

## The Invention of Protective Devices

A large fund of information concerning the methods proposed as an answer to the fouling problem is to be found in the patent literature. It is true that many patented ideas are nonsense, due largely to a misunderstanding of the problem. This is because many inventors are enthusiasts rather than experts. Barnaby (3) states that among 292 patents relating to shipbuilding, in which the profession or title of the inventor was stated, there were only 20 who were shipwrights or naval architects—the rest being a medley of colonels, wool dealers, upholsterers, fruiterers, goldsmiths, etc. Nevertheless, the patent lists provide almost the only means of tracing the development of many antifouling ingredients and devices, and are interesting as a record of ideas.

The present chapter does not pretend to represent a complete search of the patent record. It is based on three available lists of patents of ship-bottom paints which cover British patents issued between 1667 and 1872 (6), patents granted by the United States between 1842 and 1922 (4), and German patents from their beginning in 1880 to 1940 (13). A few additional patents relative to mechanical and electrical means of preventing fouling are also included. Antifouling patents as a group are discussed by Barnaby (3), Mallet (6), and Andes (2).

The first antifouling patent (2) was apparently granted to William Beale in 1625 for a composition which contained iron powder, cement, and an unnamed mineral (7). According to Rabaté (11), it is probable that this mineral was chalcocite, or copper sulfide, while Ragg (12) suggests that it was a copper-arsenic ore. However, most of the early shipbottom patents were granted for "protection against the worm," the majority being for some form of metallic sheathing.

The first metallic sheathing on the patent lists is lead. In 1670, an Act of Parliament granted to Howard and Watson the exclusive right to manufacture lead sheathing for ships (5). Some years later, rollers for milling lead into sheets were also patented (14). In 1728, another patent (12, 14) was granted for a method of "rooling" copper, tin, brass, and iron into plates. This process may have made possible the successful experiment with copper sheathing carried out on the *Alarm* (8) in 1761–1763, and the subsequent widespread use of copper sheathing as an antifouling surface.

In the 19th century, various improvements or metallic substitutes for copper sheathing appeared in the patent lists. The manufacture of zinc for sheathing was patented in 1805, (10, 14), aluminum "galvanically applied" in 1855 (15), and "coatings of the protective, or lustrous metals," including gold, silver, and nickel, in 1863 (16).<sup>1</sup> The following combinations of metals for sheathing were also patented: iron plates having small portions of zinc attached to them (17); sheets of copper and lead pressed together while hot (18); laminated zinc plates coated with tin (19); copper coated with lead, tin, or zinc (20); and iron scales covered with lead, having copper electrolytically deposited on one side (21). Other patents issued included: sheets of lead and metallic antimony painted with an amalgam of lead, antimony, and quicksilver, in 1831 (22); Muntz metal, a copper-zinc alloy, in 1832 (23); "copper and tin combined for sheathing," as early as 1817 (24); and copper or brass, in 1864 (25).

Near the end of the century, patents were granted for different ways of applying copper sheathing. One German patent (26) specified a copper coat in exchangeable sections to be set in recesses in the hull, another (27) attached copper foil with an adhesive layer, and in a third (28), a thin coating of copper was applied electrolytically.

With the growing use of iron in shipbuilding during the last half of the 19th century, various materials were patented for insulating the metallic sheathing from the plates of the hull. These included wood (29), wood and felt (30), rubber (31), and cork (32). A later patent (33) specified zinc as an intermediate layer. During this period an increasing number of patents were granted for antifouling paints and compositions as well as for sheathing; by 1870 paints formed a major part of the antifouling patent lists.

The patent mentioned above, which was granted to William Beale in 1625, was the first of the few patents issued before 1830 for paints or compositions designed to prevent fouling (7). About 1670, a British patent was issued to Philip Howard and Francis Watson for a composition of tar and resin, which used a varnish of beeswax, turpentine,

<sup>1</sup> It is doubtful that nickel sheets suitable for sheathing were being rolled in 1863. Perhaps the patentee had in mind the copper-nickel-zinc alloy, nickel silver, which was produced by one Henry Merry, Birmingham, England, after 1830. (F. L. LaQue, personal communication.)

and lacquer dissolved in grain alcohol (2, 7). A patent was granted, in 1780, for a formulation of molten tin mixed with a paste of zinc, zinc salts, limewater, and black soap (34). In 1791, William Murdock patented his composition of iron sulfide roasted in air with zinc, with arsenic as the toxic agent (2, 35).

Although few patents for antifouling paints were issued before 1830, over 300 had been granted by 1867 (14). During this period, generally unsuccessful attempts were made to use nearly every available organic and inorganic substance as an antifoulant (6, 9). Robert Mallet's British patent of 1841 for a composition using "slightly soluble coatings of toxic materials to prevent fouling" is an interesting example (36). He "preferred the oxychloride of copper and the sulphuret of arsenic" for the toxic, but he was unable to control the solution rate sufficiently to make it practicable (6).

The first successful antifouling composition to come into general use was a hot plastic, patented by McIness in 1854 (37). The antifouling coat was a formulation of copper sulfate in yellow soap. This was heated and applied over a quick-drying primer of rosin varnish and iron oxide (1). In 1863, Tarr and Wonson received an American patent (38) for their successful paint composed of copper oxide and tar in naphtha or benzene; Rahtjen's shellac-type paint, using mercuric oxide and arsenic as the toxics, was patented in 1871.<sup>1</sup>

In early British patents, as listed by Mallet, no purpose is stated for many of the formulations. Several of them, however, included one or more toxic ingredients, and may be presumed to be antifouling paints. Of those which were later patented in the United States, some were definitely specified as antifouling (39), the action being attributed either to toxicity or to exfoliation (40).

In early patents the most frequently specified toxics are copper, arsenic, mercury, and their various compounds. The copper compounds included the oxides (41) and sulfates (37) of copper, Brunswick Green (copper oxychloride) (42), and verdigris (basic copper acetate) (43). Arsenic appeared with copper as copper arsenate (44), copper arsenite (45), and Paris Green (copper acetoarsenite) (46), and in other combinations as realgar ( $As_2S_2$ ) and orpiment ( $As_2S_3$ ) (45), arsenious acid (47), and white arsenic (arsenic trioxide) (48). The

forms of mercury specified were the oxides (49), and iodides (50), calomel (mercurous chloride) (51), and corrosive sublimate (mercuric chloride) (52).

Other toxics which were tried included strychnine or atropine, patented in 1857 (53), and oxides of zinc (43), of antimony (54), and of lead (litharge) (55), patented shortly thereafter. Also claimed as toxics were: "picric acid or any picrates" (56), carbolic acid (57), potassium cyanide (58), iodine or bromine (59), phosphorus (60), sulfur (61), and copperas ( $FeSO_4 \cdot 7H_2O$ ) (62). In 1871, a patent was granted for a paint containing creosote as the toxic (63), and in 1910, for one with metallic silver (64).

Metals were also patented as ingredients of paints—powdered iron as early as 1625 (7), and molten tin in 1780 (34). In the 1860's, various formulations specified powdered metallic zinc (65), finely divided copper (66), iron powder (67), quicksilver (68), and, at a later date, metallic lead (69). Other patents included both zinc and iron (70), copper and zinc (71), and "powdered lead and copper added separately" (72). Some of these compositions were probably an effort to duplicate metallic sheathing in a paint.

In 1865, Tarr and Wonson (73) invented a "galvanic antifouling paint" which contained an alloy of zinc and "any metal below zinc in positive relation" suspended in a tarry or oleaginous medium. Henri Terrisse, a Swiss chemist, was issued a United States patent in 1911 (74) for a similar use of metals in paint. It was based on mixing a finely divided alloy or amalgam of copper and mercury in a waterproof varnish. This voltaic element was claimed to produce nascent chlorides by electrical decomposition of sea water when the attaching organisms broke through the varnish.

Among the more unusual materials claimed as toxics were powdered oyster shells (75), a powdered shellfish, *Lagamus decagonalis* (76), seaweed ashes (77), and a seaweed (kelp), "used while green and wet" (78). Patents were also granted for use in paints of concentrated extract of tobacco (79) and the active principle of plants of the genera *Tephrosia*, *Lonchocarpus*, *Derris*, and *Deguelia* (80). A patent of 1894 specified the "resinous juice of the Japan sumac," *Rhus vernicifera*, a plant related to poison ivy (81); while one of 1921 specified the sap or leaves of the Upa, *Alchorea cordifolia*, a Javanese tree yielding an intensely poisonous juice often used as an arrow poison (82).

<sup>1</sup> See Adamson (1). Ragg (12) states that this paint was introduced at Bremerhaven as early as 1860.

Of greater interest was the introduction of the more useful ideas for antifouling ingredients and devices. A metallic powder (iron) and probably some form of copper were used in William Beale's patent of 1625 (11, 12). William Murdock's patent of 1791 (35) used arsenic. Mercury was found as an oxide in a British patent of 1857 (49). Patents were issued for metallic sheathing (lead) in 1670 (5), and a metal coating (aluminum) "applied by the action of electricity or galvanism" in 1855 (15).

A British patent (83) had been granted for a copper-zinc alloy in 1830, two years before Muntz metal (also a copper-zinc alloy) was patented (23). As early as 1842, an American patent was granted for a composition to be applied hot, preceding by twelve years the introduction of McIness' widely used hot plastic paint (37, 84). Shellac and linseed oil are specified in a patent of 1837 (55). While many early patents mentioned merely copper oxide, cuprous oxide was first specified by the Benedicts' German patent (85) of 1881. Mercuric oxide was indicated in Rahtjen's patent of 1871 (1), and a German patent of 1924 specifically claimed the use of mercurous oxide to replace mercuric oxide in antifouling paints (86). Resin was patented as an ingredient in 1670 (2), rosin in 1867 (87), and a synthetic resin, which was formed of the condensation products of phenols with aldehydes, in 1908 (88). In 1861 a patent was granted for the use of magnetic or galvanic electricity to prevent fouling (89); another was issued for a single paint system that claimed to be both anticorrosive and antifouling as early as 1865 (38). The use of coal tar oil in an antifouling paint (90) was patented in 1867.

Devices other than paint systems were also designed to permit the use of poisons. In 1863, a patent was granted for a reservoir placed in any convenient part of the ship, containing a poison combined with oily substances that was to ooze constantly through perforated pipes along the bottom and sides of the ship (91). Also patented about this time were flat, open-mouthed bags to be filled with compounds of phosphorous which were to be dragged with ropes along the hull (92). Still another device used perforated pipes filled with equal parts of sulfur, resin, and fish oil; these were attached along the keel and sternpost of the boat where the compound would "generate a gas" which "destroys all animal or vegetable life in its vicinity" (93).

In the present century, a patent was granted for a special V-shaped reservoir to be lowered

over the bow of the ship, from which chlorine or other gases could be released and distributed along the hull by the ship's motion (94). Another patent was granted for pipes distributing a toxic solution from a main reservoir to outlets scattered over the underwater surface of the hull (95). A similar patent (96) proposed pipes leading to a perforated bilge keel and to other underwater parts of the hull. These were to discharge air, another gas, or any liquid lighter than water, so that the ascending bubbles could maintain the water about the hull in a state of turbulence. If desired, a toxic ingredient could be added. In 1934, a patent proposed a canvas envelope to enclose the bottom of a ship; the water entrapped by the envelope was withdrawn from around the ship, treated chemically, and returned to within the envelope (97).

Patents were also granted for nontoxic surfaces to prevent the attachment of fouling. These included sheathing the ship's bottom with canvas or other fabrics (98), with felt soaked in pitch (99), and with paper (100) soaked in copperized ammonia.<sup>1</sup> Patents were issued for surfaces of cork (101), rubber (102), cement (103), and ozocerite (a paraffin) (104), pulverized slate in pitch (105) and for sheets of graphite (106) to be cemented on the ship's bottom. Glass was patented in many forms. A surface of pounded glass had been patented in 1767 (107), and a "silicious coating of ground glass, borax, and soda" in 1855 (108). One patent specified a thin coating of glass to be formed directly on the iron hull (109), another, glass plates attached to a fabric and then cemented to the hull (110). Surfaces of enamel (111), and of vitreous glaze (112) were also proposed. One patented antifouling composition included four sizes of ground glass among its constituents (113).

About 1850, a gas jet which formed a carbonized outer surface on wooden hulls was patented.<sup>2</sup> Later patents were granted for thin veneer sheathings of ebonite or vulcanite (114), and for a surface of free sulfur on an adhesive coat (115).

Among the more curious nontoxic surfaces was one formed of nail points protruding through a rubber or leather sheathing to "tear free the organism's suckers" (116). A patent was also granted for a porous surface "to be permeated by water, on which marine animals would be unable to form a

<sup>1</sup> The inventor claimed that "the paper will desquamate under the action of sea water just as copper desquamates."

<sup>2</sup> See Masseille (7). The Portuguese charred their hulls in the time of Vasco da Gama (1469-1524). In 1720 the British built the *Royal Williams* entirely of charred wood.

vacuum, and so their suckers would be ineffectual" (117). In 1886 a patent was granted for a paint composed of a "highly oxidized oil forming an elastic surface," on the theory that "it is generally known that barnacles will adhere only to a hard or unyielding surface" (118). A composition which, on exposure to sea water, "changed into a hard stone-like surface, thus preventing the fouling of the bottom" (119) was also patented. The use of hydrazine in an antifouling paint was patented in 1893 (120), the hydrazine being claimed to act, "not as a poison, but as a means of coagulating the albumen and thereby destroying the protoplasmic masses of fouling." In 1912, another paint patented as protection against mussel fouling slowly released alkaline lyes when in contact with sea water "to keep the keratin or mussel cement from hardening" (121). A patent was granted in 1928 for a luminous antifouling paint (122), and in 1915, for one containing radioactive materials (123).

Devices for removing fouling include various systems of chains (124) or knives (125) for scraping the ships' bottoms. About 1862 patents were issued for the following: rotating brushes which operated continuously or intermittently along the bottom of the ship (126), iron scrapers which were held against the ship's bottom with cork floats (127), and crushing rollers on guides, which traversed from end to end of the ship (128). The use of steam was proposed to remove fouling in various ways: piped to scrapers pulled by ropes and held against the ship's hull by magnets (129); conveyed over the vessel's side through perforated pipes, and thus applied to the ship's bottom (130); piped to a canvas or wooden envelope which enclosed the ship (131).

In 1906, a patent was granted for a method of cleaning the ship's bottom electrolytically. A chain of zinc electrodes was held against the hull by floats, "a strong electric current loosening the oxide film of the sheathing and bringing the fouling with it" (132). In the following year, one was issued in which electrolysis of adjacent hull sections formed gases that loosened the fouling (133).

Various other methods of using electricity to prevent fouling were patented. A comprehensive patent of 1863 claimed the use of electricity "however obtained or applied" for protecting the ship's bottom from fouling and corrosion (134). Other patents were more specific, however. Thomas Edison, in 1891, was granted a German patent for an electric antifouling system having a D. C.

generator on the ship which fed multiple electric cables with electrodes at their ends. These were to be placed underwater near the hull and send sufficiently strong electric currents back through the ship's hull to prevent the attachment of organisms (135). In 1866, a patent was proposed for using an electric battery to prevent the fouling of iron ships, the ship being connected to one battery pole and the water to the other (136).

A patent issued later specified a generator which sent alternate charges of positive and negative electricity in rapid succession from one end of the hull to the other (137). Another made the hull the armature of a gigantic magnet to prevent fouling (138). And still another applied a direct current intermittently to the hull to keep off barnacles (139). A 1911 patent used a high tension apparatus with alternating current which kept the water surrounding the ship electrified (140). Later, alternating current was suggested which used a system of electrodes fixed to the hull of the ship, "a high tension discharge causing muscular fixation of the barnacles and so preventing their attachment" (141). Electrically formed deposits were also patented as antifouling devices. In 1907, a patent was granted to Schoneberger and Frazier for a device which continuously electrified the metal hull or sheathing, the resulting layer of hydrogen and sodium hydrate protecting the vessel even without paint (142). In 1940, Cox patented a method for plating out calcium and magnesium salts from sea water onto the ship's hull. There was some antifouling effect in this process, since the second and subsequent layers were less adhesive to each other than the first layer was to the metal of the ship; thereby an exfoliating surface was formed (143). Somewhat earlier a patent was granted whereby a ship's hull, or a similar conductor, was electrically coated with an adherent layer of precipitated metal and an overlying protective nonmetallic film of simultaneously formed phenolic condensation products (144).

The condensation product of phenols and aldehydes (a synthetic resin) was patented as an antifouling composition in 1908. This patent claimed an antifouling action due to the gradual splitting up of the products of condensation into their components of phenol and formaldehyde (88). In the following year, a patent was granted for a synthetic resin mixed with copper or another toxic compound to be used as an antifouling paint (40), and in 1916 for a synthetic resin combined with a toxic radical (arsenic) (145).

Most of the patents described in this chapter

have never been tested seriously. The following chapters assess the practical importance of the various methods which have been proposed to prevent fouling.

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119. MARSDEN, G. C. U. S. Pat. 341760. May 11, 1886.
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