

Introduction

If corrosion protection is the first priority for ship and other asset owner using marine paints, fouling protection will follow shortly after. Fouling is the growth of marine organisms on the underwater area of vessels outside hull. While ships carry this fouling along, they are dealing with extra drag causing increased fuel consumption and potentially spreading unwanted invasive species around the world.

Scope of this document

In this document we intend to give an introduction to the different methods for coatings to be used for reducing hull fouling on ships. We touch on regulations and technologies but do not intend to give a scientific review.

Overview

- Types of fouling
- Effect of fouling
- Solutions
 - Anti-fouling technologies and mechanisms
 - Transocean Coatings portfolio

Fouling types

Any organism capable of attaching itself to a vessel can cause fouling. Fortunately, only relatively few species are found on ships hulls. These species can be divided in three categories.

Slime fouling

As soon as any object is immersed in the sea, a film of organic molecules will settle on the object within minutes. This so-called conditioning film is believed to enhance settlement of bacteria, diatoms (such as Achnantes) and filamentous algae.

Achnantes is a diatom type that can be found in all world seas and on most ships too. A slime layer on a ship is always present but not always visible.



Figure 1: Microscopic picture of Achnantes

Algae fouling

Initially algae settle in the form of individual cells but in time they multiply to form a chain of cells and finally, may develop to strings of several meters in length. Examples are the well-known Enteromorpha (green algae) and Ectocarpus (brown algae).

Strong adhered algae fouling is a sign that the Anti-fouling has reached the end of its service life.

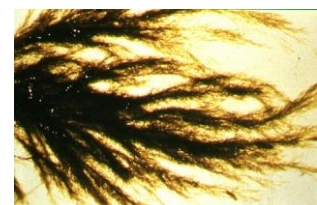


Figure 2: Microscopic picture of Ectocarpus

Animal fouling

Barnacles, tubeworms and mussels are three more notorious examples although tubeworms and mussels tend to be more proliferated in subtropical waters. Words as “hard fouling” or “encrusters” are sometimes used to describe this type of fouling due to the formation of shell-like structures by several of these species.

Barnacles is a generic name for a class of organism which have in common that after settlement of the larvae (cyprids) on a surface a hard, calcareous shell is build. Once a barnacle has adhered to a substrate it is not easy to remove. From a tiny shell of 5 millimetres in diameter a barnacle shell might grow to a diameter of 5 centimetres.

During the shell growing process enormous powers are developed to such an extent that it can undercut hard epoxy coatings. Examples are the common Acorn barnacle and the typical Gooseneck barnacles.



Figure 3: Microscopic picture of cyprid larvae

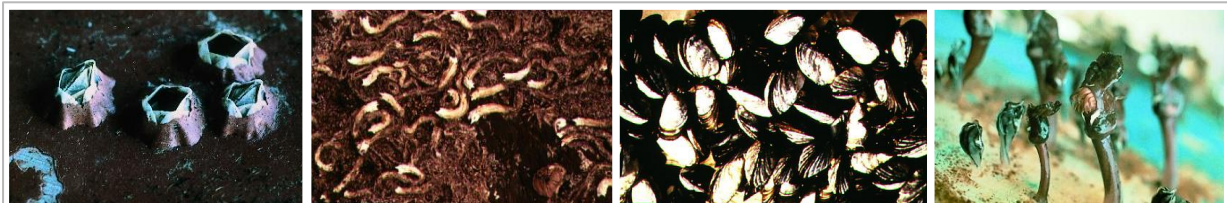


Figure 4: left to right, Acorn Barnacles, Tubeworms, Mussels, Gooseneck Barnacles

Effects of fouling

The most quoted effect of fouling on a ship hull is the increase in drag and hull roughness resulting in speed reduction. Other effects are blockage of cooling water inlets and the already mentioned corrosion initiated by bacteria and coating damage by barnacles.

However, shipowners will be more concerned about loss of speed as it influences sailing schedules and increases fuel bills. Effective solutions to prevent or reduce the fouling growth therefor quickly becomes a worthwhile investment. Solutions such as anti-fouling coatings can prevent or reduce regular hull scrubbing to remove fouling growth that may be required when water/ports with strict invasive species regulations or to bring the ships efficiency back to the design specification.

Solutions

Anti-fouling coatings for a long time were based on the principle of biocide release from the coating, creating a hostile environment at the coating-water interface. A certain minimum concentration is required to deliver effective protection. As overly high concentrations lead to overkill and may be harmful for non-target organisms (marine life that will not adhere to ships, for instance fish). Also, it will increase the cost of the anti-fouling.

The mechanism of biocide release varies between products and is selected by the manufacturer based on design lifetime, expected sailing pattern, the overall coating system and budget. Transocean delivers four ranges of Anti-fouling paints and their working mechanism is explained briefly below, separate brochures are available with more product details.

Because of the environmental pressure on the use of biocides in general, other strategies to protect a ship against fouling are gaining interest amongst paint suppliers as well as customers. The prevention of fouling by minimizing the adhesion of organism by using silicone-based coatings is a direction that has already led to commercial products such as the Transocean Ultima system.

Legislation limiting the use of specific biocides for application in yachting or regionally in commercial shipping has resulted in broad ranges of anti-fouling products to ensure suppliers can meet market requirements. Anti-fouling products in the Transocean Coatings range are not commonly available world-wide for due to these types of restrictions.

Coating Types

Coating based fouling prevention or management can be done using different mechanisms. Although different chemical components make up the binder of the coating that is often used to describe the coatings generic type, roughly there are two categories of products biocidal and non-biocidal.

The biocidal products (generally called anti-fouling) are further split in delivery mechanism and in type of biocide used. Cuprous oxide (often shortened to copper) is a commonly used biocide to prevent animal “hard” fouling or encrusters. This biocide is not allowed in certain parts of the world as contaminated became a problem in marinas (where yachts remain stationary for longer periods of time). Hence manufacturers have started to develop copper-free solutions.

Anti-fouling tends to contain a separate biocide ingredient to deal with the soft fouling (slime, algae). Local legislation often dictates registration of biocides for use in this type of coating products, products may need an adjusted biocide package for different parts of the world.

The main products in the non-biocidal fouling prevention coatings are anti-stick or fouling release coatings (FRC). Biocidal types now exist, where the use of biocide is mainly aimed at initial performance. An alternative is to use hard coatings that can allow regular cleaning (or the softer approach with grooming) without damage creating more roughness.

Working Mechanisms

The biocide release mechanisms are a key parameter for a coatings ability to fight fouling growth. A regular release throughout the lifetime of the coating is critical (between dry docking where new coats can be applied). When the biocide dissolves into the water, it leaves behind a coating with a reduced concentration and hence reduced ability to release biocide. On vessel types with a high frequency of drydocking (due to their seasonal service for instance), fouling can be kept under control while the coating is slowly depleted of biocide before a refresher is applied.

Biocidal anti-fouling coatings tend to be designed with a mechanism that allows for the coating to slowly wear away and reveal a fresh layer to the water interface. This is intended to keep the availability of biocide at an effective level. The concentration of fouling spores in the water and growth once adhering varies based on location, temperature and activity of the vessel, the need for fresh biocide may differ. To deal with this requirement, suppliers have designed products with different film thickness reduction or “polishing” rates.

The polishing may require a certain amount of water flow to mechanically assist the film wear that may be based on chemical mechanisms that to some degree just require the presence of water. There are roughly 3 types of making biocide available at the coating surface:

- Leaching, this depletion mechanism results in a “leached layer”
- Erosion, this type of film erosion is sometimes called ablative and is not controlled, biocide release varies over time
- Self-polishing
 - o Generally based on mixture of hydrophobic and hydrophilic resins
 - o Self-smoothing based on (hydrolysable) silyl acrylate

The diffusion of biocide from the coating film is called a leaching mechanism. Unless one of the DFT loss mechanisms described below is part of the design, this results in a so-called leached layer; an empty matrix of water insoluble ingredients. Deep in the film biocides are still present but diffusion through the leached layer is becoming more difficult as time goes by. At a given moment the release rate of biocides falls below a critical level and it will be increasingly likely that the paint will foul. Since these types of coatings do not erode, after several touch-ups a build-up of layers is inevitable and leads to an increase of internal stresses that may cause delamination.

The eroding type of anti-fouling are designed to have the leached layer being weak enough to break off the intact film below, resulting in a refreshed surface and more readily available biocides. The erosion rate depends on water flow and may differ around the hull and depends on other conditions such as water temperature and leaching speed. This means that biocide concentrations vary over time and location. This means the surface at a micron-scale may not be as smooth as with other technologies.

Self-polishing materials dissolve at a steady pace creating a more regular thickness loss and biocide concentration and a smoother coating surface. Well-designed binder combinations with a further reduced leaching effect add a self-smoothing-effect to this polishing resulting in an even smoother.

Figure 5 below show the polishing or DFT-loss of different anti-fouling types over time. A purely diffusion based or leaching anti-fouling would show as a horizontal line in the graph. All examples in this graph have a similar average thickness loss over time (μm per month for instance) but there is a clear difference in how steady the speed is.

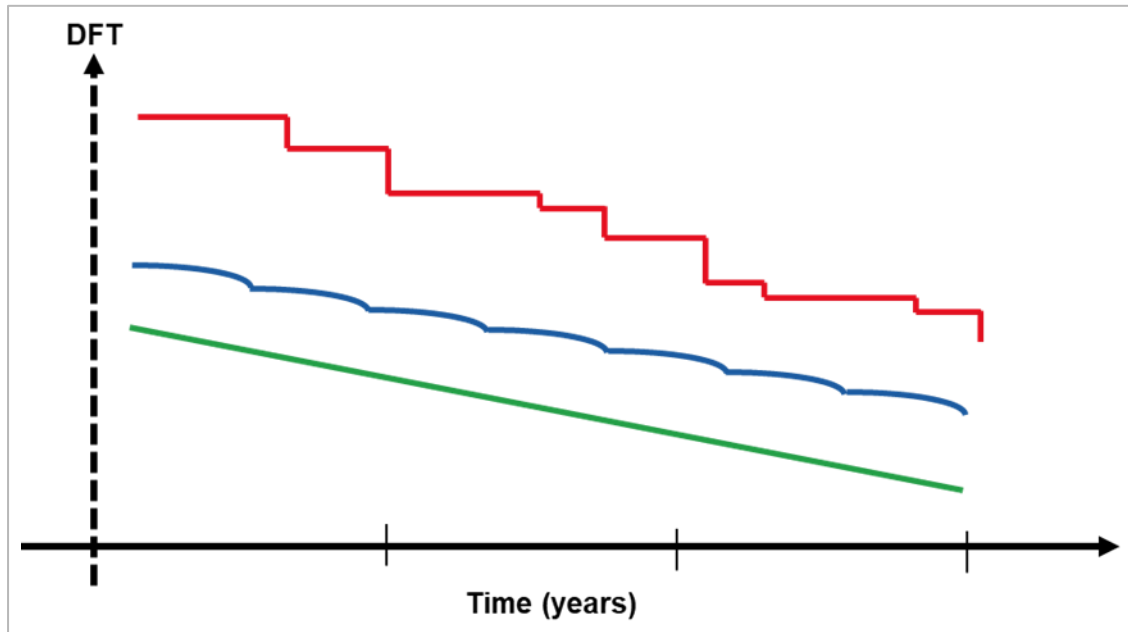


Figure 5: DFT loss mechanisms, top to bottom: ■ ablative ■ self-polishing ■ self-polishing/self-smoothing

Regulations

Due to the use of biocides, that are designed to kill or slow growth of specific aquatic flora and fauna species, there are many regulations related to the formulation of anti-fouling coatings. The most well-known and impactful was the “tin-ban” where the use of tributyltin (TBT) was banned as it had been proven to cause deformations in oysters and sex changes in whelks. The International Convention on the Control of Harmful Anti-fouling Systems on Ships, which was adopted on 5 October 2001, prohibits the use of harmful organotin compounds in anti-fouling paints used on ships. The Convention entered into force on 17 September 2008 and Transocean Coatings nowadays does not offer any “tin”-based anti-fouling.

Regionally other requirements around registrations are continuously being introduced and updated. One example is found in the active substance approval requirements in Europe under the Biocidal Product Regulation (the BPR).

The fight against invasive species has driven several regulators to call for hull inspection and cleaning requirements before vessels are allowed to enter ports.

More recent regulations from the International Maritime Organization (IMO) on energy efficiency for ships in MARPOL Annex VI are related to ships’ greenhouse gas (GHG) emissions and the drive for fuel efficiency may also impact anti-fouling (selection).

Note that the regulations for the maritime transport industry vary dramatically from those for pleasure boats and are often more local/country specific for the latter.

Transocean Products

In response to customer needs, regulations and changes in availability of raw materials, Transocean Coatings continuously innovates and renews the portfolio of anti-fouling coatings. Products based on the different mechanisms described in this document are available in our Optima, Longlife, Cleanship, Armada anti-fouling ranges and the Ultima fouling release products.

Below short overview of the available products and their specific applications needs to be read with the understanding that, partly due to regulatory reasons, not all products are available from all our members (see also the regulations paragraph).

Transocean Optima Range

Conventional Anti-fouling are essentially based on a combination of active pigments and biocides dispersed in a rosin dominated binder matrix. Cuprous oxide is the main biocide and in some cases extra fouling protection may be obtained by adding organic biocides or organic compounds. When immersed in seawater, the presence of rosin stimulates water penetration into the coating and as a result cuprous oxide dissolves and diffuses out of the coating.

The dissolving action decreases the paint film thickness as well. This simple working mechanism provides adequate fouling protection at an economic cost for a limited period of time.

Transocean offers these conventional anti-fouling as the Optima range.

There are four Optima qualities, differing in life time and activity. All Optima qualities are tin-free if so desired a version containing organic biocides is available as well.

Transocean Longlife Range

Combining lasting fouling protection and toughness, our Longlife anti-fouling are based on a combination of active pigments and biocides dispersed in a binder mixture of rosin and water insoluble resins. The structure of the dry paint film is designed in such a way that biocide particles such as cuprous oxide are in close contact with each other. Upon immersion in seawater, water-soluble compounds such as cuprous oxide and rosin dissolve first from the outermost layers and later dissolve and migrate from the depth of the film.

The whole process of dissolving and migrating of biocides through the film is in one word called 'leaching'. After the service period the coating consists of an intact, still active layer and a 'leached out' porous top layer. As the paint thickness is not decreased due to the presence of insoluble resins in the film, working action and lifetime of Longlife type anti-fouling is determined by the leaching speed of biocides. Longlife type anti-fouling offer longer service periods and stronger paint films than conventional anti-fouling.

Transocean offers anti-fouling with this working mechanism under the Longlife range. Dependent on sailing pattern, budget and desired level of fouling protection, a choice can be made between the Longlife qualities differing in type and content of biocide.

Transocean Cleanship Range

Even before the use of tin-based anti-fouling was banned for environmental reasons, Transocean was one of the first to respond (in the late nineteen eighties) with the tin-free Cleanship technology.

This Cleanship technology is based on a balanced mixture of biocides dispersed in a binder with hydrophilic and hydrophobic characteristics. When immersed in seawater, the hydrophilic/hydrophobic ratio of the binder changes, facilitating water penetration. During water penetration, the structure of the paint's top layer changes from a water-in-paint solution to a paint-in-water emulsion. Simultaneous with this so called phase-inversion biocides are released and subsequently the whole process starts again with the next layer of paint.

This working mechanism provides the following benefits:

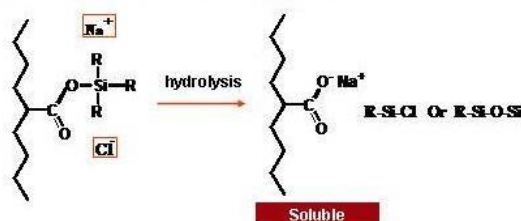
- Life time proportional with applied dry film thickness
- Efficient use of biocides
- Self-renewable surface allowing easy recoating after service life

Transocean offers the Cleanship technology in several versions differing in erosion rate and biocide content to allow for a suitable selection based on vessel sailing pattern and speed.

Transocean Armada Range

Transocean Armada is a high-performance anti-fouling based on an acrylic polymer where silyl-monomers are the active groups.

Transocean Armada is a high-performance anti-fouling based on an acrylic polymer where silyl-monomers are the active groups. The silyl polymers can be hydrolysed in seawater and thereby work in a similar manner as the tributyltin polymer of years past. As seen in the graphical representation below, this process creates in a water soluble part which results in a self-polishing effect.



The hydrolysis rate is controlled and therefore a stable erosion rate is obtained leading to a steady release of biocides. Since the silyl groups have no biocidal function, the presence of biocides is still required. Transocean Armada is compatible with standard Transocean Anticorrosive schemes and can be used to upgrade existing Cleanship systems.

Transocean Armada complies to IMO Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS/CONF/26), adopted 5 October 2001 in London.

Transocean Ultima Systems

Silicone based, biocide free anti-fouling, where fouling disappears with speed!

For decades chemist have tried to develop paints that prevent fouling but without the use of biocides. Many methods have been described in the past but only a few of them have the possibility to be translated into commercial products. The most promising direction is the approach to create a surface that is difficult for organisms to adhere to.

This direction has led to the introduction of silicone based systems on the market, also referred to as fouling-release coatings. The philosophy behind the use these fouling release systems is that although fouling organisms will adhere to the coating, the force of adhesion will be weak to such an extent that any fouling will be easily removed. However, not every silicone is the same. Transocean discovered that special silicone polymers had to be used.