nails (*18*). Shortly after, however, complaints were made of the corrosive effect of lead on iron,[1] the *Plymouth* and other ships having had their rudder irons so eaten as to make it unsafe for them to go to sea (*68, 79*). In 1682, a commission was appointed to make an investigation, and on the basis of its report, lead was officially abandoned by the Admiralty (*79, 104*).

In spite of the commission's findings, rollers for milling lead into sheets for sheathing were patented in 1687. Even after the successful introduction of copper sheathing in 1761, lead was still occasionally tried. In 1768, the *Marlborough* was sheathed with lead; but two years later, when she was docked at Chatham, the iron fastenings were found to be so deeply eaten away that the lead was stripped off and replaced with wooden sheathing (*104*).[2]

In the time of Henry VIII (1509–1547) and during the 17th century, wooden sheathing was put on over a layer of animal hair and tar. This was reported to prevent the worms from penetrating to the planking, although it greatly increased the cost of building (*22, 30, 104*).[3] An outer wooden sheathing was not new. Although it is said to have been introduced by Hawkins under Queen Elizabeth, it appears to have been used in the 15th century (*22, 49*). In the 18th century, after lead, with which it apparently alternated, had been pronounced a failure, wood sheathing was again in general use (*12, 49*). It was sometimes filled with iron or copper nails having large heads, put in so closely that the heads were touching and formed a kind of metallic sheathing (*38, 69*). This wooden sheathing also was often painted with various mixtures of tar and grease; with sulfur, oil, "and other ingredients"; or with pitch, tar, and brimstone (*12, 18, 38, 49*).

Other early shipbottom surfaces besides wood or lead sheathings were also recorded. The Vikings of the 10th century A. D., although they generally painted their boats above the water line, used nothing on their ships' bottoms (*36, 84*). They tell in one of their sagas, however, of a small boat that was protected from the worms by "seal tar" (*91*). In Aragon, a sheathing of hides was used in the 14th century (*34*). Pitch was commonly used from the 13th to the 15th centuries, sometimes mixed with tar, oil, and resin, or with tallow (*12*). The great Venetian fleets of the 15th century used tar (*63*).

Morison (*74*), in his life of Columbus, says that

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[1] Lead was also reported to be too soft to stay on the hull (*49*), and many objected to its dead weight (*89*).

[2] Hay differs in saying that the *Marlborough* was docked, not at Chatham, but at Sheerness, where the lead sheathing was found to have been nearly all lost due to its softness (*49*). (See also Fincham (*38*).)

[3] It was also believed to increase the ship's resistance. In 1663, the officers of a fleet under Sir Thomas Allen fitting out to attack the Algerians petitioned that they might not have their vessels "so encumbered" (with sheathing) as they would be unable to overtake the light-sailing unsheathed vessels of the enemy (*104*). A letter from Holland in 1666 pointed out that "the hair, lime, etc. does not altogether affright the worms while it much retards the ship's course" (*7*).

the ships' bottoms of that period were "covered with a mixture of tallow and pitch in the hopes of discouraging barnacles and teredos"—in spite of which the vessels had to be careened every few months to have the marine growths removed. In the time of Vasco da Gama (1469–1524), the Portuguese charred the outer surface of the ship's hull to a depth of several inches; and several centuries later, in 1720, the British built at least one ship, the *Royal Williams*, entirely from charred wood (*7*, *69*, *84*).

With the discovery of the antifouling qualities of copper sheathing, however, and the subsequent widespread use of copper, these earlier shipbottom surfaces fell quite generally into disuse.

COPPER SHEATHING

The first successful antifouling surface to receive general recognition was copper sheathing. Although it has been stated that copper sheathing was used in ancient times (*55*, *84*), the evidence is not clear, and its use as sheathing on ships' bottoms is denied by some authorities (*22*, *77*). The actual ships that have been recovered have been lead sheathed (*11*, *104*). The first certain use of copper on ships seems to have been in the bronze-shod rams of the Phoenician warships and as copper fastenings in the Greek and Roman boats, rather than as antifouling surfaces.

More extensive early use of copper is certainly possible. Prehistoric civilization knew copper and had shown great technical ability in casting and working copper and bronze for statues and other art work (*72*). Copper foundries of the 10th century B. C. have been excavated (*41*). Copper and tin were a staple in trade in 800 B. C., and the need for tin with which to make bronze was one of the chief reasons for the early voyages to Britain.[1] Thin sheets of copper were known to be in use for roofs from the 12th to the 15th centuries (*72*). However, no authentic case of sheathing ships with copper prior to the 18th century has been established. If copper sheathing was known to the ancients, it is difficult to understand why its use was lost while that of lead sheathing persisted.

The use of copper as an antifoulant was suggested as early as 1625 when a patent was granted for a composition that very probably contained some form of copper (*6*, *,83 84*). In 1728, another patent was obtained for "a new method of sheathing and preserving the planks of ships" consisting of "rooled" copper, brass, tin, iron, or tinned plates, although no record of its immediate use has been found (*79*, *104*). Later in the 18th century, wooden sheathing was filled with copper nails whose heads touched each other (*38*, *69*). In spite of these desultory efforts, apparently it was not until the experiment of H.M.S. *Alarm* that the antifouling qualities of copper were recognized.

In 1758 H.M.S. *Alarm*, a 32-gun frigate, was sheathed with thin copper "for an experiment of preserving it against the worm" (*70*, *75*). This first authenticated use of copper sheathing was, therefore, probably as a substitute for lead or wood sheathing, and largely for protection against ship worms. The report of the results of this experiment, made on her return from a voyage to the West Indies, is reprinted as an appendix to this Chapter.

The report took note of the plates washed off the bow of the ship where they were exposed to the full force of the sea, and the amount of waste due to the wear of the water. It recorded the soundness of the planking except for one spot that had been rubbed bare at the start of the voyage. It remarked on the freedom of the bottom from fouling, except on the rudder where iron nails had been used purposely to vary the experiment. It notes, with surprise, the corrosion of the iron where it had contacted the copper. Finally, it compared the cost of the copper with the cost of wooden sheathing, finding them about equal.

The report stated three conclusions: that copper was a protection against worms, that it did not injure the planking, and that it did not foul. These advantages were considered so important that further experiments were recommended in which thicker plates and copper nails were to be used throughout; the copper to be insulated from, or kept at a distance from, the iron.

A second ship, the *Aurora*, was coppered by the British Admiralty in 1765; a third, the *Stag*, in 1770; four more in 1776; and nine in 1777.[2] Within the next three years the use of copper became general throughout the British Navy (*38*, *49*). In 1779, the British felt that it would enable them to overtake the faster sailing French vessels that were subject to fouling (*28*). By 1789, two boats had been built in England entirely of copper, "without any planking whatever" (*104*).

The first American naval vessel to be coppered was the frigate *Alliance*. This was done in 1781.

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[1] Alexander the Great (336–323 B. C.) demanded as tribute from the Kings of Cyprus "brass or copper, flax and sails" with which to equip a fleet (*21*).

[2] Robert Bushnell's submarine is said to have been foiled in its attack on H.M.S. *Eagle* in New York harbor in 1776 because the copper sheathing prevented the penetration of the screw with which the explosive charge was to have been attached to the ship's bottom (*90*). Another account attributes the failure to the screw striking an iron bar (*13*).

The ships built under the Naval Act of 1794 for the United States Navy were also coppered (*70*). The *Constitution* was sheathed in 1795 with copper imported from England (*40*). Robert Fulton's submarine built on the Seine for Napoleon in 1801, was also copper covered (*98*). The clipper ships of 1843–1869 (*25*), and the later American whalers were coppered as a matter of course (*24*).

Although copper was the best antifouling surface known, it was by no means perfect. Its antifouling action was not always certain; and its corrosive effect on iron nearly caused it to be discontinued by the British Navy within a few years of its adoption. Although this was corrected by the use at first of mixed-metal and later of copper bolts, its excessive rate of wear proved a heavy expense. To reduce this expense as much as possible, the British Admiralty started the manufacture of copper sheathing at Portsmouth dockyard in 1803, re-working old copper sheathing and experimenting with different copper ores, and with ways of treating them. In 1823, they sought the advice of the president and council of the Royal Society to determine the best method of manufacturing copper and of preventing, if possible, its excessive wear (*10, 38, 49*).

In 1824, Sir Humphry Davy read two papers before the Royal Society detailing the results of his experiments on these questions (*31, 32*). He showed that the corrosion was due, not to the impurities in the copper as had been supposed, but to the sea water reacting with it. Knowing that copper was weakly positive in the electro-chemical scale, he considered that if it "could be rendered slightly negative, the corroding action of sea water upon it would be null." This he accomplished by attaching pieces of zinc, tin, or iron to the copper. By experiment, he found that a piece of zinc as small as a pea would protect 50 square inches of copper from corrosion; and that this was true regardless of the shape of the copper or of the position of the zinc upon it. After several experimental trials, the Admiralty adopted Sir Humphry Davy's protectors for ships in service, using cast iron surfaces of an area equal to 1/250 of the copper surface (*33*).[1]

The problem was not solved, however, for the protected copper fouled badly. Davy pointed out that the protectors prevented the solution of the copper through galvanic action, and that this was the reason why it fouled. He was thus the first to relate the antifouling action of copper to its rate of solution.

In 1831, after experimenting with shifting protectors, and protectors of mixed-metal, it was decided to use them only on ships lying in harbor. Shortly after, even this was abandoned, although experiments were still carried on with various foreign copper ores in the search for a more durable material (*38, 49*). The loss of copper was a serious expense, but it was felt that this was fully compensated for by the protection against teredos and fouling (*49*).

The introduction of iron hulls invalidated the use of copper sheathing because of the corrosive action of copper on iron. Throughout the 19th century, therefore, and in spite of the growing importance of iron in shipbuilding, it was frequently seriously suggested that a return be made to wooden ships that could be coppered (*103*). Even late in the century most warships and other ships that had to be at sea for long periods were still built of or sheathed with wood for that reason alone (*45, 62, 71*).

THE PROBLEM OF PROTECTING IRON HULLS

Iron hulls, appearing late in the 18th century,[2] developed so rapidly that in 1810 Sir Samuel Bentham proposed in Parliament that the British Admiralty start building ships of iron (*104*). At that time, however, there was widespread prejudice against the use of iron, which had not proved altogether satisfactory in shipbuilding, and the motion was voted down (*37, 104*). Nevertheless, expensive repairs, a serious scarcity of wood, and the introduction of steam engines were already forcing the change from wood to iron (*5, 12, 35, 56, 86*).

Wooden ships were limited in size and strength, and even with improved methods of construction could not compete economically with iron ships (*1, 87, 101*). Repairs frequently amounted to more than the original cost (*26*). Occasionally a ship had to be broken up because of dry rot without making even one sea voyage. The need for proper shipbuilding timbers was acute, and the lack of them often caused long delays, even to badly needed war ships. Nor were the large wooden ships strong enough to support the vibration of the early engines or the propellers (*86, 104*). It is question-

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[1] Cast-iron was used in preference to zinc because it was cheaper and more easily procured. Davy cites several successful applications of protectors in which the proportion of the protecting metal varied from 1/70 to 1/125. Differing with Davy's statement, Hay (*49*) says that the Navy Board ordered protectors of 1/80 of the copper surface.

[2] Although iron and steel were known in the 10th century B. C., iron was not used for ships' plates much before 1800, nor steel before 1865 (*44, 51, 57, 88, 96, 98*).

able whether any of them could run their engines at full speed without serious results.[1]

In spite of this, it was not until the middle of the century that the terrible destruction caused to wooden ships by explosive shells at Sinope in 1853, and the success of the French armored floating batteries at Kinburn in 1855, finally proved to the Admiralty the necessity for iron ships (*14*). But aside from prejudice, there were two serious objections to the use of iron hulls: corrosion and fouling (*50*).

Early in the history of iron ships, it was found that copper sheathing could not be used because its electrolytic action corroded the hull dangerously (*10, 79*). Among many similar cases, H.M.S. *Jackal* foundered at Greenock from the corrosion having eaten through her plates, apparently unnoticed; and H.M.S. *Triton*, in 1862, had her plates corroded to such paper thinness that, according to her commander, she was only kept from foundering by her fouling; practically sailing home on her barnacles (*104*).

Although fouling was by no means a new problem, its importance was so emphasized by the greater speeds, and by the substitution of costly and bulky fuel for sails, that many have felt that fouling became an important problem only with the introduction of iron ships. A man-of-war on commission in foreign waters for an extended period might become so fouled as to be almost unmanageable and unseaworthy before she came home and could be cleaned. The most extreme example reported was an iron whaler on the African coast, only six months out from England. Even though she had been cleaned every month with brooms and ropes, she was not safe, as she could neither sail nor steer, owing to her heavy fouling. So great did the problem become that in 1847 the Admiralty contemplated the total disuse of iron ships, and actually commenced the sale of all the iron ships then in the Navy. They were deterred, however, by the impossibility of meeting naval requirements with any other material (*8, 104*).

As a consequence of having invalidated the use of copper sheathing for an antifouling surface, the adoption of the iron hull started search for some less harmful metallic sheathing, and for some way of insulating copper sheathing from the iron hull.

Zinc, the only metal that could be used to place the plates of the ship in an electro-negative condition, was tried repeatedly as sheathing. It was claimed that when in contact with the iron hull of a ship, electrolysis increased the exfoliation of the zinc sufficiently to prevent fouling, and at the same time protected the ships' plates from corrosion (*29*). Although zinc sheathing achieved some standing as a substitute for copper, experience showed that it sometimes became brittle and wasted away too fast to be of real value (*16, 65, 67, 79*).

Muntz metal, sheet lead, galvanized iron, and nickel were tried, as well as alloys of lead and antimony, and of zinc and tin. Other metals or metallic alloys were suggested, and combinations of metals, such as iron scales covered with lead and copper, sheets of lead and antimony painted with mercury, or zinc plates coated with tin. Many of these sheathings presumably never passed beyond the experimental stage.[2]

Nonmetallic sheathings were also tried or suggested. These surfaces included felt, canvas, and rubber; ebonite, cork, and paper. They also included various forms of glass, enamels, glazes, and tiles. Cement was frequently used, but more as a protection against corrosion than for fouling.

For insulating copper sheathing from the iron hull of the ship, felt soaked in tar was often used; and sometimes cork, rubber, or plain brown paper. At one time, warships were built in a composite fashion, i.e., wooden planks were put on iron frames. While various other considerations led to this development, the practice was favored also because such ships could be coppered safely (*71, 92*). About 1862, this system was replaced by wooden sheathing put on over the metal hull. This was wedged between ridges on the hull, or bolted on in various ways, and then coppered. The wooden sheathing served only as an insulation. Although it was reported to have been satisfactory during the Spanish-American war (1898–99), and was used in both the British and the United States Navies, this method was too expensive for general use (*10, 92*).

A second and more important effect of the introduction of iron hulls, however, was to renew interest in the use of antifouling compositions. This eventually led to the development of the modern paint systems which have replaced copper sheathing almost altogether, except when special needs warrant the extra expense.

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[1] As late as 1864, at the Institute of Naval Architects, Admiral Halsted described the flagship, undergoing an engine test at Sheerness, as shaking and trembling so that the master shipwright ran out, shouting, "For God's sake stop those engines as you'll drive the stern posts out of the ship" (*48*).

[2] The invention of these many substitutes for copper sheathing is reviewed in the following chapter.

ANTIFOULING PAINTS

The use of some form of paint or composition on ships' bottoms is undoubtedly very old. An early record tells of a mixture in use about 412 B. C. composed of arsenic and sulfur, mixed with Chian oil and applied to a ship's sides so that she could sail through the water "freely and without impediment" (*27*). Many other examples could be noted, from the tar and wax of ancient Greek boats to the various compositions used on the wooden sheathing of the 18th century.

Although some were said to be for protection against shipworms, in most cases the purpose of these various compositions was not stated. The first coating recorded explicitly as a protection against fouling appears to be a composition patented by William Beale in 1625, which was composed of powdered iron, cement, and probably a copper compound (*6*, *83*, *84*). Possibly, this was the first use of copper as an antifoulant.[1] Two other patents for unknown compositions for "gravings against the worm" were also granted in the 17th century; and a third was granted in 1670 to Howard and Watson for a coating composed of tar and resin in a varnish of beeswax, crude turpentine, and granulated lac dissolved in grain alcohol (*68*, *69*).

Three more patents were granted in the following century. One was for a composition containing pounded glass in a mixture of tar, oil, and lime; and a second for molten tin in a paste of zinc, limewater, black soap, and salts of zinc (*68*). The third, granted to William Murdock in 1791, was for a composition of iron sulfide and zinc roasted in air and mixed with varnish. Arsenic was the toxic (*6*, *69*).

But even though these early patented compositions were few and scattered, other unpatented compositions are also occasionally mentioned in the literature; and the use of some form of paint or composition on ships' bottoms was not uncommon.

Nicoalaes Witsen, a naval architect, wrote of the surprise of the Dutch that a British yacht captured in 1673 was neither tarred nor painted, which was apparently most unusual (*94*). Masseille states that fishermen on the Sea of Tiberius near Palestine are said to have used a mixture of crude turpentine, resin, suet, and asphalt in the 17th century (69). He also tells of a "coat hardening under water composed of suet, resin, fish-oil, and sometimes chalk," that was used on the French coast in the 18th century and that is still occasionally employed.

Several compositions were tested comparatively at Portsmouth in 1737. The best of these, a mixture of pitch, tar, and brimstone, was successful enough against ship worms to come into general use, but it was felt that it was highly important to find some surface that would also prevent fouling. Complaints were still being made of ship worms, however, particularly in the West Indies. This was represented to the Admiralty in a letter from the Navy Board in 1761, and in the same letter it was proposed to experiment with copper sheathing on some vessel going to the West Indies (*38*, *49*). The experiment on H.M.S. *Alarm* followed immediately (*75*). Two years later, the report on this experiment established the antifouling qualities of copper sheathing as so outstanding that for the next forty years there was only negligible interest in antifouling paints or compositions.

With the growing use of iron ships in the 19th century, attempts were made at first to adopt the new methods of sheathing so as to overcome the difficulties introduced by corrosion of galvanic origin. But by 1835 the futility of these efforts began to be recognized and attention was again turned to shipbottom paints.

From that time on, the number of paints and compositions increased rapidly. According to Young, by 1865 more than 300 patents for antifouling compositions had been issued in England alone (*104*).

The early patented compositions, for the most part, were entirely useless. Their ingredients included every useable material, organic and inorganic, from guano to plain kitchen salt (*12*, *68*, *78*, *104*). Owing to the great need for protection against fouling, however, many of even the most worthless of them were tried in service; although, as Admiral Sir Edward Belcher said, they seemed designed rather to encourage fouling than to discourage it. The Admiral added that his sailors got ten shillings each for the magnificently oversize specimens of shellfish that the various antifouling paints and manures succeeded in growing on the *Ardent* at Bermuda (*15*).

Antifouling paints had a bad reputation for many years. Even as late as 1872, Robert Mallet, in presenting the Institute of Naval Architects with a catalog of British shipbottom patents, stated that the majority of them were useless or worse, and that the best were mere palliatives

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[1] The copper compound was possibly chalcocite or copper sulfide (*83*), or a copper-arsenic ore (*84*). Andes (*6*) and Massaille (*69*), however, state that this ingredient was an unknown mineral from England or Wales.

(*68*). This was due in part to wide-spread lack of understanding of the problem, but not entirely so. Mallet himself, in 1841, had patented an antifouling paint in which slightly soluble coatings of poisonous materials were applied over a coat of varnish.[1] He stated that the paint failed because he could not control the solution rate of the toxics within useful limits, and because of abrasion.

"McIness" the first practical composition to come into widespread general use, was introduced in Liverpool about 1860. It was a metallic soap composition applied hot, in which copper sulfate was the toxic. This antifouling paint was put on over a quick-drying priming paint of rosin varnish and iron oxide pigment (*3*). Soon after this, a similar hot plastic composition appeared in Trieste, Italy. Known as "Italian Moravian," it was one of the best antifouling paints of that time; and in spite of being both expensive and difficult to apply, was used well into the present century.

In 1863, Tarr and Wonson patented a successful copper paint, a composition of copper oxide in tar, with naphtha or benzene; and later Rahtjen's equally successful shellac type paint, using mercuric oxide and arsenic as the toxics, was introduced. The use of shellac as a rust-preventive coating for ships' bottoms reduced the corrosion of ships to such an extent that in 1861 Admiral Halsted stated that corrosion was no longer important (*47*).

Owing in part to the commercial value of a successful antifouling paint, nearly all were patented, and our knowledge of them is derived largely from the various patent records. A résumé of this material will be found in the following chapter.

According to these records, the most frequently used toxics were copper, arsenic, and mercury together with their various compounds. They were used both singly and in combination with each other. Often several different compounds of the same toxic would be used in a single composition. Solvents included turpentine, naphtha, and benzene. Linseed oil, shellac, tar, and various resin or shellac varnishes composed the matrix.

By the end of the century, the most widely used paints were the hot plastics such as Moravian and McIness, the shellac type paints such as Rahtjen, and the various copper paints such as Tarr and Wonson's copper oxide in tar with naphtha or benzene. These paints were generally applied over a first or anticorrosive coat of shellac or varnish, or of the same composition without the toxic. Most naval vessels were using copper over a wood sheathing, or hot plastic compositions on their ships' bottoms. Other ships used the less expensive commercial paints; and wooden ships were still frequently sheathed with copper. These antifouling surfaces, however, although reasonably successful, were expensive, often short-lived, and occasionally uncertain; and fouling was still a major problem.

The commercial shipbottom paints used by the United States Navy prior to 1908 were purchased by competitive bidding; and there were no technical specifications and no inspections other than checking the quantity of paint delivered. In an effort to standardize the quality of the ingredients as well as for various practical considerations,[2] the Navy decided to manufacture its own antifouling coatings; and in 1906, experiments were begun on both shellac and hot plastic shipbottom paints (*2*, *99*, *102*).

The first tests of its own experimental paints were begun in June, 1906, at the Norfolk Navy Yard on 21 different shipbottom paint formulations of spirit varnish paints. By October of the following year, these tests indicated that one formula was outstanding. Further tests were made on naval bottoms at various Navy Yards with paints made from this formula, comparing it with commercial shipbottom paints; and on June 8, 1908, a report was made favorable to the Norfolk test paints. Not long after, manufacture of the first naval shipbottom paints was started at Norfolk Navy Yard (*2*).[3]

The formula of an early Norfolk antifouling paint, as given by Adamson, shows that the toxic was red mercuric oxide suspended in grade A gum shellac, grain alcohol, turpentine, and pine tar oil. Zinc oxide, zinc dust, and Indian red were also added. Although the formula was continually varied, the shellac type paint was used by the Navy from 1908 until 1926, when it was abandoned (*2*, *3*).

From 1911 to 1921 further experiments were conducted at Norfolk, both to find substitutes for scarce materials and to improve the paint. In 1911, gum shellac of an excellent grade could be obtained from India, although the supply was limited. As wider use developed, it became both expensive

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[1] For toxics, Mallet used oxychloride of copper and sulfuret of arsenic.

[2] Among the practical considerations were the necessity of maintaining complete stocks of all the various brands of paint used at each of the Navy Yards, and the difficulties caused by the efforts of the competing paint manufacturers to get their paints accepted by the Navy.

[3] Convincing proof of the value of the Norfolk formula, as compared to commercial paints, came from a service test on the ships of the U. S. Fleet on its cruise around the world in 1907 (*58*).

and difficult to get. Inferior grades lacked adhesion, and experiments with various possible substitutes were carried on. Among these, rosin was of particular interest, both because of its successful use by some foreign navies, and because of the cheap and plentiful supply in this country. A substitute was also sought for the toxic, mercuric oxide, which in addition to being expensive and of foreign origin was difficult to handle (*2*).

In 1921, the American Society for Testing Materials had formed a subcommittee on antifouling paints, with the object, if possible, of setting standard specifications for the toxic ingredients. They found, however, that factors other than the toxic were almost equally important (*3*); and an extensive investigation of the entire problem of fouling was begun in September, 1922, under the direction of the Bureau of Construction and Repair, U.S. Navy (*97*). At this time, most foreign navies were reported to be using commercial paints such as Holzapfel, Rahtjen, and Hempel; and the average effectiveness of the shellac type antifouling paints was said to be about nine months (*2*, *3*).

At the same time, the U. S. Navy renewed experiments with hot plastic paints. In the beginning of the century, the consensus of opinion had been that the Italian Moravian hot plastic was the best antifouling paint available. Analyses of commercial paints of this type had been made at the Brooklyn Navy Yard in 1906, and ways of producing them worked out; but with the official acceptance of the Norfolk shellac type paint in 1908, work on hot plastics had been dropped (*99*).

In 1922, at the request of the Navy Department experiments in hot plastic antifouling paints were begun again by the Chemical Warfare Service at the Edgewood Arsenal. Various hot plastic compositions, based on analyses made at Edgewood in 1922, were made up and tested on steel panels at the Beaufort, N. C., station of the Bureau of Fisheries during the next two years. As a result of these tests, the Navy Department sent representatives from the Edgewood Arsenal to supervise a test application of the U. S. S. *King*, at the Norfolk Navy Yard. After nearly a year's cruising, the ship was docked at Mare Island on April 10, 1925; and it was reported that although the antifouling qualities had been excellent in the panel tests, the paint was not as successful in actual service. The film adherence, however, was good and further experiments were planned (*99*).

About 1926, the Navy substituted a coal tar-rosin formulation[1] for the shellac type antifouling paint (*2*). Although coal-tar-rosin paints were used by the Navy until comparatively recently, the Mare Island Navy Yard, interested by the experiment on the U. S. S. *King*, had also developed a hot plastic shipbottom paint which used cuprous oxide and mercuric oxide as the toxics. Repeated tests have proved the Mare Island hot plastic superior to other available coatings. Extensive experience during the early years of the war has confirmed this superiority, and the hot plastic formula is currently the preferred paint for naval use on steel bottoms.[2]

Hot plastic paints are troublesome because they require elaborate apparatus for application. Since the availability of such apparatus is limited, a need is still felt for superior antifouling coatings which may be applied by brush. This need led to the development of several satisfactory formulations known as cold plastics, which dry by evaporation of the solvent yet produce heavy films having much of the virtue of the hot plastic coatings.

As a result of the improvement in the coatings it is reported that naval vessels are now able to remain out of dry dock as long as 18 months with no reduction in speed or increase in fuel consumption due to fouling (59).

RESEARCH AND DEVELOPMENT

The earliest published works concerned with the prevention of fouling of which we are aware are the papers of Sir Humphry Davy which appeared in the Philosophical Transactions of the Royal Society of London in 1824 (*31*, *32*). Doubtless many reports of practical tests, such as that on the *Alarm*, and the tests of bottom compositions made at Portsmouth in 1737, existed in naval archives prior to this date (*38*, *75*). Davy's studies are noteworthy, however, because he made experiments, based on the best scientific knowledge of the time, to develop the principles controlling the fouling and corrosion of copper sheathing, and only then tested the methods which these experiments suggested on ships in service.

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[1] Visscher (*97*) gives the formula of a Navy standard coal tar-rosin antifouling paint of 1925 as:

1,196 grs. mineral spirits
306 grs. pine oil
564 grs. coal tar
923 grs. resin
923 grs. zinc oxide
616 grs. iron oxide
410 grs. mercuric oxide
515 grs. cuprous oxide
329 grs. silica

For coal tar-rosin formulas of 1937, see Adamson (*3*).

[2] For an account of the history of the development of plastic paints by the Navy and a discussion of their merits, see Reference 42.

No man of Davy's scientific stature has since concerned himself with the fouling problem, and for more than three-quarters of a century no one approached the problem from the scientific angle followed by Davy. It is interesting to note in passing that a generation later another great English scientist, Charles Darwin, became the authority on barnacles and thus contributed valuable knowledge of the subject without apparently becoming concerned with its practical aspects.

The development of antifouling compositions during the 19th century appears to have been strictly empirical. The publications of this period consist of general discussions based on the experience of practical men: naval officers, naval architects, and shipbuilders. There was some speculation on how fouling is prevented, but never any controlled experiment designed to test principles or theories. The paints themselves were developed privately as proprietary products. How much systematic investigation underlay the patented or secret formulations is not recorded.

When paint research was first undertaken by the Navy, in 1906, the data available consisted largely of records of submersion tests which compared one commercial paint with another. Very little was known about the formulae. In starting tests, it was necessary to try many combinations of ingredients, and through a process of substitutions, eliminations, and alterations finally to arrive at formulae which would produce satisfactory paints (*2*). Some additional information was obtained by analyzing paints of commercial origin which showed promise (*19*, *20*, *99*), but because of the nature of paint ingredients the knowledge to be gained in this way was limited. Performance on panel test and in service remained the only guide to performance, and no means of judging the cause of failure was at hand.

The trial and error method of research gradually led to formulations which became more and more complicated, since each component which was introduced into a promising formulation tended to be carried along into subsequent modifications. In 1939 this tendency was reversed by an experiment conducted jointly by the Mare Island Navy Yard and W. F. Whedon of the Scripps Oceanographic Institution at La Jolla, in which the currently accepted hot plastic formulation was broken down into a series of simplified mixtures of its components (*100*). The object was to determine which ingredients were really essential. The outcome was the demonstration that the mercury and Paris green present in the original formula added nothing to its antifouling characteristics. The tendency to simplification which this experiment initiated is illustrated by a comparison of the composition of formula for a standard Navy paint of 1925, given as a footnote on page 218, which contained nine components, with the present standard wood bottom formula, 16X, which has only five specified ingredients.

Prompted by a desire to obtain more fundamental knowledge of how to prevent fouling, the Navy arranged, from time to time, for biological investigations. This work supplied valuable information on the toxicity of potential paint ingredients to marine organisms, on the nature of the fouling population, its rate of growth, its seasonal and geographical incidence, and the relation of the service in which ships are employed to their tendency to foul (*17*, *97*). Similar studies were also conducted in Germany at the Laboratorium für Bewuchsforschung in Cuxhaven, in Turkey, Russia, and Japan (*76*), and in England (*39*, *80*).

The proposal that slimes, produced by bacteria and diatoms on submerged surfaces, had an important bearing on subsequent fouling aroused much interest and led to investigations which culminated in the establishment of the Naval Biological Laboratory at San Diego, and also initiated work at the Woods Hole Oceanographic Institution.

While this earlier biological work provided useful background knowledge that was requisite to intelligent attack on the problem, the idea that it would produce some unthought-of method of circumventing fouling proved illusory. However, the study of slimes led indirectly to two important results. First, the variability in the tendency of various paint surfaces to slime, and an apparent relation between slime formation and fouling, focused attention on the question of what property of the paint is responsible for its antifouling action. Second, experiments which were made to study the tendency of slimes to accumulate copper led to the development of techniques for measuring the rate at which copper or other toxics are given off by the paint surface. These methods, in turn, appear to have provided the answer to the above mentioned question: the antifouling action of currently successful shipbottom paints depends upon the rate of solution of the toxic material (*61*).

Armed with a definite physical objective, the problem of formulating antifouling coatings can now proceed in a more rational manner. What needs to be discovered is how to formulate so as to control correctly the discharge of toxic from the paint surface. The problem becomes one of applied physical chemistry rather than a game of permutations and combinations. Like Sir Humphry Davy, the paint technician can make experiments, based on the best available scientific information, to develop and employ the principles controlling the fouling of paint surfaces. Subsequent chapters contain an account of the first steps toward the development of such principles.

APPENDIX: NAVY BOARD'S REPORT TO THE ADMIRALTY ON THE FIRST COPPERING EXPERIMENT[1]

31st August 1763

Sir

His Majesty's Ship ALARM whose bottom has been covered with Copper for an experiment of preserving it against the Worm, and this Ship being returned from her Voyage to the West Indies to Woolwich, and that We might examine her bottom, and be informed how far the Experiment had answered the intention; We sent directions to Our Officers there, to take an immediate Survey of the State and condition of the Copper, also an Account of the number of Plates that might be rubbed off; and the number that should be continued on, and to distinguish such as were in a State of decay from those which should appear unimpaired, to examine likewise with regard to the Copper being Clean or foul'd with Barnicles, Weeds, which usually collect and grew upon the bottom of Ships in long Voyages, and in case of finding any of the Plates rubbed off, to observe the effect the Worm had on that part. They were then to cause all the Copper that should be remaining to be carefully taken off and collected: And these several Injunctions being complied with, they were strictly to inspect the Ships bottom, and report their Observations, as well on the Heads aforement'd as on every thing else that might occur in the course of their examination: And having received their report, We send you enclosed a Copy thereof with a profile sketch of each side of the Ship, shewing the manner in which the bottom was at first covered, the part that remains so, and also that which was found uncovered when the Water left her in the Dock; all which We desire you will please to lay before the Rt. Honble the Lords Commissrs. of the Admiralty, for their information.

And their Lordships having directed Us on the 21st October 1761, to report Our remarks upon this Experiment, We beg you will upon presenting the Sketches, observe that the Copper is most deficient upon the Bows; from thence ranging Aft a little beyond the Midships, and for four or five Strakes under the surface of the Water all which parts are most exposed to the force of the Sea. Upon discoursing the Officers on board the ALARM; We find the plates began to wash off from the Bows in fifteen or sixteen Months, after She sailed, gradually wasting in the middle, till reduced to the substance of the finest paper, and too thin to resist the wash of the Sea; the Edges and fastenings only remaining as when first put on.

The plates upon the lower part of the bottom also in the run of the Ship, quite Aft (except a few whose defects can be imposted to Workmanship), are wasted very little.

In two hundred superficial feet that were taken from these parts and Weighed, the plates were found to have wasted in Twenty Months only 13lb 12oz which seems to confirm that the quick Waste of those Plates laid on the Midships forward, can only be from the Wear occasioned by resistance of the Water to those parts. We are further to observe that the Copper which was remaining upon the bottom had been on near twenty Months and had kept perfectly clean without any means whatever having been used to render it so. But the Copper which covered the Rother was foul'd with Barnicles; and this difference We cannot Account for unless it may be supposed, that the Plates there being fastened with Iron Nails which was done to vary the Experiment the rust from thence with what might come from the Straps of the Pintles, draining down and spreading the surface of the Rother should have occasioned it.

The Copper being every where taken off the Plank of the bottom was very carefully examined, so likewise the Caulking, and in neither was there found the least Impair from Worm or any other Cause. The Plank was entirely sound, and the Seams and Butts were full of Oakam, hard and good, except upon one Spot on the Starboard side, distinguished on the Sketch by a red Circle, where the Copper for about a foot diameter being rubbed off the Plank was covered with Barnicles as close as it was possible; and upon inspection it was found the Worm had then made a deep impression.

The Copper upon this Spot, We apprehend must have been rub'd off very early, probably before the Ship went out of the River, as in all other parts of the bottom where the Copper had remained till gradually worn away as before described, the Worm had but slightly gribled the Surface, which plainly shews that it was owing to the Copper only that they were preserved from being in the same Condition.

We were greatly surprized to percieve the Effect the Copper had had upon the Iron where the two Metals touch'd; but it was most remarkable at the Rother Iron and in the fastenings of the false Keel, upon the former, the pintles and Necks of the Braces were as coroded and Eat.—particularly the two lower Ones, that they could not have continued of sufficient strength to do their Office many Months longer, and with respect to the false Keel it was entirely off.

The loss of the false Keel was at first supposed to have happened from the Ship having been on Shore, but upon examining it, the Nails and Staples that fastened it were found dissolved into a kind of rusty paste; which was also the Case of every Nail that had been used in fastening on the thick Lead to the Gripe and fore part of the Knee.

The same effect, but not to so great a degree; was observable upon all the Bolts and Iron under water, except where brown paper (with which the bottom was Covered) remained undecayed, and thereby separated the two Metals; and where this Covering was perfect, the Iron was preserved from Injury.

Having now informed their Lordships of the most material Observations We have made upon this subject, We shall observe upon the whole.

1st That as long as Copper plates can be kept upon the bottom, the Plank will be thereby entirely secured from the Effect of the Worm.

2nd That neither the Plank or Caulking received the

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[1] William L. Clements Library, Ann Arbor, Michigan. Reprinted from *The American Neptune*, July 1941.

least Injury with respect to its duration, by being covered therewith.

3^{d} That Copper bottoms are not incident to foul by Weeds, or any other Cause.

All which are Advantages very desireable to be attained, provided Methods could be fallen upon to obviate the difficulties we have before pointed out; the greatest of which is, the bad Effect that Copper has upon Iron.

It has been shewn that where brown paper continued perfect between them, the Iron was not injured; whence We presume, if the Heads of the Bolts and other surfaces of Iron were covered with flannel and a very thin leaf of Lead, they could be better secured from the corosion of the Copper, and with respect to the Rother Irons, if the back and sides of the Stern port and sides and beardings of the Rother were also covered with thin Sheet Lead instead of Copper, the effect that has appeared upon the Pintles and Necks of the Braces would be kept at least a greater distance and though We doubt it would not answer the end of entirely securing the Rother Irons, and it might lengthen their Service beyond the hazard of failing within a three Years Station.

As to the difficulty about the false Keel, that may be got over by having all the Staples made of Copper.

There is still another difficulty which is the Accident that Copper Sheathing has been found liable to in the Course of this Experiment, but as We imagine these have been partly owing to the thinness of the Plates made use of, which were only twelve Ounces to the foot, it appears to Us this difficulty would be removed by adding to their substance; which would render the Plates stiffer, not so liable to rub off, and also consequently of greater duration, with respect to their Wear.

We must not in Our Observations to their Lordships upon this subject forget the Expence that attends covering a Ships bottom with Copper; That upon the ALARM amounted to about £650. and to increase the Plates to the thickness that would be requisite to answer the aforement^{d} Advantages and bring the Charge to about £945. which is at least an Expence of four times the cost of Wood; but when it is considered how much more durable Copper will be than Firr Sheathing, also the worth of the old Copper when returned, We are inclined to think the difference (if any) in the end will be immaterial, the intrinsic value of the Copper rece^{d} back from this Experiment is £199.15.9.

And having maturely considered all the Circumstances that attend the Sheathing Ships with Copper, and seeing the extensive advantages it is capable of; supposing it can be brought into Use, We are induced to recommend it to their Lordships consideration,—whether a further tryal may not be made of it, with the improvements We have mention^{d} And in Case a Ship of 32 Guns should be wanted on the West India Station, We would propose that the ALARM may be again made use of for the Occasion, All which is nevertheless submitted to their Lordships by &c^{a}

JS. WB. HB. RO.

Philip Stephens Esq^{r}

P.S. We have ordered a Box to be sent to their Lordships containing several Plates in their different degrees of Wear.

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