(BIO)FOULING AND ANTIFOULING MEASURES

Antifouling agents for marine applications: a NeverEnding Story

The use of something toxic to combat specific biological species causing adverse effects on the human activities is quite unavoidable, but sooner or later problems caused to the environment and to not target organisms must be faced. In the case of the antifouling coatings, there is a cyclical development/production of new "products", initially considered as the final solution of the problem, and then discovered responsible of new unpredicted adverse effects. A NeverEnding Story

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Marine biological fouling, usually called marine bio-fouling, can be defined as the accumulation of microorganisms, plants, and animals on artificial surfaces (ships, submerged pipelines, ...) immersed in sea water. In the case of ships, the adverse effects caused by this biological settlement are well known:

- Frictional resistance, which leads to subsequent potential speed reduction. As a result, higher fuel consumption is needed, with less energy-efficient systems, and the consequent increase in emissions and transport overall costs.
- Increase in the frequency of dry-docking operations. A large amount of toxic wastes is easily generated during this process.
- Introduction of species into environments where they are not naturally present (invasive or non-native species).

The antifouling (AF) technology has developed in close association with increased maritime transportation of people and goods but, as for many other technologies, its development can be considered a NeverEnding Story. This is typical of the approach based on the use of something toxic for specific biological species causing adverse effects on human activities (agriculture, industry, transport, ...). Sooner or later, problems caused to the environment and to not target organisms (sometimes modifying biological equilibria and diversity) must be faced.

This historical development of AF strategies has been very well resumed by Diego Meseguer Yebra, Søren Kiil and Kim Dam-Johansen in *Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings* [1]. In the following, a rapid summary of the main stages.

Problems caused by bio-fouling for the maritime transportation system were rapidly understood by ancient people, and so were the strategies to combat these adverse effects for more than 2000 years. In a broad sense, as already suggested in literature [2], we can find something that could be considered as the earliest citation of coating used for extending the life of vessels and preventing against bio-fouling in the first book of the Bible (Genesi 6:14)! God said to Noah "…..make yourself an ark with ribs of cypress; cover it with reeds and coat it inside and outside with pitch" (Figure 1).

Many authors and historians (e.g., P. Cintas in several studies on ancient civilizations in the Mediterranean Sea, and F. Braudel in *Les Mémoires de la Mediterranée* [3]) attribute the incredible fame of Phoenicians as

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the best sailors in the world to the use of pitch from the Black Sea for protecting the hulls of their boats. In fact, Phoenicians and Carthaginians widely used pitch. There is some evidence that metal sheets on wooden vessels were probably used also in the 1500–300 BC period [4], but this is more difficult to prove. In a translation from the Aramaic of a papyrus dated about 412 BC, concerning boat repairs, the following note was found: "And the arsenic and sulphur have been well mixed with Chian oil thou broughtest back on thy last voyage and the mixture evenly applied to the vessel's sides that she may speed through the blue waters freely and without impediment" [5].
Greeks and Romans used similar approaches sometimes, including arsenic and sulphur mixed with oils to prevent against the attack of shipworms [6].
The Chinese Admiral Cheng Ho had the hulls of his junks coated with lime mixed with poisonous oil to protect wood from worms [5]. From the 13th to 15th century pitch, blended with several other components such as oils, resin, tallow, were widely used.
It is interesting to remind that Leonardo da Vinci invented a rolling mill for making sheet lead. One of the first attested reference about underwater use of copper was in 1618, during the reign of the Danish King Christian IV, mentioning the use of copper for sheltering keel and rudder. In the same period we can find one of the first record of the use of copper (copper sulphide or a copper/arsenic compound) as an antifoulant in a British patent (William Beale, 1625).
In the second part of 1700's copper was widely used, especially in British Navy, even if only later its antifouling mechanism of action (based on the dissolution of copper in the seawater) was studied and demonstrated (sir H. Davy).
The good results of copper sheltering were evident in the famous Trafalgar battle. Among the factors contributing to the victory of the British Navy, the use of copper was considered one of the most important. 3923 copper shelters were fixed to the hull with more than 550.000 rivets on the vessel Victory, commanded by Adm. Nelson.
Actually, copper is an effective and (still) widely used biocide, however its effectiveness is relatively short (maximum 2 years, but often a few months), so dry dockings of vessels for cleaning and paint reapplication are frequently required.

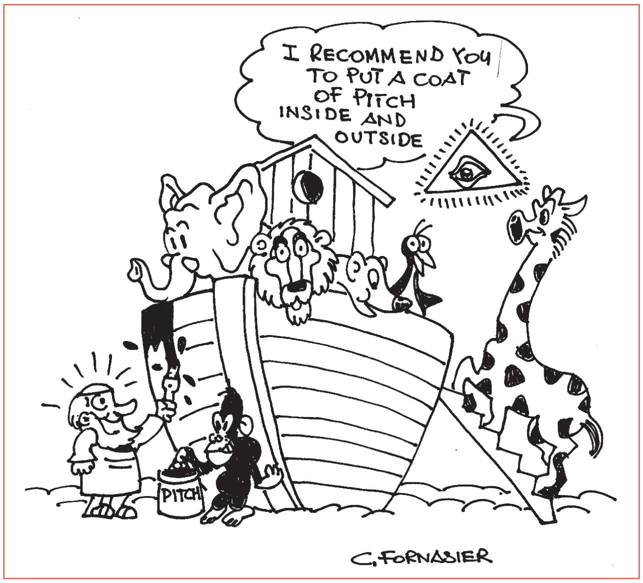

FIGURE 1 God said to Noah "….. .make yourself an ark with ribs of cypress; cover it with reeds and coat it inside and outside with pitch" (Genesis 6:14)

After the introduction of iron ships at the end of the 18th century, the use of copper sheathing was drastically reduced [4, 7, 8], due to its corrosive effects on iron, and several alternatives were tried, including sheathings of zinc, lead, nickel, arsenic, galvanised iron and alloys of antimony, zinc and tin, followed by wooden sheathing, which was then coppered [1, 6].
Consequently, in this period a variety of paints based on the mixing of one or more toxicants in a "polymeric" matrix started to be developed. So, by the late 18th and into the 19th centuries, coatings containing copper, arsenic and mercury were increasingly applied to vessel hulls [5].
It is easily understandable that until recent times, the environmental concern on the use of these toxicants was absolutely disregarded.
Mallet in 1841, William John Hay in 1847, James McInness in 1860 patented antifouling paints based on the use of different "poisonous materials", mixed with or applied over a coat of varnish, and James Tarr and Augustus Wonson in 1863 patented an A/F paint using copper oxide in tar with naphtha [5].
The "Italian Moravian" and McInness' "hot-plastic paints", shellac type paints (active in the prevention

of rust), and various copper paints have been widely used for a long time.
For about 50 years a considerable number of products based on these principles have been developed, thereafter substituted by the so-called "cold-plastic paints", easier to apply and effectively decreasing fouling and extending up to 18 months the period between dry-dock times for re-painting.
After World War II, important changes took place in the AF paints industry. During this period, studies on organotins and their AF properties improved the performance of AF paints and offered a great contribution to the solution of the problem. Van de Kerk and co-workers [9, 10] already described the efficacy of the TBT-containing products in the 1950s. Organotins have been widely used in copper-based paints, at first in the so-called "free association form" [11]. The paints used at that time can be classified into insoluble matrix type and soluble matrix type, according to their water solubility.
In the following, a rapid description of different types of TBT paints, based on different approaches, just to give an idea of the level of complexity of the technologies investigated.
Tributyltin Free Association Paints: in these paints the antifouling agents are dispersed in a resinous matrix from which they can, more or less, slowly leach. The control of the rate of release of biocides from a free association paint system and the constant leaching level is quite complex to achieve and it is difficult to make theoretical previsions in terms of environmental risks. However, results of monitoring programs suggest that paints containing freely associated biocides (the most widely used copper compounds and TBT), can be considered as the main cause of relatively high initial concentrations of biocides in the marine environment.
TBT Self Polishing Copolymer Paints (SPC): in these paints copolymer systems are based on a combination of biologically active resins and antifouling agents, such as TBT copolymer resins and copper compounds. TBT react by hydrolysis with the seawater, resulting in the slow release which combats fouling. The remaining surface of the paint is continuously eroded by the seawater action, resulting in the exposure of a fresh surface of TBT polymer. This hydrolysis/erosion process continues until no paint is left on the surface and this process confers two key properties on the TBT copolymer paint system: increased ability to control/regulate the biocide leaching rate and smoother surfaces as a result of the erosion process [12-13].
As already mentioned, the development of TBT (tributyltin) as an antifouling agent in conventional coatings started in1960s. TBT-based coatings allowed to control the biocide release rates, but quite early adverse effects on the marine ecosystems appeared: already in 1974, oyster farmers reported abnormal shell growth while in the 1980s TBT was clearly demonstrated to be linked to shell abnormalities in oysters *(Crassostrea gigas)* and imposex in dogwhelks *(Nucella lapillus)*. So in 1987–90 TBT coatings were prohibited on vessels <25 m in France, UK, USA, Canada, Australia, EU, NZ and Japan, followed by other Countries worldwide.
Several studies demonstrated the problems caused to the marine environment and monitoring campaigns also started in Italy [14-16].
In the meanwhile, from the 1990s to present time, copper release rate restrictions were introduced in Denmark and considered elsewhere (e.g., California, USA).
The International Maritime Organisation (IMO) adopted (2001) the "AFS Convention" to eliminate TBT from AF coatings from vessels imposing the following steps: 2003 – prohibition of further application of TBT; 2008 – prohibition of active TBT presence; finally the IMO "AFS Convention" entered-into-force (2008).
Coming back to the NeverEnding Story, starting from the 2000's, the research into "environmentally friendly" AF alternatives increased, but as frequently happens in these situations, the alternatives themselves started to pose new "alternative" problems [16-17]. Again, in the last few years eco-toxicological assessments have been made in Italy's marine coastal environment [18-24].
One of the approaches widely used, considering that some algal groups are tolerant to copper [25], was based on the fortifying paints with additional 'booster' biocides, aimed at targeting hull colonisations by micro- and macro-algae. Several algal toxic compounds have been tested worldwide including chlorothalonil, dichlofluanid, Irgarol 1051, TCMS pyridine, thiocyanatomethylthiobenzothiazole (TCMTB), diuron, dichloro-octylisothiazolin (DCOIT, Sea Nine 211), zinc and copper pyrithione (Zinc and Copper Omadine) and zineb [26-29].

These are often herbicides (e.g., Irgarol 1051 and diuron, but also fungicides) that have negative effects on the growth rate of photosynthetic organisms. Legislation now exists in some countries to regulate the use of some 'booster' biocides in AF paints such as, for example, diuron and Irgarol 1051. In the UK, a review of booster biocides in 2000 resulted in only four biocides gaining approval (dichlofluanid, DCOIT (Trade name: Sea Nine 211), zinc pyrithione and zineb). Approvals of chlorothalonil, diuron and Irgarol 1051 were revoked due to their high toxicity at low concentrations and their persistence in the environment [30]; Irgarol 1051 and diuron are also banned in Denmark (DEPA, 2008), and diuron is banned in the Netherlands. The use of Irgarol 1051 in AF paints is not permitted in Australia as it was not granted approval for use as an AF biocide by the Australian Pesticides and Veterinary Medicines Authority (APVMA), when its presence was detected and the risks it posed assessed in the 1990s. Applications for approval have been submitted to the European Union for eleven AF biocides, including copper (II) oxide, copper thiocyanate and Irgarol 1051, but not diuron [31].

The increased consciousness of the impacts on the marine environment resulting from the use of toxic AF paints has induced investments on research and development of non-toxic alternatives, such as foul-release coatings that incorporate silicone elastomers, waxes or silicone oils, and "natural" coatings in which AF compounds are sourced from algae and other marine organisms [32].

Foul-release coatings currently on the market include silicone (e.g., Intersleek 700, Sealion and Bioclean), fluoropolymer (e.g., Intersleek 900), hybrid (e.g., Phasecoat UFR) and hydrogel silicone (e.g., Hempasil X3) coatings (Townsin and Anderson, in [32]).

"Natural" coatings however are not currently in commercial use due to the difficulties in sourcing a supply of natural AF compounds at a reasonable cost in addition to meeting the requirements of environmental regulation agencies [1].

At the moment no alternatives seem to be promising to replace biocide-based A/F coatings [33]. Hence, a considerable part of the efforts are still concentrated on the study of new binder systems better regulating the release of booster biocides. Future regulatory decisions in favour of non-toxic alternatives in antifouling paints could shift the balance and force these products into commercial use.

One possibility is the attempt to prevent the adhesion of fouling organisms by developing ultra-smooth surfaces, making the settling of organisms difficult. Brady made a summary of the most significant properties of coatings necessary to obtain satisfactory results [34], but again the main requirement is to be physically and chemically stable for prolonged periods in the marine environment. These properties are owned by fluoropolymers and silicones, but many other materials are being continuously developed. Nevertheless, modest results evidenced the still limited efficacy of fouling release properties of these coatings; moreover, the advantages of these technology seems limited to fast-moving vessels, at the moment.

The other interesting approach is the study of the AF natural protection of marine living organisms such as wales. The attempt to reproduce the microtexture of the surface of their body is fascinating, but again results are modest so far.

The use of microstatically charged microfibres to obtain the "furry" surface effect was supposed to prevent hard biofouling from settling. Again doubtful results were obtained.

In theory the application of UV, ultrasonic, laser beams could be used by automated systems (robot technology): underwater cleaning is potentially cost-effective with respect to the cleaning procedures in a dry-dock. This approach needs further developments.

The last research frontier could be the development of a coating capable of selectively releasing bioactive substances after artificial (electricity, ultrasound..) or natural (temperature or fouling adhesives themselves) stimulation [1].

Conclusions

Two main topics, of scientific/technological and philosophical/ethical nature and both related to the environmental concerns, will probably drive research on A/F coatings. The optimization of a reliable A/F paint performance model could be a powerful tool for a rational screening of new ideas eliminating the weak ones at the early stages of the development process. At the same time, studies on the adhesion mechanisms and biological characteristics of the fouling processes need to be continued. It is however fundamental to find a compromise between industrial and academic needs: environmental eco-toxicological assessment as well as scientific investigations are necessary even if costly and time-consuming. This can only be achieved defining clearly the acception of the term "sustainabilty" on a global scale, also in the case of A/F coatings development, production and use addressing research towards acceptable alternative solutions, balancing economic and environmental sustainability.

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