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Antifouling Technology & Vessel's Performance

ΓΕΛΕΓΕΝΗΣ ΑΒΡΑΑΜ

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Ευχαριστίες

Με την ολοκλήρωση της παρούσας διπλωματικής εργασίας θα ήθελα να ευχαριστήσω τον κύριο Δημήτριο Παντελή, Καθηγητή του Τομέα Θαλασσίων Κατασκευών της Σχολής Ναυπηγών Μηχανολόγων Μηχανικών του Εθνικού Μετσόβιου Πολυτεχνείου, για τη δυνατότητα που μου έδωσε να ασχοληθώ με αντικείμενο του άμεσου ενδιαφέροντός μου.

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Περίληψη

Στόχος της παρούσας διπλωματικής εργασίας, με τίτλο «Αντιρρυπαντική Τεχνολογία και Επίδοση Πλοίου», είναι η παρουσίαση της βιομηχανίας των αντιρρυπαντικών συστημάτων, καθώς και αυτή καθαυτή η επιρροή των ίδιων των αντιρρυπαντικών συστημάτων στην καθημερινή λειτουργία των σύγχρονων ποντοπόρων πλοίων.

Με δεδομένο τον παραπάνω στόχο, γίνεται μια ολοκληρωμένη προσπάθεια παρουσίασης της ιστορίας των αντιρρυπαντικών επιστρώσεων και της κατηγοριοποίησής τους με βάση τα χημικά τους χαρακτηριστικά και τις επιμέρους ιδιότητές τους. Συγκεκριμένα, δίνονται ορισμοί για τις βασικές έννοιες γύρω από το θέμα της ρύπανσης και αναλύονται οι μηχανισμοί πίσω από το φαινόμενο αυτό. Επίσης, καταγράφονται τα σημαντικότερα αντιρρυπαντικά συστήματα που έχουν χρησιμοποιηθεί από την απαρχή της παρατήρησης του προβλήματος της θαλάσσιας ρύπανσης έως σήμερα.

Επιπροσθέτως, αυτή η διπλωματική καλύπτει το θέμα της χημικής σύστασης μιας αντιρρυπαντικής επίστρωσης, λαμβάνοντας υπόψη τα επιμέρους συστατικά της. Επιπλέον, παρουσιάζονται οι δύο πιο διαδεδομένοι τύποι επιστρώσεων αντιρρυπαντικής προστασίας (δηλ. με βάση τον χαλκό και με μη τοξική απελευθέρωση ρυπαντή). Εστιάζοντας πλέον όλο και περισσότερο στη ναυτιλιακή βιομηχανία και στη σχέση της με την αντιρρυπαντική τεχνολογία, γίνεται λεπτομερής παρουσίαση των απαραίτητων βημάτων για την ορθή επιλογή και εφαρμογή μιας αντιρρυπαντικής επίστρωσης σε ένα ποντοπόρο πλοίο. Επίσης, γίνεται αναφορά στα διεθνή πρότυπα ISO που σχετίζονται με την αντιρρυπαντική τεχνολογία, καθώς και στην ταξινόμηση των αντιρρυπαντικών επιστρώσεων.

Εν συνεχεία, και επικεντρώνοντας πλέον καθαρά στα ίδια τα ποντοπόρα πλοία γίνεται μια λεπτομερής παρουσίαση του θέματος της «επίδοσης» ενός πλοίου, καλύπτοντας τόσο τον ορισμό όσο και την παρακολούθηση αυτής, καθ' όλη τη διάρκεια ζωής του πλοίου. Ο συσχετισμός των επιδόσεων ενός πλοίου με τις αντιρρυπαντικές τεχνολογίες γίνεται μέσω της παρουσίασης των επιπτώσεων που έχει η θαλάσσια ρύπανση στην αντίσταση τριβής του πλοίου κατά τον πλου σε ποικίλα στάδια της ζωής του. Μια λεπτομερής επισκόπηση της «αντίστασης του πλοίου» (ορισμός και μαθηματικές εξισώσεις) πραγματοποιείται και παρατίθενται παραδείγματα από θεωρητικά μοντέλα, καθώς και από πραγματικά πειράματα, που έχουν γίνει σε λειτουργικά πλοία ώστε να παρατηρηθεί και να στοιχειοθετηθεί η επίδραση που έχει η θαλάσσια ρύπανση στις επιδώσεις ενός πλοίου και οι επακόλουθες οικονομικές επιπτώσεις στην πλοιοκτήτρια εταιρία. Τα πραγματικά παραδείγματα εστιάζουν στην παρατήρηση των επιδόσεων (α) ενός ή περισσότερων πλοίων με την πάροδο του χρόνου, υπο διαφορετικές συνθήκες, χρησιμοποιώντας μια συγκεκριμένη αντιρρυπαντική επικάλυψη και (β) όμοιων πλοίων χρησιμοποιώντας διαφορετικές αντιρρυπαντικές επιστρώσεις.

Τέλος, παρουσιάζονται κάποιες καινοτόμες ιδέες και τεχνολογίες γύρω από την αντιρρυπαντική βιομηχανία καθώς και τα πεδία εφαρμογής τους. Οι καινοτόμες αυτές ιδέες αφορούν νέα προϊόντα από τη βιομηχανία των αντιρρυπαντικών επιστρώσεων, προερχόμενα από νέες προσεγγίσεις στο πρόβλημα της υποθαλάσσιας ρύπανσης, αλλά και λύσεις βασισμένες σε εξωγενείς τεχνολογίες που μπορούν να αποδειχθούν χρήσιμες στη μάχη κατά της ρύπανσης.

Μια σύνοψη των παραπάνω καθώς και τα ανάλογα συμπεράσματα που εξάγονται παρατίθενται στο τέλος της παρούσας διπλωματικής εργασίας

Abstract

The aim of the present thesis entitled "Antifouling Technology and Vessel's performance" is to present the antifouling industry and the relevant antifouling systems involved, as well as to point out the influence of the antifouling systems in the daily operation of modern seagoing vessels.

Taking into account the above stated aim, a complete effort is made into presenting the history of antifouling coatings and their categorization based on their chemical characteristics and their properties. More specifically, definitions are given for the basic concepts surrounding the issue of fouling and the functioning mechanisms behind the fouling process are being analyzed. The most significant antifouling systems implemented since the first fouling observations until nowadays are, also, recorded.

In addition, this thesis covers the topic of the chemical composition of an antifouling coating taking in consideration its different components. More than that, the elements of the two most well-known antifouling coatings (i.e. copper-based and nontoxic fouling-release) are presented. While focusing more and more on the shipping industry and its direct relationship with the antifouling technologies, a detailed presentation is made on the necessary steps towards the proper selection and application of an antifouling coating on a seagoing vessel. The international ISO standards related to the antifouling technology, as well as the classification of antifouling coatings are also reported.

Moving on, and clearly focusing on the seagoing vessels themselves, a detailed presentation on the topic of "vessel performance" is made, covering its definition and its monitoring throughout a vessel's seagoing life. The connection between a vessel's

performance and the applicable antifouling technologies is made through the presentation of the effects of marine fouling on the frictional resistance of the vessel during sailing in various stages of its life. A detailed overview of the "vessel's resistance" (definition and mathematical formulas) is given, as well as various examples from theoretical models and real-life examples of operational vessels, so as to observe and record the actual effect of fouling on a vessel's performance and the subsequent financial impact for the ship-owning company. The real-life examples focus on the observation of the performance of (a) one or more vessels over time, under different circumstances, while using the same antifouling coating, and (b) similar/identical ships using different antifouling coatings.

Finally, some innovative technologies and ideas around the antifouling industry and their fields of application are presented. Those innovative technologies refer to new products that have risen in the antifouling coating industry by a radical change of approach on the marine fouling issue, as well as extrinsic technologies that may prove useful in the fight against fouling.

A summary of all the above as well as the relevant conclusions extracted are presented in the end of the present thesis.

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List of Abbreviations

A/C:	Anti-Corrosive
A/F:	Anti-Fouling
Al_2O_3:	Aluminium Oxide
$C_{20}H_{30}O_2$:	Abietic Acid
C_A:	Correlation Allowance
CASPER:	Computerized Analysis of Ship Performance
CFD:	Computational Fluid Dynamics
C_{Fm}:	Frictional Resistance Coefficient of model
C_{FS}:	Smooth Frictional Resistance Coefficient
CO_2:	Carbon Dioxide
C_T:	Total Resistance Coefficient
C_{Tm}:	Total Resistance Coefficient of model
DFT:	Dry Film Thickness
EA:	Environmental Auditing
EL:	Environmental Labelling
EMS:	Environmental Management System
EPE:	Environmental Performance Evaluations
EPI:	Environmental Performance Index
EPS:	Eco-Pickled Surface
FR:	Foul-release
GHG:	Greenhouse Gas
H_2SO_4:	Sulfuric Acid
HCl:	Hydrochloric Acid
HF:	Hydrofluoric Acid
HFO:	Heavy Fuel Oil
HNO_3:	Nitric Acid
IMO:	International Maritime Organization
ISM:	International Safety Management
ISO:	International Organization for Standardization
ITTC:	International Towing Tank Conference
k^+:	Reynolds Roughness Number

KPI:	Key Performance Indicator
LCA:	Life-Cycle Assessment
LNG:	Liquefied Natural Gas
MARPOL:	Maritime Pollution (International Convention for the Prevention of Pollution)
MCR:	Maximum Continuous Rating
MDO:	Marine Diesel Oil
MEK:	Methyl Ketone
MEPC:	Marine Environment Protection Committee
MIBK:	Methyl Isobutyl Ketone
NMR:	Nuclear Magnetic Resonanse
1HNMR:	Nuclear Magnetic Resonanse using 1H hydrogen isotope
13CNMR:	Nuclear Magnetic Resonanse using Carbon-12 isotope
NO_X:	Nitric Oxides
PDMS:	Poly-Dimethyl-Siloxane
P_E:	Effective Power
PEG:	Poly-Ethylene Glycol
QAS:	Quaternary Ammonium Salts
Re:	Reynolds Number
ROV:	Remotely Operated Vehicle
R_T:	Total Resistance
S:	Wetted Surface Area (WSA)
SCS:	Smooth Clean Surface
SEP:	Safety and Environmental Protection
SMS:	Safety Management System
SNAME:	Society of Naval Architects and Marine Engineers
SO_2:	Sulphur Dioxide
SOG:	Speed Over Ground
SOLAS:	Safety Of Life At Sea
SPC:	Self-Polishing Copolymer
TBT:	Tributyltin
TEU:	Twenty-foot Equivalent unit
UV:	Ultra Violet
V:	Speed

VOC:	Volatile Organic Content
ΔCF:	Frictional Resistance Increase due to Roughness
ΔU+:	Roughness Function
ϱ:	Density

Introduction

Since the beginning of mankind, humans have engaged in various ways of trading in order to satisfy their needs. What began innocently as an act of trading between products that one had in abundance and another lacked of, has now after centuries evolved into a huge industry spreading all over the world employing hundred thousands of people.

Shipping is without doubt the bigger form of trading occupying almost 60% of current global trading. The number of deadweight capacity offered by the contemporary fleet in combination with low cost prices (compared with other means of shipping such as aviation) and technological advancements, render shipping the No.1 choice when it comes to transporting any sort of merchandise from one point to another.

The art of shipbuilding and shipping in general is very complicated and complex and is affected by a huge number of factors. One of the elements which has always played a major role in the evolvement of the shipping industry has been the application of antifouling coatings.

During the last decades an additional factor has been introduced in the subject of antifouling coatings and this is no other than the environmental consciousness. This has led a significant number of chemically oriented companies that engage in antifouling coating production to reassess their approach on the matter and change their orientation in order to implement specific standards aiming to the protection of the environment.

A significant milestone in this change of approach was the ban of environmentally detrimental TBT (tributylin) – based coat products which led to various changes in the antifouling industry.

Since then a number of TBT-free products have gained their spot in the commercial market and have asserted a certain level of effectiveness when it comes to prevention of marine bio-fouling in the most environmentally friendly way.

Furthermore, another aspect has risen to be a top priority in the shipping community over the last years due to the increasing costs of marine fuels and that is none other than the vessel's performance which is now consistently monitored and recorded in most major ship-owning companies so as to ensure a cost-effective operation of the vessel. The vessel's performance is directly related to the frictional resistance of the hull itself thus the protection of the hull against fouling by the most effective means (and the maintenance of the hull condition over time) has risen to be one of the most important priorities during a ship's life, especially when taking into consideration the relevant costs that are involved.

This thesis gives to the reader the opportunity to go through the basic principles of the antifouling science and coatings, their evolution within time, as well as the chemistry involved. Its main objective is to study the direct connection between a vessel's performance and the condition of the hull (fouling, antifouling coatings, maintenance), through many different case studies. The target is clear: an efficient and cost-effective vessel operation.

Chapter 1 – Introduction to antifouling technology

1.1 Fouling definition and history

Fouling is defined as the unwanted growth of biological material, such as barnacles, algae and mollusks, on a ship's surface when it is immersed in water.

In order to provide a better picture of the fouling process and the antifouling technology basics, Table 1.1 sums up the main aspects and definitions of fouling.

EXPLANATION of FOULING	
Definition of Fouling	The unwanted growth of biological material such as barnacles and algae on ships' surface which is immersed in water
The amount of fouling on an unprotected ship	The ***amount of fouling*** that can be gathered on vessels' bottoms, which are not protected by antifouling system, is of 150kg/m^2 in less than six months of being at sea. Specifically, on very large crude carriers with 40.000m^2 underwater area the amount of fouling can be measured at 6.000t
The need of antifouling systems	Even a small amount of fouling can lead to an ***increase*** of ship's ***fuel consumption*** up to 40% ~ 50% as long as there is a ***resistance to movement***. It's true that a clean ship can sail faster with less energy.
The cost effect of antifouling systems	An appropriate and effective antifouling system can be a ***cost saver*** for an industry in clear-cut ways such as:

on marine industry	➢ Prompt fuel savings by keeping the hull free from fouling micro-organisms. ➢ Wide dry-docking interval when the antifouling system ensures several years of use. ➢ Increased ship's availability *(because of shortage of time in dry-dock).*
The good biocide in an antifouling system	The ***main characteristics*** of a good biocide in an antifouling system are: ➢ Profound spectrum activity ➢ Low levels of toxicity ➢ Low water solubility ➢ Compatibility with coatings' raw materials ➢ Propitious price / attribution ➢ No bio – accumulation in food chain ➢ It is not persistent in the environment

Table 1.1: A short explanation of fouling [1]

Table 1.2 demonstrates the levels of attachment of marine micro-organisms on any kind of surface that is submerged into water.

Type of Process	Attached Micro - Organisms	Substance of formed film	Time of Formation
Level 1: Substantially physical forces such as electrostatic interactions, Van der Walls forces and Brownian	Accession of organic molecules like proteins, polysaccharides and proteoglicans	Presumptive	~ 1min

movement			
Level 2: Revertible aspiration of attached species from previous level, basically by physical forces and their interaction with protozoan and rotifers	Bacteria like Pseudomonas putrefactions, Amphora coffeaeformis, Amphiprora paludosa and Licmophora abbreviata	Microbial bio - film	1 up to 24h
Level 3: Settlement of micro – organisms with greater protection from predators, toxicants and environmental variations	Spores of microalgae such as Ulothrix zonata, Enteromorpha intestinalis, Vaginicola and Vorticella	Bio - film	~ 7 days
Level 4: Increase in the taking of more particles and organisms, like the larvae of marine macro - organisms	Macro – organisms like Balanus amphitrite, Laomedia flexuosa, Mytilus edulis and Styela coriacea	Mature and well structured film	From 2 to 3 weeks

Table 1.2: Levels of formation of marine biofouling [2]

Figure 1.1 shows a representation of the evolution of micro and macro organisms depending on time and size.

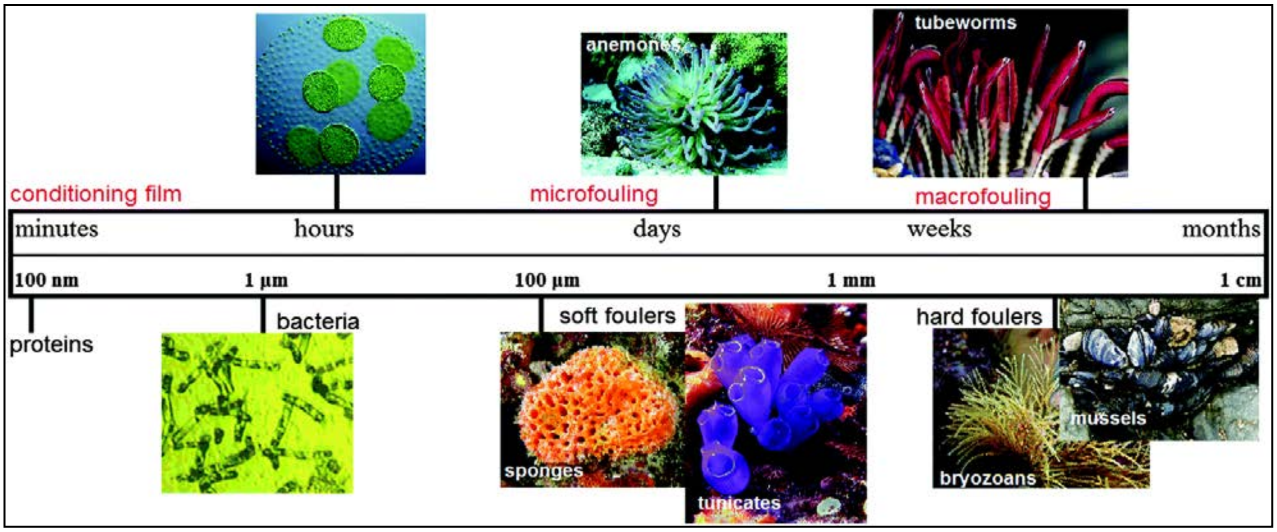


Figure 1.1: Characteristics of marine macro and micro-organisms [3]

In Figure 1.2 fouling is divided into categories of different macro and micro-fouling organisms.

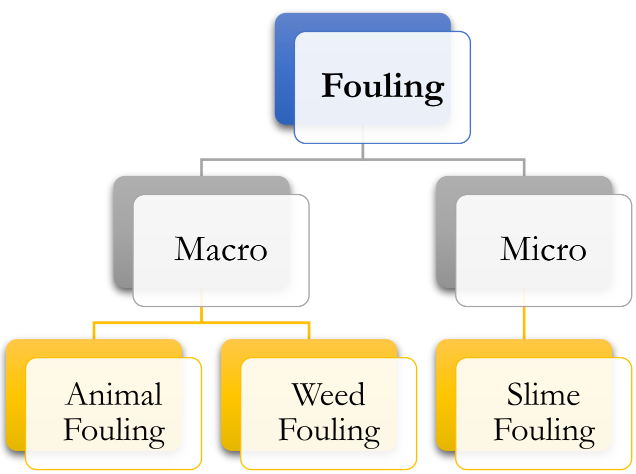


Figure 1.2: Macro and Micro Fouling Organisms [4]

Since the early days of sailing, it became obvious that ships could travel faster and consume less fuel (or energy in general, depending on which time we are referring to) as long as their hulls remained clean and free from any sort of fouling organisms. This same observation led to the beginning of the development of what is today referred to as "anti-fouling" technology.

Ever since vessels were introduced in order to be used for military or trading activities the control of the fouling growth on their hulls became an important issue.

The first recorded civilization which exploited the sea as a means of travelling was the ***Phoenicians***, who were the first to become a well-recognized maritime power. These were the times when the first recorded forms of antifouling "coatings" actually took place. What was used back then was a mix of copper lead and other toxic material, which of course had a huge impact on the maritime environment.

Another historic finding related to antifouling in early history is an ***Aramaic papyrus***, which give us information about the use of antifouling methods based on toxic substances around the 5th century BC [4]:

"... the arsenic and sulfur have been well mixed with Chian oil that you brought back on your last voyage, the mixture evenly applied to the vessel's sides, that she may speed through the blue waters freely and without impediment ..."

Centuries after the Aramaic papyrus, a message from ***Christopher Columbus***, who was also suffering from fouling problems, gives us details about the antifouling methods used [4] :

"All ships' bottoms were covered with a mixture of tallow and pitch in the hope of discouraging barnacles and teredo and every few months a vessel had to be hove-down and graved on some convenient bench. This was done by careening her alternately on each side, cleaning off the marine growth, re-pitching the bottom paying the seams."

Throughout the 19th century the importance of protecting a vessel's hull became even more obvious. New methods were introduced and the first recorded antifouling coating came into existence in the middle of the 19th century and was a mixture of readily available components of copper, arsenic and mercury dispersed in an oil based resin, such as linseed oil.

Through the release of toxic compounds around the vessel's hull, these coatings were effective against the growth of marine organisms.

The successor of this toxic mixture of compounds, the gum rosin, was introduced in the early 20th century, but the evolution of antifouling coatings was moving really slowly until the 1970's when the advent of the tributyltin self-polishing copolymer antifouling (TBT-SPC) first came in place. This is actually the first recorded synthetic antifouling composition. It quickly became the industry's benchmark, due to its prolonged periods of protecting the hull, thus increasing the intervals between the need for docking the vessel.

1.2 TBT antifouling compounds

In the past, ships' hulls were protected by the use of arsenical or mercurial coatings and a variety of other pesticides which served as antifouling systems. As years progressed these substances were replaced with the well-known TBT (tributyltin) compounds. So around the 70's, the new "era" in the antifouling industry was defined by the use of metallic compounds with the ultimate goal of providing efficient fouling protection. In this regard, it is useful to make a short description in order to define those TBT compounds which were for many years the main ingredient of a variety of antifouling coatings.

The tributyltin (TBT) is an organometallic compound (Figure 1.3), commonly used in antifouling marine coatings. It is highly toxic and it can remain in the marine environment for years, affecting aquatic species in a detrimental way.

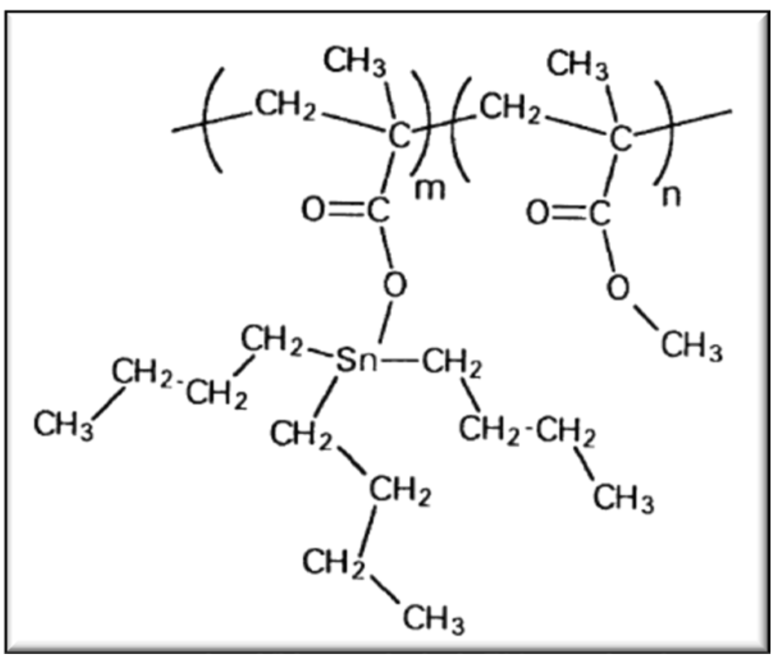
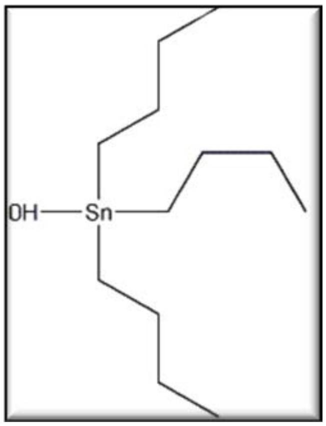
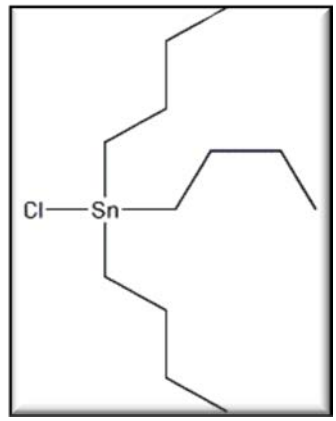


Figure 1.3: Chemical formula of TBT [5]

Two of the most common TBT compounds are the tributyltin hydroxide and the tributyltin chloride (Figure 1.4).





Tributyltin Hydroxide

(predominant species in seawater)

Tributyltin Chloride

(~3% in seawater)

Figure 1.4: Tributyltin Hydroxide and Tributyltin Chloride, two of the most common TBT compounds [6]

The TBT compounds have served during many years as a booster, along with cuprous-oxide (a substitute of lead-based products which is far more toxic), arsenic and organo-mercury compounds, so as to enhance the biocide characteristics of the antifouling coatings. In Figure 1.5, one can see the biocide-based antifouling coating system's behavior when this type of coating is exposed to sea water.

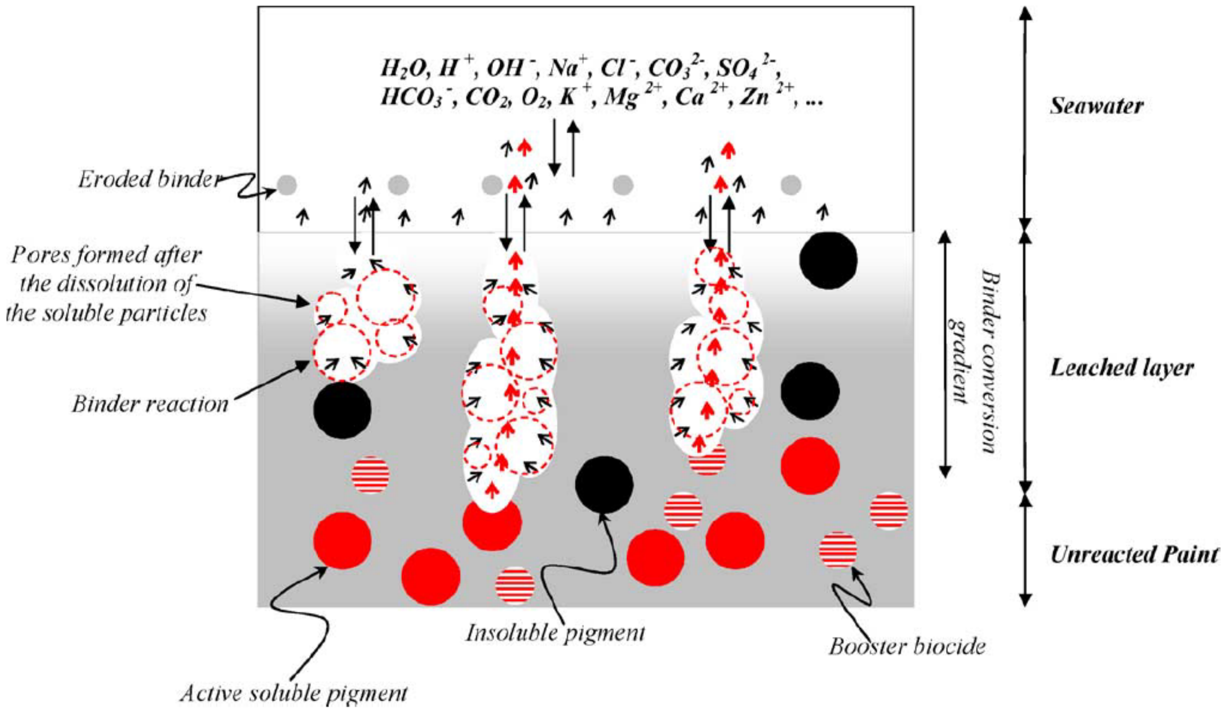


Figure 1.5: The behavior of biocide-based antifouling coating system exposed to sea water [5]

The TBT-based coatings can break down in two main categories [7]:

1) **Free association coatings**: The main characteristic of the free association coatings is their ability to permit to their biocide to percolate freely into the water at an unstable rate.

2) **Self-polishing copolymer coatings**: The main characteristic of the self-polishing copolymer coatings, which also differentiates them from the free

association ones, is that the biocide components chemically encompass and are diluted in a slow pace as the coatings' surface decolorizes.

Figure 1.6 provides an illustrative demonstration of the mechanism of the two different TBT-based coating types described above.

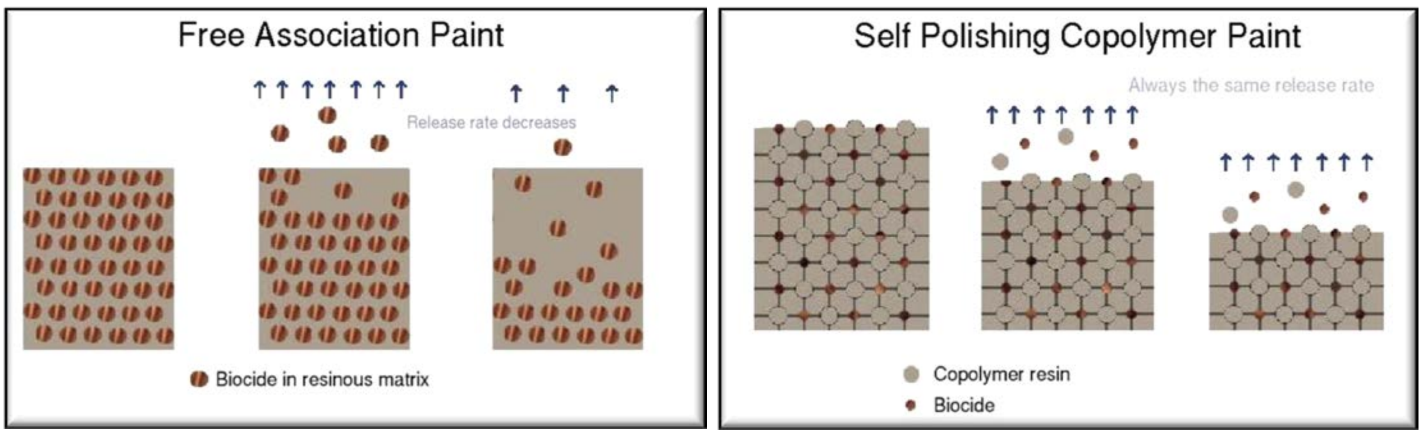


Figure 1.6: Illustration of the free association and the self-polishing copolymer coatings [8]

What also made the TBT-SPC antifouling coatings significantly special, was their ability to create a smooth layer between the vessel's hull and the seawater, thus reducing the overall resistance of the vessel and the power requirements, which leaded to lower consumption and operational cost.

The two main kinds of antifouling coatings, at that time, were the "Insoluble Matrix Coatings" and the "Soluble Matrix Coatings" (Figure 1.7), which are explained here below. [2], [5], [9]

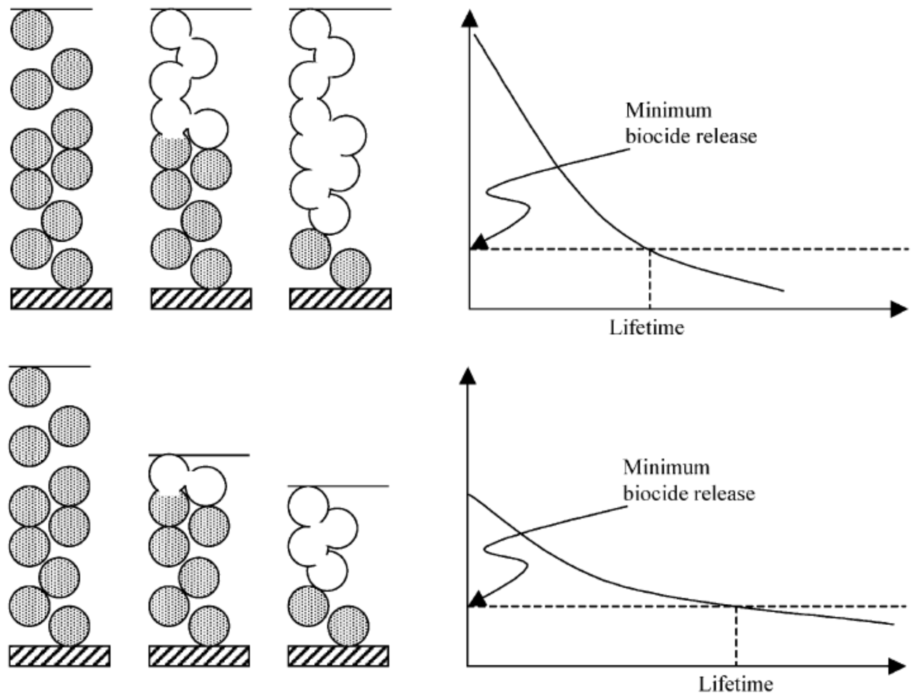


Figure 1.7: Working scheme and biocide release rates of traditional insoluble and soluble matrix paints. "Minimum biocide release" indicates the limit for efficient protection against fouling (dependent on the fouling conditions). [5]

Insoluble Matrix Coatings: In insoluble matrix coatings, the polymer matrix does not polish nor erode after the ship's immersion into water. In these coatings, profuse molecular weight polymers can be used, like vinyl, epoxy resin, acrylic and chlorinated rubber. It was soon noticed that, during the ship's operation, the dissolved tincture ions diffused through a slightly thick leached layer, while the rate of release was falling under minimum value in order to restrain the process of fouling. Coatings of such composition and type have good mechanical characteristics as well as resistance in cracking and stability to oxidation and photo–degradation.

The only disadvantage is the short lifetime of these coatings (approximately 12 to 18 months on seagoing operation), which is the main cause why marine companies do not prefer their application on vessels.

Soluble Matrix Coatings. Soluble matrix paints were developed in order to avoid the loss of A/F efficiency with time by incorporating a binder which could be dissolved in sea water. The classical film-forming material in these systems contains high proportions of rosin. Rosin is a natural and very compatible resin obtained from the exudation of pine and fir trees [26]. Its variable composition, which contributes to a rather unpredictable performance of natural rosin-based paints, consists generally of about 85–90% of acidic materials, of which the abietic and levopimaric acids are the most important [4].

Resin acid is the general name for all kinds of acids that share the same basic skeleton, a three-fused ring and the empirical formula $C_{20}H_{30}O_2$. The resin acids may be classified into two types, abietic and pimaric. The abietic-type group includes levopimaric, l-abietic and neoabietic.

Each of these acids contains two double bonds and a carboxyl group. These conjugated double bonds affect the stability of the resin, and make it oxidable when exposed to air. This undesirable feature had to be taken into account during dry-docking, as the application of the paint could only be performed a short time before immersion. Once in contact with sea water, the carboxyl groups reacted with sodium and potassium ions present in the sea water, and thus gave resins of high solubility.

It should be pointed out that the introduction of TBT-SBC coatings came in place at the same period when fuel prices were rising almost 200% in under a year (from 15$ to 45$/barrel) and the fact that an antifouling coating could reduce fuel consumption and at the same time protect against fouling growth was of vital importance.

Nevertheless, it was not long until the negative environmental effects, caused by the use of TBT coatings, were observed and this revealed the need for a more environmentally friendly approach in the coating industry. Many studies, which supported this idea, showed that the use of TBT compounds was the main reason of aquatic pollution that resulted in the extinction of vital micro-organisms and was also proved to cause serious shell deformation in oysters, mussels, clams, sex change (imposex phenomenon) in sea-snails, immune response, as well as neurotoxic and genetic effects in other marine species.

Some of the most harmful effects of the TBT coatings are summed up in Table 1.3 [8]:

Water and sediments	Tributyltin-organotin compound (TBT) is a broad spectrum algicide, fungicide, insecticide and miticide, used in anti-fouling paints since the 1960's. It is toxic to humans. It can be decomposed in water under the influence of light (photolysis) and micro-organisms (biodegradation) into less toxic di- and mono-butyltin. Its life varies from a few days to a few weeks, but decomposition is slower when TBT has accumulated in sediment - if oxygen is completely excluded, TBT half-life may be several years. Therefore waters with heavily sedimented bottoms - such as harbors, ports, estuaries - are at risk of being contaminated with TBT for several years.
Shell malformations	TBT causes thickening of shells in sea oysters, caused by disturbance of calcium metabolism.
Imposex	Females develop male sexual characteristics. Imposex has been recorded in 72 marine species. Concentration of just 2.4 nanograms of TBT per liter is needed to produce sexual changes in dog-whelks, leading to sterility.

Marine mammals	Traces of TBT have been found in whales, dolphins and members of the seal family in the United States, south-east Asia, the Adriatic Sea and the Black Sea. The TBT is absorbed via the food chain.
Reduced resistance to infection	Research has shown that TBT reduces resistance to infection in fish, such as flounder and other flatfish which live on seabed and are exposed to relatively high levels of TBT, especially around areas with silty sediment like harbors and estuaries.

Table 1.3: Effects of TBT in the marine environment [8]

During the 80's, this problematic scheme was brought to the attention of the Marine Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) and the United Nations Agency, which were at that time troubled with both the safety of shipping, the protection of the environment and the prevention of marine pollution.

Soon after that, in the early 90's, the IMO applied pressure to all governments worldwide to take imminent actions in order to eliminate harmful antifouling technologies and invest money towards the development of new technologies in this field.

TBT-SBC coatings were banned worldwide on January 1st 2003, when it became clear that the tin-free options could replace them effectively. Copper and silyl acrylate-based-tin free SPCs were developed in the early 1990's.

Reaching the second decade of the 21st century the market is dominated by biocide-containing antifouling coatings. However, this dominance is slowly being eroded with the creation of viable non-toxic biocide free technologies, known as "foul release coatings". It should be noted that foul release coatings are as old as TBT-SBC ones but high components' cost did not allow them to become highly commercial.

The first foul release coatings became available in 1996 and were silicon based. The growth prevention mechanism of such coatings was different, as it was based on their hydrophobic properties. This means that they effectively prevented the strong adhesion of fouling organisms through influencing the strength of the adhesive they used to attach on surfaces.

Silicon based coatings were modified in the early 21st century so as to be used on large commercial ships, such as containers and reefers, which were engaged in high activity. Most recently, the foul release coatings have been modified so as to take advantage of the hydrophobic nature of the silicones, as well as hydrophilic properties of various added polymers, with the intention of confusing the fouling organisms when they needed to make a choice as to where to settle.

1.3 Marine oriented coatings

When it comes to paint technology, there is a huge range of different types of coatings, each for different types of application and with different properties. Those properties (and thus the different application categories) derive from the different ingredients that are used for each coating and their unique characteristics.

The marine industry needs coatings that demonstrate several properties, such as "smoothness", "durability", "adhesion", etc., when they are in contact with sea water (a corrosive and fouling environment). The main types of marine oriented coatings are summarized and reviewed synoptically below [10]:

1. **RFT – 380 / PEGylated Compounds and Process for making antifouling biocompatible materials** ***(Application:** General/ Marine/ Biomedical)* [10]

PEG is the acronym for polyethylene glycol polymer.

Researchers have developed a new class of PEGylated polyurethane materials using a novel process, which is much more effective than traditional procedures. The resulting compounds are novel siloxane-PEG copolymers having terminal amine functionality and a backbone of siloxane having a varied number of pendant hydrophilic PEG chains. The low surface energy siloxane can help in bringing PEG chains to the surface, and the terminal amine functionality can be bound into the polyurethane by reacting with isocyanate. Therefore, the surface of the material will be amphiphilic, while the underlying polyurethane base will give toughness to the system.

This approach allows the precise control over the number of hydrophobic PEG chains, the siloxane and PEG chain lengths, and the final amine functionality.

2. RFT – 319 / Amphiphilic Fouling Release Coatings *(Application: Marine)*[10]

Scientists have found that incorporating oligo (ethylene glycol) segments and per-fluorinated siloxane segments into moisture-curable poly-siloxane coatings results in a synergistic enhancement in fouling-release properties towards a series of marine organisms. Also, the addition of the moieties does not negatively affect the mechanical properties of the coating after immersion in water. This invention has led to the development of novel amphiphilic fouling release coatings that exhibit superior fouling release properties.

3. RFT – 283 / Polymer for Non-Fouling or Fouling-Release Type Coatings *(Application: General/ Marine)* [10]

Scientists have recently invented a novel zwitterionic/amphiphilic pentablock copolymer coating that exhibits superior anti-fouling and fouling release properties.

The invention combines the low surface energy of poly-dimethyl-siloxane (PDMS) and the protein resistance properties of both zwitterionic and amphiphilic compounds.

Since the amphiphilic substance has both hydrophobic and hydrophilic moieties on one compound, the polymer forms nanoscale heterogeneities, creating a surface topography that is unsuitable for the proliferation and adsorption of proteins and marine micro-foulers.

The main benefits of this type of coatings are summed up below:

- ✓ They exhibit superior anti-fouling and fouling release properties due to unique surface topology.
- ✓ Pseudo-barnacle measurement demonstrates a weak adhesion on the surface of the coatings.
- ✓ High water contact angle values indicate a surface enriched with poly-dimethyl-siloxane (PDMS).

4. **RFT – 271 / Linear Glycidyl Carbamate (GC) Resin for High Flexible Coatings** *(Application: General/ Marine)* [10]

Scientists have invented a low-VOC (Volatile Organic Compound), chromate-free, solvent borne, highly flexible coating resin system of low viscosity. This resin system has the functionality of an epoxy resin while providing the performance of a polyurethane coating without exposing the end-user to isocyanates. When cross-linked with amines, these GC coatings have excellent adhesion, hardness, solvent resistance, gloss, and flexibility on cold-rolled steel and aluminum substrates (Figure 1.8). This polymer technology was specifically developed to be used to obtain highly flexible coatings while maintaining good solvent and chemical resistance.

The benefits of this type of coatings are summed up below:

- ✓ Low VOC
- ✓ Chromate-free
- ✓ Low viscosity
- ✓ Corrosion resistant
- ✓ Solvent resistant

Figure 1.8: Images of coating on steel and aluminum after 240 hours of salt spray [11]

5. **RFT – 254 / UV – Curable Low Surface Energy Coatings with Fouling Release** *(Application: General/ Marine/ Anti - Graffiti)* [10]

Scientists have invented a novel polyester composition that is UV-curable and exhibits low surface energy. The composition contains polydimethylsiloxane (PDMS) and involves mixing polyesters with co-reactants and photo-initiators, and curing the compounds using either visible or ultraviolet (UV) light (Figure 1.9).

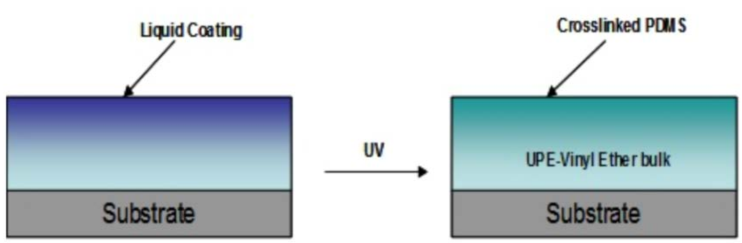


Figure 1.9: Illustration of the UV curing of PDMS functional coating using donor-acceptor chemistry [12]

These coatings are useful in applications where low surface energy is desired, such as marine ship hulls, anti-graffiti surfaces, release coatings, and protective wood coatings with easily cleanable surfaces.

The benefits of this type of coatings are summed up below:

- ✓ They are solvent, water, and acrylate free, eliminating health hazards associated with acrylates.
- ✓ They have low cost of manufacturing, due to low levels of siloxane used.
- ✓ They do not suffer from oxygen inhibition.

6. RFT – 231 / Siloxane Polyurethane Coatings for Antifouling Applications *(Application: General/ Marine/ Anti - Graffiti)* [10]

This invention describes a novel siloxane-urethane composition developed at the North Dakota State University (NDSU) that may be used to form fouling-release coatings for applications such as protecting ship hulls and creating anti-graffiti paints. The coatings were developed from unique single-end-functional siloxane polymers, which are incorporated into polyurethane coatings and result in coatings having low surface energy but good adhesion and mechanical properties (Figure 1.10).

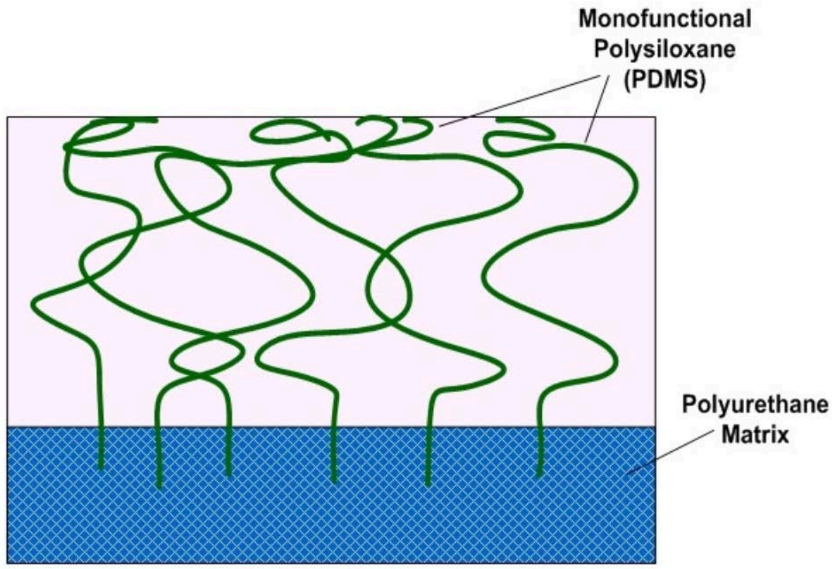


Figure 1.10: Cross section of a novel coating with a mono-functional poly-siloxane (PDMS), anchored in a polyurethane matrix to combine desirable attributes of both components [13]

The benefits of this type of coatings are summed up below:

- ✓ It improves adhesion and mechanical strength, and low surface energy, significantly improved over currently available silicone-based fouling release coatings.
- ✓ Coatings are self-stratifying (self-organized into two or more distinct layers upon application), with a low surface energy, low modulus top layer and a tougher lower layer.
- ✓ They have potential commercial significance in applications related to marine antifouling coatings, anti-graffiti and others.

7. RFT – 214 / Unique Antifouling and Antimicrobial Coatings for Marine Applications *(Application: Marine/ Biomedical)* [10]

This invention pertains to the development of stable polymeric anti-fouling surface coating formulation that contains Quaternary Ammonium Salts (QAS) as the primary disinfectant.

The main benefits of such coatings are summarized below:

- ✓ Confer anti-microbial effect to a diverse array of polymers and coatings, ranging from medical devices to underwater instruments
- ✓ Broad efficacy against gram+ gram- bacteria, and yeast
- ✓ Tethered QAS disrupts outer membranes, meaning the anti-microbial surface can kill microbes on contact, making attachment to surfaces (and eventual biofilm formation) less likely/rapid

8. RFT – 197 / Thermoset Siloxane – Urethane Fouling Release Coating *(Application: General/ Marine)* [10]

Scientists have invented a novel non-toxic, cross-linked thermoset polysiloxane-polyurethane coating that exhibits properties as a foul release (FR) coating and allows organisms to be sloughed off by shear forces obtained at a ships cruising speed. In addition to exhibiting its fouling release behavior, these coatings have been demonstrated to provide improved durability to its coating surface.

9. RFT – 157 / Coating Formulations Exhibiting Antifouling Properties for Marine Vessels *(Application: Marine)* [10]

Scientists have invented a group of novel polymeric coating formulations that has been found to demonstrate its effectiveness in preventing marine-life fouling on surfaces exposed to salt and fresh water. This invention involves novel poly-siloxane-poly-caprolactone block copolymers where the linking group between the blocks is a carbamate group. This linking group provides better compatibility of the block copolymer with polyurethane coating compositions. Also included are star branched block copolymers where the linear poly-siloxane polymer forms the central segment and multiple caprolactone polymers radiate from the two end groups, and cross-linked polyurethane coatings prepared from these block copolymers.

The benefits of this type of coatings are summed up below:

They reduce significantly the amount of fouling on the ships' hulls. This reduces the water resistance and, as a consequence, the fuel consumption and the fleet costs.

10. RFT – 133 / Environmental Friendly Coatings for Marine Applications *(Application: Marine)* [10]

Scientists have developed novel, silicone-based compounds which incorporate tethered biocide moieties, and which can be used in coating formulations to prevent or reduce marine fouling on ship surfaces.

The benefits of this type of coatings are summed up below:

- ✓ It is considered "Green Technology", since the tethering of biocide may reduce leaching of hazardous chemicals.
- ✓ NSDU anti-fouling coatings improve fuel economy for marine vessels.

- ✓ It prevents or reduces fouling of ships' hulls and other surfaces by aquatic organisms.
- ✓ It has effective anti-fouling properties.

1.4 Common types of marine antifouling products used nowadays

As stated previously, when choosing an antifouling coating, various factors have to be taken into consideration such as the temperature, the aquatic environment salinity, the trim of the vessel, the presence of silt (in case of vessels operating in fresh water) and the marine environment (attachment of either micro or macro organisms).

These factors can affect the vessel in numerous ways such as speed, fuel efficiency, emission augmentation and generally compromise the ship owner's investment (for example if the vessel cannot achieve the speeds or consumptions agreed in the charter party).

There are two main types of antifouling coatings that are most commonly used nowadays and they are summed up in Table 1.4.

Traditional Leachable Coppers	Ablative Polymers
• They can be either hard or soft	▪ The ablative polymer coatings are more sustainable
• The drastic ingredient can leach out while the coating film remains mostly intact	▪ In these coatings, both the toxicant and the coating film perish
• They lose their performance and effectiveness as time passes by	▪ These coatings maintain more enduring performance through time

• They are repainted after dry reposition	▪ These coatings can be used in every season and climate
• They do not require drift so they can work equally right at the dock and underway	▪ These coatings require the movement of the vessels in order to be effective
• The hard leachable copper coatings resist in chaffing which make them ideal for trailer use	▪ The ablative polymer coatings tend to be smooth after their application on vessels' hulls

Table 1.4: The two most common types of antifouling coatings on the market and their main characteristics [14]

1.5 Characteristics of antifouling coatings

The importance of certain traits, when it comes to marine antifouling coatings, has been brought forward before in this thesis. Although the essential characteristics of an effective antifouling coating are more or less well known, there is still dispute over their actual composition and what ingredients should and should not be used in order to achieve the needed properties. The effectiveness and durability of an antifouling coating are multivariable problems and some of the parameters involved are the application thickness layer, the rate of diluteness, the area of application and the area of operation.

The effectiveness of the antifouling coatings is defined by their ability to "kill" the marine bio-fouling organisms from the time of first contact with the aquatic environment and for as much time as possible after that. As the effective duration of an antifouling coating plays a very important role, the chemical industry is searching ways in order to extend the protection period even more.

The main characteristics of an effective marine antifouling coating are presented below [23]:

- **Durability**. This is one of the biggest aspects that affect the antifouling coating and depends on the resistance to mechanical damage, the water's erosive impacts, by its movement and the diluteness of its mixture.

- **Adhesion**. It is widely accepted that, this attribute has to be liturgical on both wooden and steel ships' hulls. Most of the times the application of the new coating is done in prevailing weather conditions which are far from ideal for this purpose. For that reason, the antifouling coating must always be applied under strict supervision by a specialized technician. Researchers often observe big deviations in the performance of the same coating due to different weather conditions during application.

- **Impact on Corrosion**. It is vital that when an antifouling coating is applied on a steel vessel, it should primarily protect the vessel from corrosion. The weak effectiveness of a coating can lead to excess rusting of the surface and fouling of the exposed areas. The coating's contribution depends on both its thickness and resistance to the penetrability of sea water. Moreover, the elements of antifouling coatings should not precipitate steel's corrosion.

- **Smoothness**. It is of vast importance for an antifouling coating to have smooth surface so as to maintain the frictional resistance of the vessel to a minimum level. This specific characteristic is by far the most crucial when the vessel's speed is essential and this is the case with many modern vessels. When it is mandatory, the application of a thick antifouling coating must be tenderly formulated in order to permit flexible operation (in different areas, with different speeds etc.)

- **Convenience on Application**. The antifouling coatings have to be formulated in such way so as for the specialized technicians to be able to apply them either by brush or spray equipment. Spraying the area is far more convenient as it results in major time saving. It should also be noted that the strenuous changes in temperatures can highly affect the application's convenience since vessels must be coated in all seasons and climates.

- **Drying Time**. It is proved that the time which is available for application of the coating is generally of narrow limits so the process of drying has to be rapid. Many maritime companies commonly restrict the docking period to one day during of which the vessel has to be cleaned and coated. In case the coating film is not hardened before the vessel's entering into the water, its effectiveness can be reduced dramatically. It has been observed that many coatings are hardened under water, so the constant period following the undocking may serve in preventing enormous erosion or flow of the coated surface.

Chapter 2 – Antifouling coatings - Composition, application, selection criteria, standards and classification

In Chapter 1, an extensive presentation about the historical retrospect of antifouling coatings, the types that have been used till nowadays in the marine industry, as well as their main characteristics has taken place. Chapter 2 will focus on the composition of the antifouling systems, their application, selection criteria and principal standards.

2.1 Composition

While the composing compounds of an antifouling coating can be unlimited and combined in various ways, they can be divided in three main categories:

1) Pigments and extenders
2) Solvents
3) Other additives

In order to have a complete understanding of the purpose of each category, in the next paragraphs they will be studied one by one.

2.1.1 Pigments and extenders

The pigments and extenders are used in the form of fine powders. Depending on the coating type, they are dispersed into the binder in different particle sizes, for example:

for a finishing paint their size is about 5-10 microns, while for primers the size is up to 50 microns.

These materials can be divided in different main types, as shown in Table 2.1.

Type	**Purpose**
Anticorrosive pigments	To prevent corrosion of metals by chemical and electrochemical means
Barrier pigments	To increase impermeability of the paint film
Coloring pigments	To give permanent color
Extending pigments	To help give film properties required

Table 2.1: Types and purpose of pigments and extenders [15]

A short presentation for each type of pigment will follow.

<u>Anticorrosive Pigments</u>

As one can easily understand the main purpose of these compounds is to enhance the corrosion-resistance properties of the end product. The main components used in this type of pigments are red lead, zinc chromate, zinc phosphate and zinc.

Red lead is most probably the most commonly used anticorrosive pigment. However, its use has raised environmental and health considerations and, during the last years, its use has been significantly reduced, especially in the most developed countries. Besides red lead, the use of metallic lead is often encountered. Nevertheless, the corrosion protection mechanism of the metallic lead is uncertain and its use affects the environment in the same way as red lead.

Zinc chromate pigments are divided in two types: the zinc potassium chromate and the zinc tetroxy chromate. Both are functioning as anticorrosive pigments by releasing water soluble chromate ions, which help to passivate the steel surface. Once again health considerations weight out any benefits these types of pigments might have and their use is steadily being phased out.

Zinc phosphate is, also, a widely used anticorrosive pigment, but its actual corrosion protection mechanism is still under doubt. The main benefit is that zinc phosphate can be incorporated into almost any binder and, because of its low opacity and transparent nature, paints of any color can be produced.

Metallic zinc is also widely used in primers and gives excellent resistance to steel corrosion, with its initial protection being originated by galvanic action. It should be noted however that while being exposed to the atmosphere a progressive buildup of zinc corrosion products occurs, producing an impermeable barrier with zero or close to zero galvanic protection.

Some other anticorrosive pigments that have also made their appearance through the years, but have not been accepted in general, because of their lack of cost effectiveness, are: Barium Metaborate, Calcium Molybdate, Zinc Molybdate and Lead Silicochromate.

Barrier Pigments

When it comes to barrier pigments the most common types are aluminum (leafing aluminum) and micaceous iron oxide (MIO). Both of these types have particle shapes which are termed lamellar (Figure 2.1) and they are often used in combination. The MIO pigmented films present high durability, while aluminum has been used for many years as the principle pigment for paints used in underwater applications.

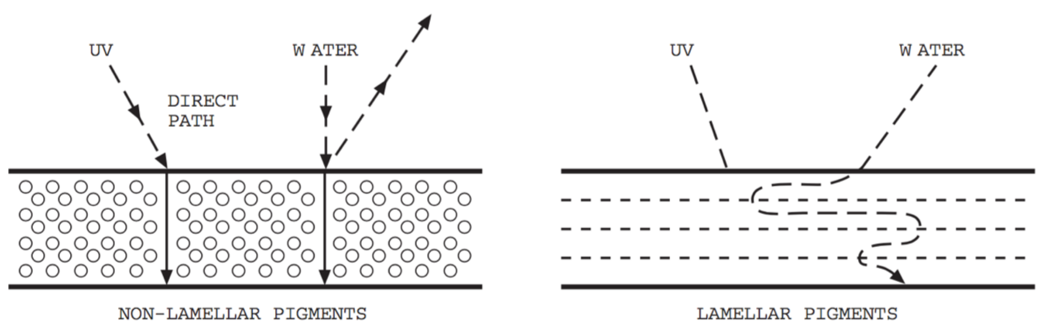


Figure 2.1: Increase of the impermeability of the film and binder protection due to lamellar structure of pigment [15]

Coloring Pigments

This type of pigments provides both color and opacity and can be divided in inorganic and organic types. Inorganic pigments can be naturally occurring or synthetically produced, while all organic pigments are nowadays synthetically produced. The most common coloring pigment is titanium dioxide. Coloring pigments are generally bright in color and their low toxicity makes them more acceptable compared to other types of pigments.

Extended Pigments

They are most commonly known as extenders and, as their name suggests, they are used to "extend" the pigmentation of the paint until the required pigment volume concentration is achieved. They are all inorganic powders with various shapes and sizes and the most common types are presented in Table 2.2.

Extender	Uses
Barytes (Barium Sulphate)	A medium hard powder which helps to reinforce the film.
China Clay	Sometimes used to vary the level of gloss. Has a relatively high oil absorption.
MICA	The lamellar properties of this material enable it to act to some extent as a barrier pigment to reduce permeability. It can also improve film durability by preventing cracking.
TALC	Can have a similar effect to MICA but to a lesser degree.

Table 2.2: Most common extender types and their use [15]

2.1.2 Solvents

Traditionally, solvents have constituted a major part of organic coatings. Solvents are added to coatings to dissolve or disperse the other constituents of the formulation (such as viscous polymeric binder materials and pigments). Furthermore, the solvents reduce the viscosity of the liquid coatings, thereby enabling application of the coating by spraying or dipping [16]. Liquids used as solvents in paints can be described by one of the three ways below [15]:

True Solvent

A liquid which will dissolve the binder and is completely compatible with it.

Latent Solvent

A liquid which is not a true solvent. However, when mixed with a true solvent, the mix has stronger dissolving properties than the true solvent alone.

Diluent Solvent

A liquid which is not a true solvent. It is normally used as a blend with true solvent/latent solvent mixes to reduce the cost. Binders will only tolerate a limited quantity of diluents.

Table 2.3 presents the main types of solvents and their use in typical paint types.

Solvent Type	Typical Solvent Name	Typical Paint Types
Aliphatic	White Spirit	Most conventional paints based on vegetable oils
Aromatic	Toluol	Quick drying primers for automatic plants
	Xylol	Modified alkyds. Chlorinated rubbers, some stoving paints. A diluent solvent for epoxies, vinyl, polyurethanes
Ketones	Acetone	Quick drying primers for automatic plants
	Methyl Ketone	True solvent for vinyls. Quick drying primers

	(MEK)	
	Methyl Isobutyl Ketone (MIBK)	True solvent for vinyls used sometimes for epoxies
	Cyclohexanone	A slow evaporating true solvent to give good flow in vinyls and epoxies
Alcohol	Isopropanol	Latent solvents for vinyls, wash and etch primers
	Butanol	Some stoving paints used for epoxies in conjunction with aromatics
Esters	Butyl Acetate, Cellosolve Acetate	Polyurethane and vinyls
Water	Water	Emulsion paints-some special epoxies

Table 2.3: Solvent types and their uses [15]

2.1.3 Other additives

As we have already stated, a number of additional compounds can be added to the main ingredients of an antifouling coating, so as to enhance some of its properties, such as shelf life, film formation or film curing.

Table 2.4 gathers typical paint additives according to their use [15].

Enhanced Property	Paint additive
Aids to Manufacture	Dispersion agents
	Defoamers
Aids to shelf life	Stabilizers
	Anti-setting agents

	Anti-skinning agents
	Preservatives
	Thickening agents
	Moisture absorbers
Aids to application	Flow promoting agents
	Solvent retarders
	Conductivity controllers
	Antistatic agents
Aids to smoothness	Anti-floating agents
	Pattern additives
	Matting Agents
	Thixotropes
	Anti-gas Checking agents
Aids to Film Curing	Driers
	Curing agents/catalysts
	Adhesion promoters
Aids to Film Formation	Heat stabilizers
	Fire retarders
	Optical brighteners
	Slip and anti-slip agents
	Anti-fouling agents
	Fungicides
	Bactericides
	Absorbers
	Anti-scuff agents
	Corrosion inhibitors

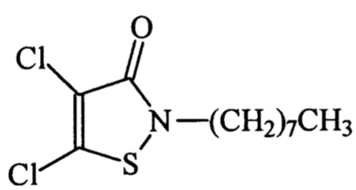
Table 2.4: Paint additives and their use [15]

2.1.4 Composition of the two main antifouling coating categories

The antifouling coatings are divided into two main categories: copper-based coatings and nontoxic fouling-release coatings.

1. **Copper-based Coatings**

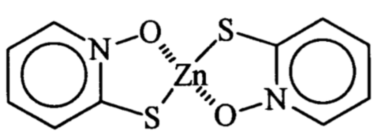
   Such type of coatings has been used in the marine industry for over 200 years and it has been reported that the British Navy used copper sheathing on ships since 1779. The modern copper based coatings are effective due to three important factors: (1) the toxicity of copper (very effective for fouling organisms), (2) the subordinate biocides (which also offer a protection of the surface against marine organisms) (Figure 2.2) and (3) the ablative resin system (which slowly but steadily removes fouling by means of dissolving).



4,5-Dichloro-2-*n*-octyl-4-isothiazoline-3-one

Synthesis of the product

Sea Nine 211 – Rohm and Haas Company, Spring House, PA U.S.A.



Zinc complex of 2-pyridinethiol-1-oxide

Synthesis of the product

Zinc Omadine – Arch Chemicals, Norwalk, CT U.S.A.

Figure 2.2: Chemical composition of two subordinate biocides [17]

2. **Nontoxic Fouling-Release Coatings**

   Nontoxic hull coatings involve fluoro-polymer and siloxane based products. These coatings have been tested in laboratories for over 25 years and are the so called "fouling release" coatings, so as to discriminate them from hazardous (previously mentioned) coatings. Mainly, these coatings obstruct in the most adequate way the attachment of fouling. It is noticed that, such coatings substantially limit the strength of the attachment between the hull and fouling organisms by making it so loose that it can be drifted away by the weight of the fouling or by the movement of the ship through seawater. The effectiveness of such coatings is subject to the thickness of the coating and the area of operation.

Figure 2.3 presents the mechanisms of biocide-release-based antifouling coatings and non-biocide-release-based antifouling coatings.

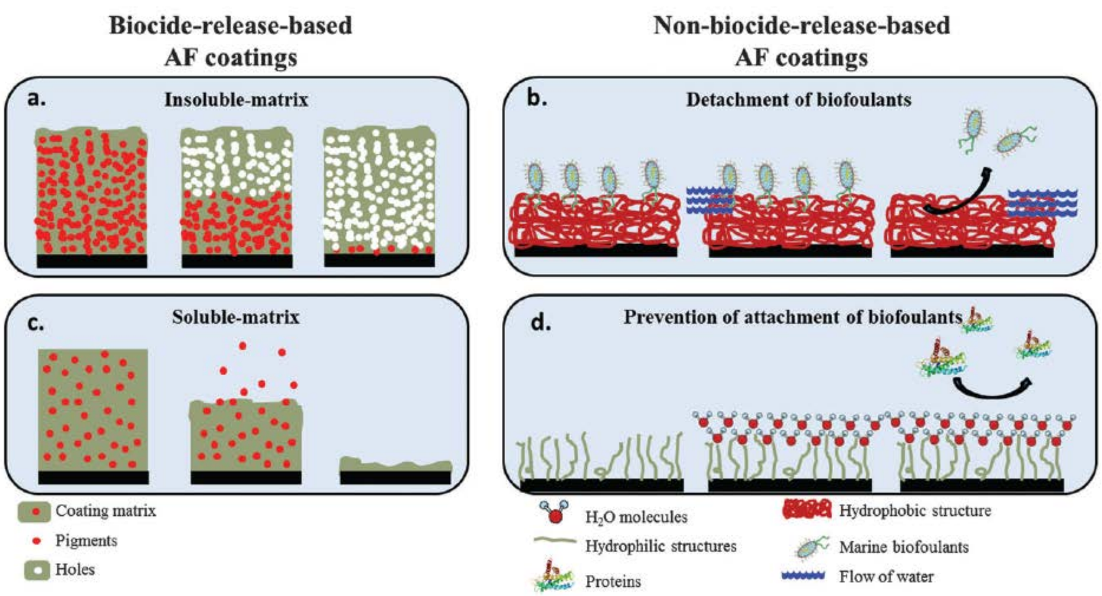


Figure 2.3: AF coatings with and without biocide-release [3]

Figure 2.4 shows different types of matrices in antifouling coatings.

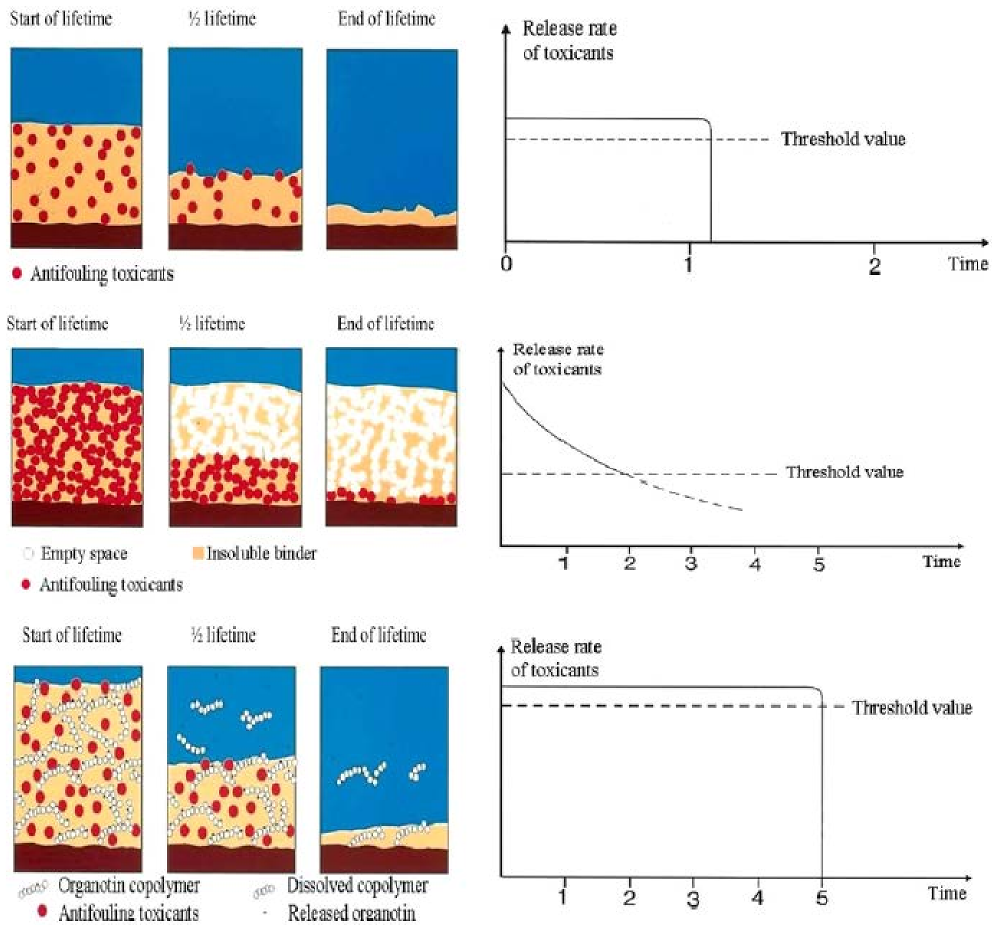


Figure 2.4: Different types of matrices in antifouling coatings [2]

Finally, the chemical elements of antifouling coatings according to the performance specification MIL–PRF–24647D (16 Feb 2005) for the ship's hulls are presented in Table 2.5.

Antifouling Coating Composition

Element / Requirement	**Maximum** *(soluble)* **mg / L**	**Metals Content** *(total)* **/ weight % maximum**
Antimony	15	0.015
Arsenic	5	0.005
Asbestos	-	0.0005
Barium	100	0.10
Beryllium	0.75	0.0002
Cadmium	1	0.0005
Chromium *(non-ablating antifouling)*	5	0.001
Chromium *(foul-release)*	560	0.56
Cobalt	50	0.005
Copper	25	0.01
Fluoride salts	180	0.18
Lead	5	0.005
Mercury	0.2	0.0002
Molybdenum	350	0.35
Nickel	20	0.02
Selenium	1	0.002
Silver	5	0.001
Tantalum	100	0.10
Thallium	7	0.007
Tungsten	100	0.10
Vanadium	24	0.01
Zinc	250	0.25

Table 2.5: Chemical elements of antifouling coatings according to MIL – PRF – 24647D [18]

2.2 Application

2.2.1 Surface preparation

One of the most important aspects regarding the adequate operation of the antifouling coating is the proper preparation of the surface that the coating is actually going to be applied to. The preparation consists of (a) the cleaning of the surface (in case of a vessel already in operation) from any already existing fouling and (b) the actual "foul-free" steel surface treatment prior to the application of the coating. Within this section the most common ways of preparing a surface will be presented.

1. **<u>Abrasive Blast Cleaning</u>** [15]

   It is by far the most efficient and effective method of removing paint, rust, mill scale, etc. from substrates while being generally considered to provide the proper surface profile to promote coating adherence. However, compared to other methods of surface preparation it is also the most expensive one. For this reason, it is chosen when the main focus is to reduce the time for surface preparation, or to achieve certain high standards of cleanliness. It should be noted that the first recorded abrasive blasting process was patented by Benjamin Chew Tilghman as early as the 1890's. The main types and methods of abrasive blast cleaning are summed up in Table 2.6.

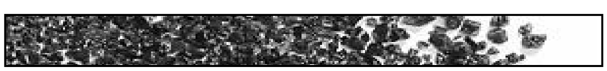
Wet Abrasive Blasting
Bead Blasting
Wheel Blasting
Hydro – Blasting
Micro – Abrasive Blasting
Automated Blasting
Dry – ice Blasting
Bristle Blasting

Table 2.6: Types of Abrasive Blasting [19]

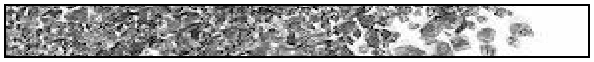
When it comes to abrasive blast cleaning there is a variety of abrasive materials on the market many of which are used in the maritime industry for cleaning purposes. A short presentation of them follows [20]:

- **Black Blast – Coal Slag**. It is an aluminum silicate blast cleaning abrasive which is made from coal slag a by-product of coal-fired power plants.

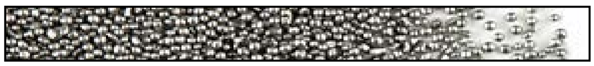
- **Ebony Grit – Copper Slag**. It is a disposable high-density blasting slag made from a by-product of copper production.



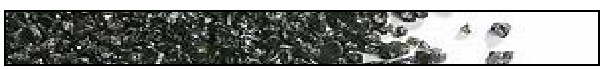
- **Ultra Blast – Nickel Slag**. It is a high-density disposable blasting slag made from a by-product of nickel production. It is an ideal abrasive for general-purpose use including shipyards, bridges and general industrial cleaning.



❖ **Power Blast LS – Staurolite**. It is a blast that contains less than 1% of crystalline silica. Its hardness and unique grain size make it suitable for new steel and mill scale removal or other general blasting applications with low to average surface profile requirements.



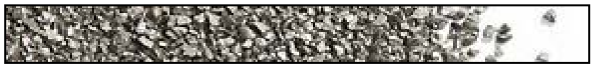
❖ **Aluminum Oxide**. It is the 2nd hardest mineral after diamond. Aluminum oxide is fused in an electric arc furnace by high temperature. The resulting oxide is over 95% Al_2O_3. Aluminum oxide abrasive grains are made for maximum toughness and hardness to provide superior performance in blasting.



❖ **Corn Cob**. It is a low-density granular product made from the hard wood ring of a corn cob. It is an organic product that can be used both as an absorbent and abrasive. It is used to de-burr, burnish, de-flash, and polish a wide variety of products.

❖ **Green Blast – Crushed Glass**. It is a medium-density crushed glass grit made from 100% recycled material. It is crushed, cleaned, sized and packaged in order to provide the ideal blast media for many applications.

❖ **Chilled Iron Grit**. It is made from thoroughly selected alloy-free iron scrap which is re-carbonized in a hot blast furnace. It is a white iron structure that shatters on impact rather than wearing round. The fresh edges, exposed by this process, combined with a high degree of hardness, result to a faster cutting/cleaning process.



❖ **Garnet**. It is a semi-precious stone of high density with physical properties that make it a good abrasive for wet or dry blasting applications.

❖ **Stainless Steel Shot & Grit**. It is one of the most rigid abrasives available on the market that is manufactured from 300 series cast stainless steel. The molten material is poured in streams through high pressure water jets that break the stream into individual shots. After that, shots are re-heated, refined and tempered to a martensitic structure obtaining eminent consistency, density and hardness.

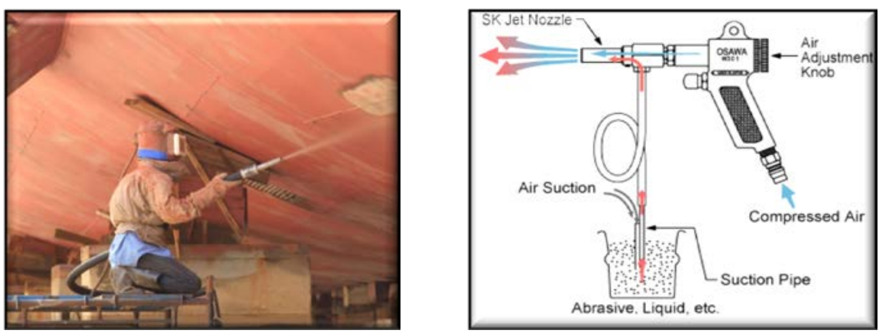
❖ **Super Steel Shot & Grit**. The sharp angular structure of super steel grit offers raw cutting power, offering many of the same benefits as the stainless steel shot.

❖ **Sodium Bicarbonate (Soda Blasting)**. Soda is a crystalline structured abrasive, inorganic compound, with high purity and of angular particle shape. It often appears in fine powder composition.

❖ **Plastic Media.** It is a non-aggressive granulated plastic abrasive for use in applications where the underlying substrate cannot be damaged. Cleaning with Plastic Media is fast, environmentally sound and a cost-effective alternative to traditional chemical and hand stripping.

❖ **Walnut Shells**. It is a hand and fibrous product which is made from crushed walnut shell in compliance with the International Trade Standard. It is the most usual soft abrasive for industrial use. Moreover, it has an excellent durability and can be used for polishing soft metals, glass, fiberglass, wood, plastic and stone products.

In Figure 2.5, one can see a picture of an in-situ abrasive blasting cleaning and a sketch of the blasting equipment.



(a) (b)

Figure 2.5: (a) The process of abrasive blasting cleaning and (b) the equipment used for the blasting process [21], [22]

2. Pickling [23]

It is a surface treatment which can be applied on metal constructions and surfaces from ferrous metals, copper and aluminum alloys. It removes stains, inorganic contaminants and rust. The most commonly used pickling method is the "Acid Pickling" and the most regularly acids used are the Nitric Acid (HNO_3), the hydrofluoric acid (HF), the sulphuric acid (H_2SO_4) and the hydrochloric acid (HCl). When planning an acid pickling operation, it is necessary to know the type of stainless steel and its metallurgical and physical condition. Most of the steels have different alloy compositions and are subject to present different behavior when exposed to pickling acids. It should be noted that no single acid solution or process is effective for all situations. The most appropriate acids according to surface material's composition are presented below:

- ***For carbon steels with alloy content ≤ 6%*** : Hydrochloric or Sulfuric acid
- ***For steels with alloy content > 6%*** : Phosphoric, Nitric or Hydrochloric acid
- ***For chromium-nickel steels*** : Hydrochloric and Nitric acid
- ***For copper alloys*** : combination of Sulfuric and Nitric acid with Sodium Chloride and Soot

Disadvantages of this method

The cleaning process by acid pickling has various constraints, which derive from: (a) the inherent difficulty of handling elements with high corrosiveness and (b) the limitation of application on different steel grades and types. Relatively to its high reactivity to treatable steels, concentrations of acid and solution temperatures have to be controlled in order to secure desired pickling rates.

Alternatives for pickling

The most common alternatives to pickling are the Smooth Clean Surface (SCS) and Eco-Pickled Surface (EPS). During the first process, surface oxidation is removed by using an engineered abrasive which results in a surface more resistant to sequential oxidation without the need of applying an oil film or any other protective coating. The second process is a far more environmentally friendly approach in comparison with acid pickling. It renders the carbon steel surface rust resistant, excluding the need to apply an oil coating.

3. **Flame Cleaning (or Flame Gouging)** [24]

It is a process of cleaning a steel surface by crossing over a strenuously hot oxyacetylene flame. Basically, it is an oxygen-fuel torch which is used in order to melt and remove any possible defects from the surface. In Figure 2.6, one can notice that the actual direction of the oxygen-fuel torch determines the outcome of the process and is the only difference between the process of gauging and cleaning. Even though the equipment is the same, the flame, which is used in cleaning process, is vigorously reduced to prevent excess removal of the surface. Many kinds of fuel can be used with oxygen with the most commonly used one being acetylene.

This particular process can be applied on a number of different surface qualities and steel grades. It helps to remove various substances, such as lubricants and greases. This method can also be applied for the cleaning of ceramics, steel constructions and concrete structures. The only drawback of flame cleaning is the burn marks from the oxy-flame that appear on the surface (Figure 2.7). Such marks however can be removed by applying a coating layer or by further grinding.

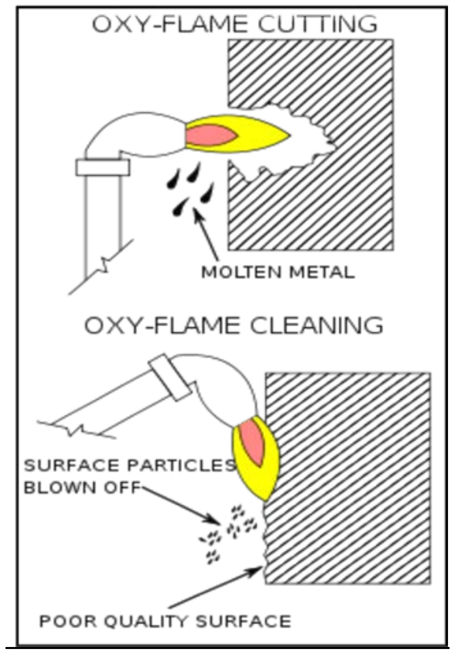


Figure 2.6: Flame cutting and flame cleaning processes [24]

Figure 2.7: Burn marks during the process of flame cleaning [25]

2.2.2 Application method

At this point, it would be useful to mention that there are few types of structures exposed to the marine environment that need protection, as it is depicted in Table 2.7.

Structure	Category	Service
Vessel	▪ Commercial ▪ Defense ▪ Pleasure	Cargo vessel, Tankers, Hydrofoil, Motor launch, Boats
Field	▪ Exterior ▪ Interior ▪ Deck	
Underlay	▪ Steel ▪ Aluminum ▪ Wood ▪ Fiber glass	
Offshore structure	▪ Drilling platforms ▪ Structure of navigational services	
Dock facilities	▪ Tanks ▪ Piling	
Terminals and Storage facilities	▪ Exterior ▪ Interior	

Table 2.7: Types of structures exposed in marine environment [9]

As for the application of an antifouling coating system special attention has to be given in order to avoid application early in the morning, late in the afternoon and during cold/humid/rainy weather. In addition, the antifouling coating should rest for adequate time in order to ensure proper drying.

During the application of an antifouling coating, it is essential to use means of self-protection. These include special uniforms, gloves and masks that will be worn from technicians who will undertake this task and from people in close proximity to the operation.

Prior to application, the coating should be stirred thoroughly, in order to achieve lean flow. Especially in cases of cold weather, the coating has to be warmed up using special equipment for about 6 hours or by placing the tin can into warm water of at least 30 - 40°C [20].

It is advisable, not to apply the coating directly to the surface from the tin can but to place a small amount into a roller tray or in a spray equipment, so as to prevent its contamination.

Furthermore, the application of the selected coating system is carried out on three layers: (1) primer coating (for metal surface), (2) anticorrosive coating and (3) final antifouling coating. These three layers will be analyzed below:

1. **Primer Coating for Metal Surface** *(using as an example the product RUST – OLEUM SKU 207016).* Before applying the primer coating on the metal surface, consideration should be given to the careful cleaning of the surface from dirt, grease, oil, salt, wax and chemical contaminants. This can be ensured by washing the surface with simple detergent or another applicable method. Then the surface should be rinsed with fresh water by pressure and shall be allowed enough time so as to dry completely.

   Then the loose coating and rust shall be removed using a wire brush, sandpaper or even by sandblasting. The application of such a coating has to take place when the external temperature is between 10 - 32˚C and the level of humidity is strictly below 85%.

   Also, as already mentioned, the primer has to be mixed thoroughly in order to secure that the settled pigment is well scattered before use. For the application, it is advisable to use a top quality brush or an air-spray equipment (Figure 2.8). Should the coating be applied by brush or roller it can be diluted by adding 5% mineral mix *(only for hot weather)* so as to remain liquid.

   Additionally, on an ample smooth surface and when using conventional spray equipment, it is recommended to dilute the coating by adding 5% xylene. In case of air –spray application, the pressure must be under 1.6 - 2.4 psi and the nozzle's tip between 0.013 - 0.017 inches.

Figure 2.8: Application in situ of the Primer Coating on a tanker by spray equipment [73]

Table 2.8 gathers the technical data of the primer coating RUST-OLEUM SKU 207016, which is adequate for application on metal surfaces.

Technical Data		
Primer Coating for Metal Surface / ***RUST – OLEUM SKU 207016***		
	Resin type	Modified Alkaline
	Pigment type	Titanium Dioxide and Fillers
	Solvents	Aromatic Hydrocarbons
Weight	**Per Liter**	1.23 kg
Solids	**By Weight**	62.7%
	By Volume	39.8%
	Volatile Organic Compounds	464 g/l
	Recommended Dry Film Thickness *(DFT)* **per coat**	1.0-1.5 mils
	Wet Film to Achieve	2.5-4.0 mils

	DFT *(unthinned material)*	
	Practical Coverage at Recommended DFT *(assumes 15% material loss)*	100 sq.ft / quart
Dry Times at ***(21-27°C)*** **and 50% Relative Humidity**	**Touch**	1-2 hours
	Handle	4-6 hours
	Recoat	24 hours
	Shelf life	3 years
	Flash point	40°C

Table 2.8: Technical data of the primer coating RUST-OLEUM SKU [27]

2. **Anticorrosive coatings**. Anticorrosive coatings are comprised of manifold layers of various coatings with unlike properties and purposes. These individual components, which can determine the anticorrosive coating's properties, can be organic, inorganic or metallic. Such coatings that are being used in maritime industry *(with high anticorrosive deportment)* consist of a primer, one or few medial coats and a topcoat.

   The primer coating protects the underlayment from corrosion and retains a good adhesion to it. This is the exact reason why elements like metallic zinc and inhibitive pigments are frequently added to primer coatings and applied particularly to structures close to the splash zone or to those which are being exposed to atmospheric environment.

The medial coating is used mostly to build up the thickness of the coating system and blot out the adhesion of marine species on the surface. Also, the medial coating acts as a good adhesive between the primer and the topcoat.

As for the topcoat, which is exposed to the external environment, it has to provide high protection and resistance against extreme weather conditions, various micro-organisms, objects and ultraviolet radiation.

At this point it is useful to mention that, the environmental degradation, which is a result of moisture, temperature and ultraviolet radiation, leads to the reduction of the coating's lifetime. It is true that, both performance and durability of a coating system are hard to be assessed because they are affected from a variety of internal and external factors. Furthermore, in an anticorrosive coating system, mechanical, chemical and physical properties can be reacting with the solvents, pigmentation and the additives in order to put up a stated operation. It is very important for an anticorrosive coating to operate successfully as well as for the surface to be in a very good condition, free of contaminants, cracks, enclosed air, weak areas and pigment resins. Additionally, the internal stress of an anticorrosive coating is one crucial factor that ought to be considered, due to its inefficiency to shrink and to make the performance more complicated. Table 2.9 summarizes the factors that affect the durability of an anticorrosive coating system.

Anticorrosive Coating System			
Environmental Properties	**Underlayment Properties**	**Coating Properties**	**Mechanical Properties**
Exposure	*Surface Condition*	▪ Micro Structure ▪ Macro Structure	▪ Hardness ▪ Flexibility ▪ Abrasion Resistance
▪ **Atmospheric** ▪ **Splash** ▪ **Immersion**	▪ Cleaning ▪ Preparation ▪ Treatment ▪ Roughness		
Factor of Exposure	**Type of Structure**	**Coating Type**	**Physical Properties**
▪ **Temperature** ▪ **Moisture** ▪ **Gas** ▪ **Salt** ▪ **Chemicals** ▪ **Bacteria** ▪ **UV Radiation** ▪ **Time**	▪ Stainless steel ▪ Mild steel ▪ Aluminum	▪ Organic ▪ Inorganic ▪ Metallic	▪ Adhesion ▪ Cohesion ▪ Penetrability
		Rheology	**Chemical Characteristics**
		▪ Application ▪ Thickness of coating ▪ Drying	▪ Solvents ▪ Pigments ▪ Additives

Table 2.9: Factors which affect the performance of an anticorrosive coating [16]

Figure 2.9 schematically shows the protective mechanisms of anticorrosive coatings.

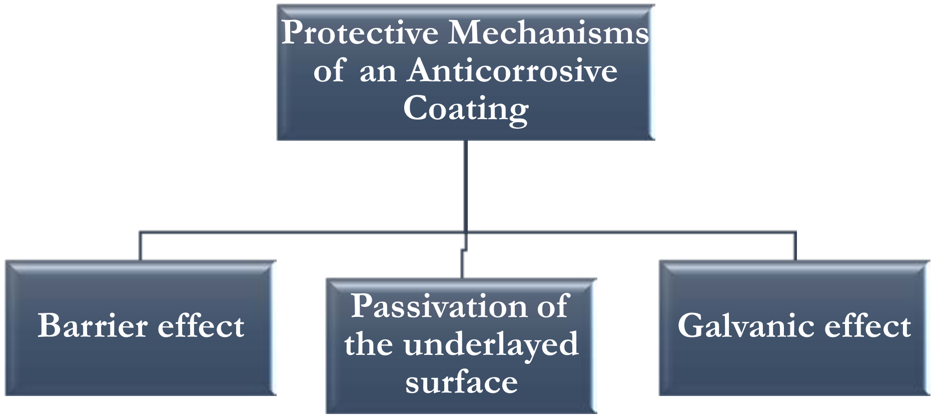


Figure 2.9: Protective mechanisms of anticorrosive coatings [16]

3. **<u>Final antifouling coating</u>**. The last type of coating that is used for protection against fouling is the so-called Antifouling Coating. While the primer and the anticorrosive coatings are used so as to protect the steel surface of the vessel, the antifouling coating is used so as to protect against fouling and secure proper hull performance. The most common types of antifouling coatings have already been analyzed in the previous chapter and are those which use a mechanism of protection based on an insoluble or a soluble matrix. The choice of the proper antifouling coating is a difficult task and one must have deep understanding over the properties of each component used, in order to have a complete overview of the coating. The most convenient type of ingredients in soluble matrix-based coatings are the resin-based ones whose main property is to harden the coating and create a solid film between the aquatic environment and the vessel's hull. As for the pigments of such types of coatings, they are divided into two categories: toxic and non-toxic. Toxic pigments should only

be used in small amounts and should also be completely soluble into sea water but at the same time dissolute in a small rate in order to secure efficient operation for as much time as possible. In connection to this, some of the toxic pigment elements that were and are commonly used, such as corpus oxide and metallic copper-based ones, often present superior solubility properties when compared with sulfates, chlorides, mercuric oxide and mercuric chloride-based ones, since the latter tend to dissolute really fast in the marine environment. Often non-toxic pigments are also used in order to improve the coatings' mechanical and physical properties so as to achieve bigger durability and effectiveness. Table 2.10 presents the minimum amount of cuprous oxide and mercuric oxide that an antifouling coating must contain in various environments

	General Operation	**North Temperature Waters**	**South Temperature Waters**	**Tropical Waters**
Cuprous Oxide *(oz. per U.S Gal.)* **not less than**	14	25	20	14
Mercuric Oxide *(oz. per U.S Gal.)* **not less than**	7	1.5	5	14

Table 2.10: ASTM specification on the amount of toxic pigments in an antifouling coating [28]

2.2.3 Maintenance of antifouling coatings

There are three categories of coatings on the market that can be used on a variety of structures for onshore and offshore applications:

- **Soft coatings**. This type of coatings stands soft. They can be detached easily with a low mechanical impact or even by touching them with the hand. They provide temporary protection from rust on steel surfaces and ought to be maintained on regular intervals. The steel surfaces which are painted using soft coatings must be recoated every 2 years.
- **Semi-hard coatings**. These coatings dry in a specific way, so they lie soft and flexible. They do not either wear away or erode by ballast water motion. They provide temporary protection of rust on steel surfaces and on most occasions the interval for recoating the steel surface is around 3 ~ 4 years.
- **Hard coatings**. This type of coatings has a special chemical synthesis (with several metals and chemical combinations), which practically protects the steel surfaces from corrosion in a very efficient way. The maintenance of such coatings depends on the environment, the steel structure and the operational conditions. The approximate time for maintenance is about 5 ~ 7 years. Such coatings have been the main focus of studies with an orientation towards bigger dry-dock intervals (from 5 to 7.5 years).

It is important to mention that antifouling coatings are very diverse and they vary in terms of:

- ***Chemistry*** → They consist of one or a combination of products such as lanoline / wool grease, petroleum, vegetable oil, organic and inorganic components. It is true that, each of the aforementioned products has its unique characteristics and corrosion protection aptness.

- ***Method of protection*** → A big variety of corrosion inhibitors *(that interact with oxide to halter further oxidation)* are used, as well as various corrosion barriers *(that obstruct oxygen from attaching to a metal surface)*. It should be pointed out that pure corrosion barrier products permit a corrosion cell to be active under the product while corrosion inhibitors block out this activity.

- ***Thickness*** → The final thickness of the antifouling coating system can differ from a thin film of 3mm up to 80mm depending on the surface. This factor is very important particularly when inspecting a coated surface, since the surface must have the same paint thickness in order to avoid any abnormalities. A thicker coating will provide longer protection but one should weight out the extra costs included. Generally, when applying coating products on the vessel, the painting specification of the vessel should be followed. Figure 2.10 shows several initial specifications for the painting of a vessel. One of them is the dry film thickness (D.F.T.).

PAINTING ITEM		MATERIAL OF TOP SURFACE	SHOP PRIMER	SURFACE PREPAR-ATION	COAT	BRAND NAME OF PAINT AND ITS COLOR SHADE	DFT (μm)	REMARK	FACE CODE
FLAT BOTTOM		STEEL	SPR	B3	1	JOTAMASTIC NB (AL.RED)	200	* BEFORE ERECTION	511A
(UP TO BILGE KEEL LEVEL)					2	SAFEGUARD TF KS (YELLOW)	150		
					3	SEAQUANTUM PLUS (DARK RED)	150		
					4	SEAQUANTUM PLUS (LIGHT RED)	150		
					5	SEAQUANTUM PLUS (DARK RED)	100		
SIDE BOTTOM & BOOTTOP		STEEL	SPR	B3	1	JOTAMASTIC NB (AL.RED)	200	* BEFORE ERECTION	511B
(UP TO DESIGN DRAUGHT(12M))					2	SAFEGUARD TF KS (YELLOW) A3	150		
					3	SEAQUANTUM PLUS (DARK RED)	125		
					4	SEAQUANTUM PLUS (LIGHT RED)	125		
					5	SEAQUANTUM PLUS (DARK RED)	125		
					6	SEAQUANTUM PLUS (DARK RED)	125	* BEFORE LAUNCHING	
SEA CHEST		STEEL	SPR	B3		SAME AS SURROUNDING HULL			511F
RUDDER	OUTSIDE	STEEL	SPR	B3		SAME AS SIDE BOTTOM			511K
	INSIDE	STEEL	SPR	NP		TREATED WITH V.C.I POWDER			511L
RUDDER TRUNK		STEEL	SPR	B3	1	JOTAMASTIC NB (AL.RED)	200	A4	511M
					2	SAFEGUARD TF KS (YELLOW)	150		
					3	SEAQUANTU PLUS (DARK RED)	150		
RUDDER TRUNK (RECESS)		STEEL	SPR	T3	1	JOTAMASTIC NB (AL.RED)	125		511N
					2	JOTAMASTIC NB (AL.GREY)	125		

Figure 2.10: Initial Painting Specification of a Hyundai Built Vessel [29]

- ***Opacity*** → The antifouling coating can be opaque *(dark or black)*, gray or transparent. This proper feature has an effect on the inspection of the coated surface. The opaque products require spot removal in order to permit the inspection of the steel surface, whereas the transparent products give the inspector the ability to view most of the steel surface without taking off the coating.

- ***Application of products of maintenance*** → The coated surface can be maintained by using products that contain metals like magnesium, zinc, aluminum, tin, brass, copper, nickel, silver and titanium. These products promote both the effectiveness and the durability of the coating. It is important that, prior to that process the steel surface should be completely dry which may be accomplished by ventilation or dehumidification.

2.3 Selection criteria

The type of the complete antifouling system has to be prescribed thoroughly by specifying the discrete primers, anti-corrosive mid-coatings, tie coatings and antifouling top coatings. One should always take into consideration that each component shall be selected carefully in order to perform a particular function and to result in a totally compatible and environmentally friendly system.

The marine environment consists of highly destructive factors such as salt water, steady washing, sunlight and fouling which make the decision of choosing the appropriate antifouling system a very crucial task for the maritime industry in way of protecting any kind of vessel.

The above factors exist in permutation with high condensable humidity, chemical pollution that occurs in ports, radical variations in service and temperature within a vast corrosion and fouling-full environment.

For that reason, marine antifouling coating systems have to provide protection to vessels, offshore structures, docks, storage facilities and terminals.

Additionally, the antifouling coating should ensure the following elements [9]:

- Enough electrical resistance among metal and sea water
- Withstand the alkaline condition

The ship owner should always assume that the vessel will operate and be exposed in the most hostile conditions in way of fouling so as to choose the most efficient coating that will ensure durability and proper performance. In this direction much consideration has to be given on the following points:

- Selecting the appropriate materials based on specifications
- Rigorous and adequate surface preparation
- Ensuring satisfactory application method
- Persisting on adequate time schedules to implement the system

Before the selection of the correct coating system all economic and technical restrictions must be seriously taken into account. For that reason, the most important factors to consider before making a choice are the following:

- **Environmental Corrosiveness**. It is very important to study the conditions in which the structure, facility or installation will function. In order to "measure" the environmental corrosiveness the following factors should be designated.
    - Humidity and temperature
    - Presence of UV radiation
    - Chemical exposure
    - Mechanical damage

  It is widely accepted that the environmental corrosiveness level has considerable impact on:
    - The type of coating
    - The total thickness of the coating system
    - The requirements as for the surface preparation
    - The minimum and maximum re-coating intervals

The categories of water and soil corrosiveness based on the ISO 12944 standard are depicted in Table 2.11.

Categories of Corrosiveness	Environment	Examples of Environments and Structures
lm1	Fresh water	River installations, hydro – electric power plants
lm2	Sea or brackish water	Vessels, piers, offshore structures, sluice gates, boats, etc.
lm3	Soil	Underground tanks, steel sheet pilings, pipelines, etc.

Table 2.11: Categories of water and soil corrosiveness in accordance with ISO 12944 [30]

- **Type of protected surface**. The choice of the appropriate coating system usually involves the conformity with the surface's materials, like steel, hot dipped galvanized steel, spray – metalized steel or stainless steel. The surface preparation, the coating products that can be used *(especially the primer coating)* and the total thickness of the system depend on the core material that has to be protected and on the vessel's area of application (sides, decks, hull fuel tanks, ballast tanks, lubricants' tanks, etc.). Table 2.12 gives a short overview of conventional coating systems in relation to the area of application.

Pivotal areas of coating	Primary requirements	Conventional coating system
Sides and Super – structures	Appearance, anticorrosive protection, UV resistance	▪ Pure or modified epoxy primer / epoxy topcoat ▪ Aliphatic poly – urethane / acrylic ▪ Poly – siloxane / epoxy hybrid
Decks	Appearance, anticorrosive protection, UV resistance, nonslip	▪ Zinc silicate ▪ Elastomer *(1 ~ 3mm)* over high primer ▪ Topcoat enhanced with aluminum oxide or silica
Tanks	Resistance to staggering contact with sea water and transported products	▪ Modified epoxy ▪ Aluminum epoxy ▪ Solvent free epoxy ▪ Cement reinforced acrylic
Cargo • **Crude or Petroleum** • **Oil or Hydrocarbon** • **Very inquisitorial products**	Resistance to conduct with particular types of cargo	▪ High solid / Solvent free polyamine epoxy ▪ Epoxy cyclosilicone

Table 2.12: Typical coating systems according to areas of vessel's coating [9]

- **Required durability of the coating system**. The lifetime of a coating system is considered to be the period of time from the first application up to the time of maintenance. The ISO standard 12944 traces an essential range of three time frames in order to categorize the durability (Table 2.13).

Category	Period of Time *(in years)*
Low *(L)*	2 ~ 5
Medium *(M)*	5 ~ 15
High *(H)*	> 15

Table 2.13: Coating system's durability as per ISO 12944 [30]

- **Planning the coating application system.** The creation of the schedule and the miscellaneous stages of construction of any respective project determine both the way and time of the coating system's application. It is essential to plan the process of application well in advance so as to ensure that there will be enough time for proper surface preparation. Furthermore, the drying and curing time of the coatings in connection with the weather conditions (temperature and humidity) are also very important factors that must always be taken into consideration when planning the application or maintenance of a coating system. Figure 2.11 shows the temperature range in which the coatings (depending on the binders and pigments they contain) show a good resistance against fouling.

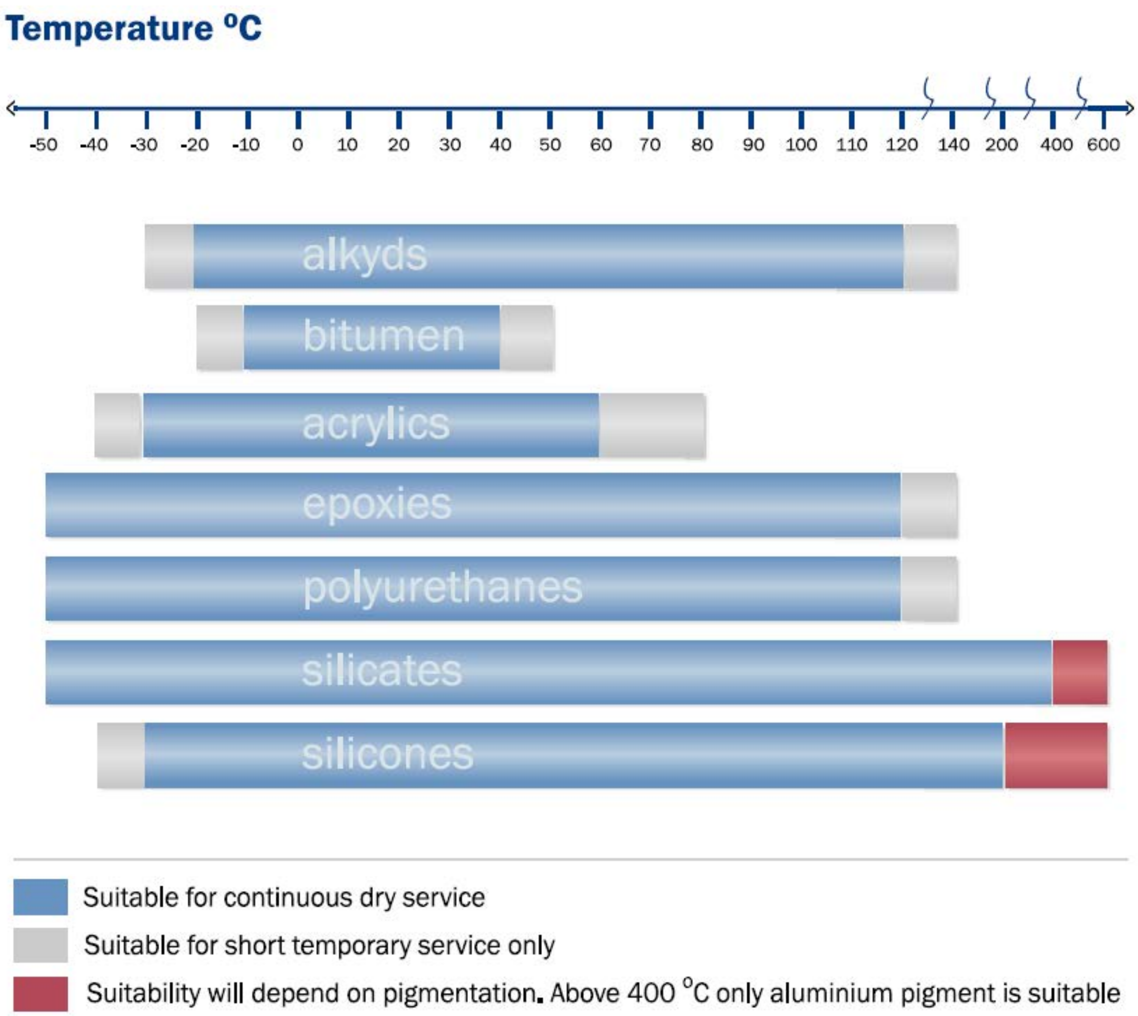


Figure 2.11: Range of temperature resistance of coatings based on binders and pigments [30]

2.4 Standards and classification

During the past four decades, much consideration has been given to the protection of the environment from the maritime industry. The protection of the environment can be achieved through optimization of operations like shipbuilding, transportation of hazardous products, application of antifouling coatings on vessels, maintaining and of course the scrapping process.

This protection of the environment became feasible through the enforcing of specific standards that nowadays all involved parties no matter their field of operation must follow.

As far as the maritime industry is concerned, the most broadly used standard for a variety of applications is the ISO 14000 family of standards. The scope of this specific standard is to convert the environmental performance to a management system. Standards from the family of ISO 14000 have been implemented by the most companies related to maritime activities regardless of their size, process, economic condition or regulatory requirements.

The most well-known standards from the family of ISO 14000 are the following:

1) Environmental Management System (EMS) ISO 14001-04
2) Environmental Performance Evaluation (EPE) ISO 14031
3) Environmental Auditing (EA) ISO 14010-12
4) Life Cycle Assessment (LCA) ISO 14040-43
5) Environmental Labelling (EL) ISO 14020-24
6) Environmental Aspects in Product ISO Guide 64

Their relation is shown in Figure 2.12.

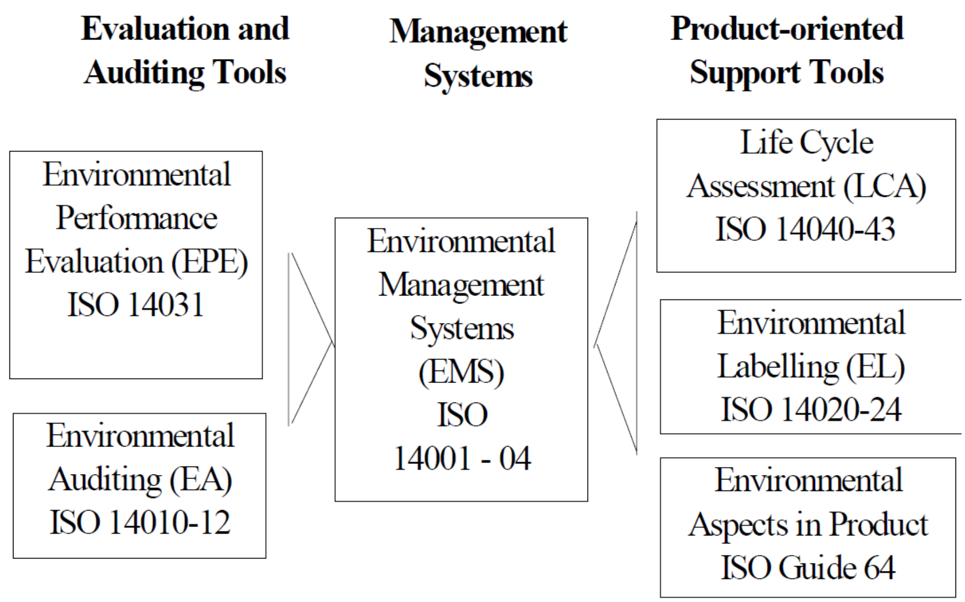


Figure 2.12: Relation between the ISO 14001 standards in the maritime industry [31]

ISO 14000 represents a new consensus position for the business and the environmental communities. It is a "package" tying the mandatory requirements of environmental performance to a management system. The standards have been designed for application by all organizations regardless of their size, process, economic situation or regulatory requirements.

ISO 14001-04 concerns the Environmental Management Systems (EMS). It mainly refers to the specifications of the EMS along with a relevant guidance for use. The methodology for implementation of the EMS for any company consists of three phases:

- Planning *(including the identification of regulatory requirements)*
- Implementation *(with obligation to continuous improvement)*
- Evaluation of environmental performance *(on regular intervals)*

The Environmental Performance Evaluation (EPE), **ISO 14031**, provides tools for measuring the environmental impacts that can be controlled by any company. It is the same process that can be used in order to measure, analyze and assess the company's environmental performance in connection with certain criteria and goals that are set. EPE can also be used even without the presence of an EMS and is often referred as an internal management process that compares the past and present environmental performance of the organization while setting future objectives and goals.

The two basic evaluation areas to consider when selecting Environmental Performance Indicators (EPIs) are the management area and the operational area. Furthermore, there are additional tools called Environmental Condition Indicators (ECIs) which describe the direct strains and impacts an activity has on the environment. The condition of the environment covers the quality of air, soil, fauna, flora and the human health while the operational area includes physical facilities and equipment, operation and energy flows. Environmentally related inputs and outputs to the management area include information from the operational system and information about the condition of the environment (Figure 2.13). Finally, it should be noted that the EPE process consists of several steps including commitment, planning, application, review and improvement.

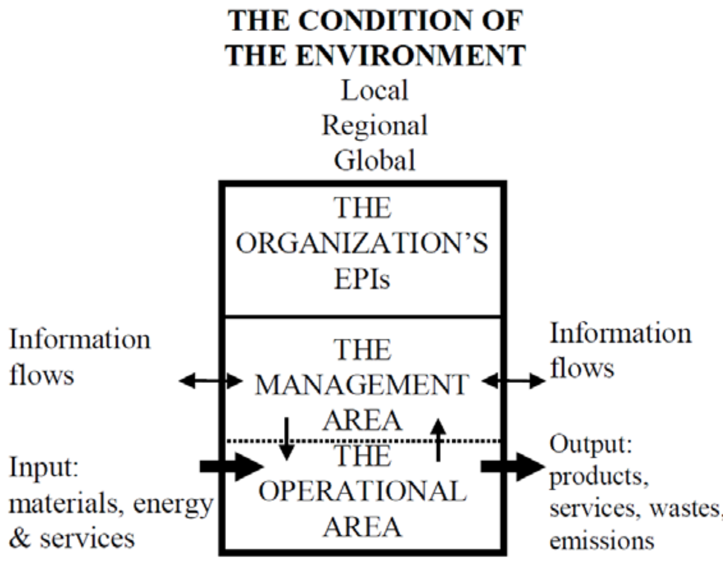


Figure 2.13: Environmental performance evaluation areas to consider in selecting EPIs and ECIs [31]

The main stages of ISO 14001, as a procedure, are the below:

- Description of environmental policies
- Identification of the environmental factors in comparison to external material protection and waste treatment
- Establishment of the necessary objectives and goals such as the exertion of available energy, waste reduction, the assessment of environmental impact during coating and blasting

These stages are in tight connection with the potential EMS implementation.

As shown in Figure 2.14, the reporting parameters are at the lowest level of the informational structure of ISO 14001. They are used for measuring the environmental standings on a short-term basis and are the management tools for every day issues.

This information can be used and communicated both within the company and the stakeholders and, furthermore, it is considered a means of comparing the company's real environmental performance with the environmental targets that are set for a specific period.

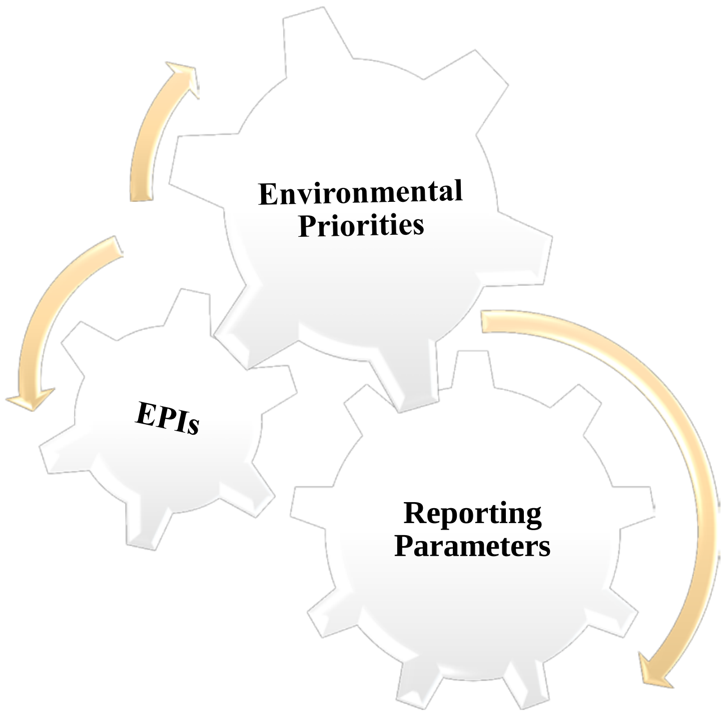


Figure 2.14: Informational structure of ISO 14001 [31]

Table 2.14 is an example of EPIs used in the shipbuilding industry.

Corporate Level	
Index	**Index**
Material use	External material protection
Local Management	
Indicators	**Indicators**
▪ Material utilization ▪ Energy use per unit of material	▪ Emission of noise ▪ Emission of dust ▪ Emissions of solvent ▪ Use of coating per unit area
Reporting parameters	**Reporting parameters**
▪ Profit excess material ▪ Purchase of cut steel plates ▪ Purchase of complete hull ▪ Transport of materials *(t*km)* ▪ Means of transportation from steelworks to the yard	▪ Number of complaints ▪ Degree of covering during blasting or coating ▪ Amount of generated waste material from specific factions like blasting, coating, maintaining, etc. ▪ Recycling ▪ Number of accidents

Table 2.14: Appropriate EPIs for shipbuilding [31]

Two examples for assessing EPI's, in terms of materials and emissions:

Examples of assessing EPIs

1. ***Material utilization*** = 1 – Weight of excess material / Total weight of steel product

2. ***Emission of dust*** = Measured emissions *(in dB or gr / m^3)* * 100m from the site of blasting

EPIs can also be used for a subsystem of a vessel for example the main engine (Table 2.15), which is considered the biggest machinery equipment of a vessel. In the same frame of thought EPIs can be developed for other subsystems such us diesel generators, hull, waste handling systems, etc.

Indices	
• Contribution to global warming • Contribution to acidification • Contribution to eutrophication	• Contribution to smog formation • Material efficiency

Table 2.15: EPIs for main engine system [31]

The main role of ISO 14001 is to promote attitudes relative to environmental actions within companies or organizations. Up to now, this ISO standard has resulted in models for EMS especially in maritime industry. Shipping companies (and more specific shipyards) with an efficient environmental management practice have eliminated their loads through better planning.

Moreover, they have accomplished economic return from increased profitability of resource use and waste treatment action. Some of the consequences of incorporation of the ISO 14001 standard for the maritime industry in the years to come may be:

- Increased knowledge about environmental issues and performance
- Better conditions for loans and insurance
- Cost savings through better resource utilization
- Better reputation in the local community and within the maritime industry
- Procedures for continuous improvement and specific code of practice for shipyards
- Better health and safety conditions at yards resulting in better recruiting of labor to the industry

Both, ISO 14031 and EPIs are crucial tools aiming to the communication of environmental performance among interested parties (suppliers, customers, public organizations, governments, etc.) within industrial groups such as the maritime industry.

As far as the remaining ISO standards, as stated above, are concerned, ISO 14010-12 deals with the principles, qualification criteria and procedures for internal and external auditing, the ISO 14020-14 standard establishes principles for the development and use of environmental labels and declarations while the ISO 14040-43 standard describes the principles and framework for the life cycle assessment.

The ISO 14040-standard has already provided significant data input to ship design as well as improvement of maintenance routines. It has contributed to optimization of fuel consumption and bottom hull coating and to cost/environmental optimizations for the vessels taken under study.

At this point, it would be practical to look over some recommendations for the future use of the ISO 14000 standards as strategic tools within the business of shipping and shipbuilding [31]:

- Use of the ISO 14000 standard to develop environmental profiles for different scenarios of ship's performance within its life cycle.
- Harmonization of ISO 14001 standards with the ISM code.
- Develop EPIs that reflect requirements that will be enforced in the shipping industry in the future, and practice the use of relevant EPIs as reporting parameters to and among interested parties.
- The use of ISO 14040 – 43 in combination with "Design for Environment" principles in the early planning of vessels.

It should, also, be noted that over the last years there has been an increasing number of international contracts and regulations which refer to vessels' safety and environmental protection. The International Marine Organization (IMO) has the responsibility for most requirements within the maritime industry. The most crucial contracts and codes in this sector are:

- Safety of Life at Sea *(SOLAS)*
- Prevention of Pollution from Ships *(MARPOL)*
- The International Safety Management Code *(ISM)*
- Safety and Environmental Protection *(SEP)*

The ISM system has been one of the biggest changes in way of operation of the shipping industry. It has affected the maritime industry for several years and will certainly be in practice in the years to come. Its ultimate role is to reduce the risk of human error and in that way it is a useful managerial tool for all shipping companies worldwide. The complete and successful implementation of the ISM code is achieved when all levels and departments of a company comply with it.

Both ISO 14001 and ISM should be based on the top management's formulated environmental policy which focuses on continual improvement, prevention of pollution, and compliance with rules and regulations. ISO 14001 emphasizes that an organization must identify its most significant environmental aspects, define objectives and targets for improvements of these, and develop management programs to reach these targets.

The main purpose of the ISM code is to designate the rules that a shipping company ought to incorporate through the development of a Safety Management System (SMS). SMS is most concerned with the safety and security systems of the ship and the environmental impacts caused by accidents during the operation phase. Thus, the scope of the ISO 14000 standards is broader than the ISM code.

For that reason, many shipping companies around the world take special attention on efficient environmental management practices like:

- Use of coating systems without organotin
- Use of cooling water systems so as to impede fouling on hull instead of using antifouling coating systems with toxic compounds that harm the environment
- Use of waste operating systems on vessels
- Implementation of educational programs for the employees, aiming to the guidance on environmental issues

Finally, according to the performance specification ***MIL – PRF – 24647D*** for the ship's hulls the classification of antifouling coatings is based on the type of coating, the class, the grade and the application, as presented below [18].

TYPES

Type I. Coating systems having topcoats which contain biocide(s) other than copper that ablate or self-polish.

Type II. Coating systems having topcoats which contain biocide(s) (copper or other not cited in type I) that ablate or self-polish.

Type III. Coating systems having topcoats that are foul-release and contain no biocide.

Type IV. Coating systems having topcoats that contain biocide(s) (copper or other), which do not ablate or self-polish.

CLASSES

Class 1. Coating system for use in rigid, fiberglass, wood, or metallic substrates other than aluminum.

Class 2. Coating systems for use on aluminum substrates.

Class 3. Coating systems for use on elastomeric substrates.

GRADES

<u>Grade A</u>. The volatile Organic Content (VOC) of the antifouling topcoats shall not exceed 400gr/L and of any other individual coating in the system 340gr/L.

<u>Grade B</u>. The VOC of the antifouling topcoats shall not exceed 400gr/L and of any other individual coating in the system 250gr/L.

<u>Grade C</u>. The VOC of the antifouling topcoats shall not exceed 400gr/L and of any other individual coating in the system 100gr/L.

APPLICATIONS

<u>Application 1</u>. Coating systems for use on the underwater hull – operation life 3 years.

<u>Application 2</u>. Coating systems for use on the underwater hull – operation life 7 years.

<u>Application 3</u>. Coating systems for use on the underwater hull – operation life 12 years.

<u>Application 4</u>. Coating systems for use on high-speed vessels – operation life of minimum 2 years.

Chapter 3 – Effect of antifouling coatings on a vessel's performance

The previous chapters dealt with the theoretical approach of antifouling coatings. They focused mostly on the history behind them, their various categories and most common types, their chemical aspect and composition, the various steps involved for their application, their selection criteria, as well as the relevant standards and classification. However, what has not been examined, and will be in this chapter, is the actual effect an antifouling coating has on the operation and performance of a sailing vessel.

3.1 Vessel performance

Before studying the effect of antifouling coatings on a vessel's performance, the definition of "vessel performance" shall be given.

A simplified approach of "performance evaluation" is the comparison of operational data of a vessel under real-time conditions against a set of theoretically and/or practically gained set of benchmark data.

The above definition might sound easy, however it raises additional questions about the necessity of the performance evaluation, the identification of the operational and benchmark data and the meaning of the real-time conditions.

3.1.1 The necessity of performance evaluation

There are many good reasons why the performance of a vessel should be monitored and evaluated and the most apparent one is that it provides a good overview enabling to proceed with corrective actions when/where needed.

The aspect most easily affected from a "poor" vessel performance is the fuel consumption of the vessel, since a poor performance leads to increased fuel consumption.

To begin with, one has to take into consideration the rapidly increasing fuel prices (reaching at the moment 450$/t), an increase that is not likely to stop in the near future given the ongoing diminution in the global crude oil reserves. Moreover, the marine industry is responsible for approximately 5% (data from 2006) of the global oil consumption, a percentage that cannot, under any circumstances, be ignored.

Example

An operational scenario for a typical 6500 TEU container vessel with 25 steaming days per month:

25 steaming days/month x 12 months = 300 steaming days/year

Assuming a modest average operational speed of 20 knots and a main engine consumption of 90 t/day at scantling draft at such speed, the annual expenses raised from the vessel's fuel consumption can be calculated as below:

300 steaming days x 90 t/day = 27.000 t/year

27.000 t x 450 $/t = 12.150.000 $/year

The above example is a solid way of understanding how critical the fuel consumption is towards an economically viable vessel.

As mentioned before, the performance is directly related with the fuel consumption and in order to stress the importance of the performance monitoring, one can assume that the vessel is under-performing or over-performing in such way so as to lead to a relevant respective increase or decrease of fuel oil consumption by 1% (the actual deviations percentage-wise are much bigger).

Following up on the above case-scenario, a 1% in fuel oil consumption would lead to an additional expense in the area of 121.500$ while a decrease in the same percentage would lead to equal saving in a yearly cycle. Considering that the life-expectancy of a vessel is 25 years, the number grows to 3.037.500$ of additional cost or savings by 1% deviation to the vessel's performance.

Besides the economical aspect related to the vessel's performance, another very important perspective that should not be ignored is that the increased consumption also leads to the production of additional greenhouse gases (GHG). The GHG are harmful to the environment and contribute greatly in the so-called global warming phenomenon, which has detrimental effects in the Earth's atmosphere. Figure 3.1 presents the annual global contribution of ship emissions, i.e. CO_2, SO_2, NO_X and soot.

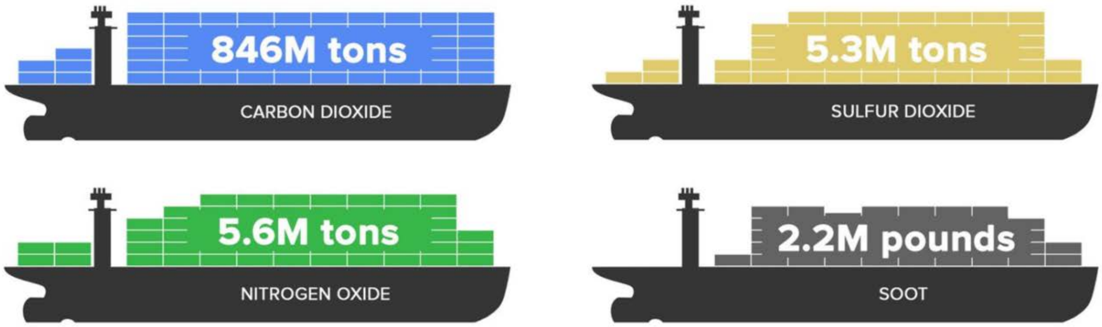


Figure 3.1: Annual global contribution of ship emissions [32]

3.1.2 Operational data and real-time conditions

In order to evaluate a vessel's condition, the two key values that need to be monitored are: (1) the attained speed and (2) the required power in order to attain that speed.

Most shipping companies have established procedures for speed/power monitoring, for example by measuring the fuel consumption and the daily distance covered. In such way, the daily mean power and mean speed may be calculated and the results may be plotted in a speed/power diagram for further comparison with the "benchmark set of data" that is available An example of such a plotting is presented in Figure 3.2.

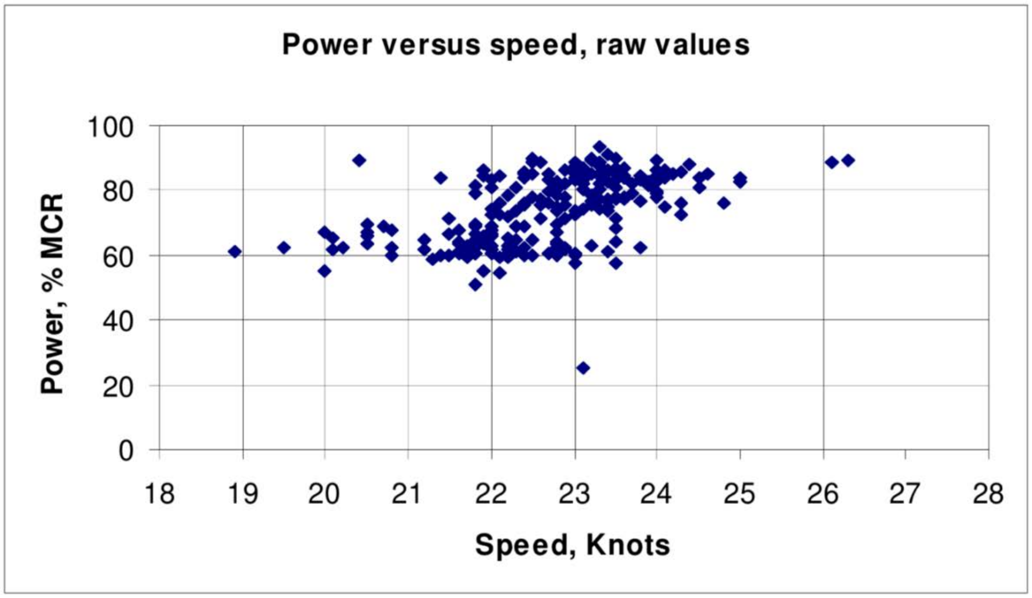


Figure 3.2: Typical power vs speed operational values of operating vessel [33]

As seen in Figure 3.2, the data are really scattered. For example, a ship appears to need 50% of the engine's MCR to reach a certain speed in one occasion and 60% in another. This is due to the so called "real-time" conditions. Some of the factors related to the "real-time" operation of the vessel that differentiate the measurement results are presented here below:

Draft: Mean draft and trim have a great influence on a ship's resistance. While it is reasonably easy to adjust the results for differences in mean draft, differences in trim are very difficult to deal with.

Weather: Wind and waves (Figure 3.3) also have their part in the equation of a ship's performance. While corrections for wind effects are easy to be made, waves can neither be measured nor corrected.

Figure 3.3: Vessel facing severe adverse weather [34]

Sea Current: Today's technology offers very effective ways to measure the speed over ground (SOG) of a vehicle. However, in the case of sailing vessels the SOG is not the "true" speed of the vessel since the effect of the sea currents is present. The "true" speed is the speed over water and this is more difficult to deal with.

Temperature & Salinity: The temperature and the salinity also have an effect on the analysis of the results, however their effect being small is rarely taken into consideration during analysis.

Last but not least, even if all the above were taken into consideration and the speed/power values were corrected, the interpretation method of the results, in order to describe the degradation in the vessel's performance, is missing. The ship's resistance can be roughly divided into frictional resistance and wave-making resistance. The fouling affects only the frictional resistance, and as the frictional resistance, which is a fraction of the total resistance, depends on the speed and draft, the additional power demand, expressed as percentage of the total power requirement, will not be the same for different loading conditions and different speeds.

In order to deal with the above raised issues as efficiently as possible, other performance measuring procedures have been established with longer intervals. Power is measured more accurately by cylinder indication and speed may be measured over a given period at constant power on a constant course. Some operators also make analysis by calculating the "slip" of the propeller, however differences in slip may be related to various aspects such as weather. Continuous data logging is used in many cases, excluding possibility of human error, however certain data (e.g. wave data) cannot still be made available.

3.1.3 Benchmark data

The actual data, acquired in the previous stage, shall now be compared with the benchmark data. The procedure to acquire the latter ones is described below.

For most ships leaving the shipyard after their initial construction, a diagram is provided showing the relation between speed and required power for one or more loading conditions. This diagram is prepared based on theoretical calculations and in most cases confirmed by a model test. It is then verified by performing a "speed-trial" test just before the final delivery of the ship to the owner. An example of such a diagram is presented in Figure 3.4.

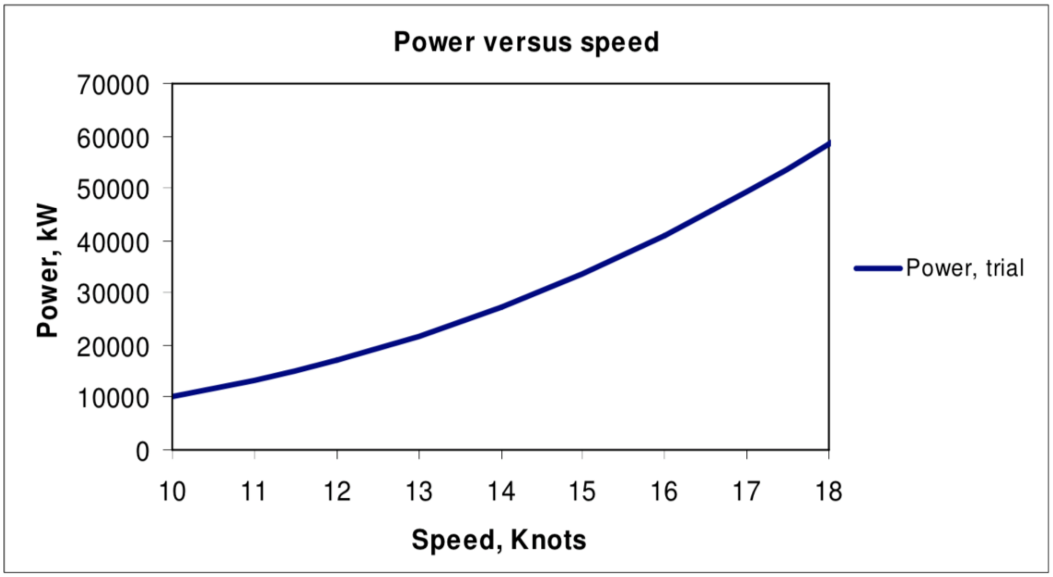


Figure 3.4: Power vs Speed diagram from "speed-trial" tests [33]

The next step would be to plot the engine's maximum continuous rating (MCR) in the above diagram in order to attain the maximum speed of the ship in question. Such a combined diagram is illustrated in Figure 3.5.

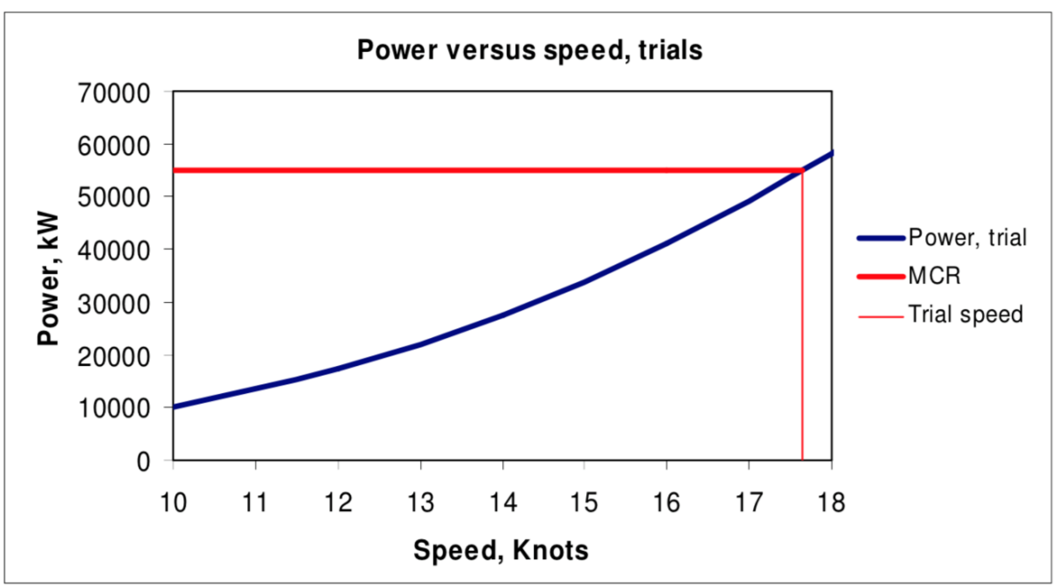


Figure 3.5: Typical Power vs Speed diagram incorporating diesel engine's MRC [33]

Finally, and since the vessel is not expected to sail in the diagram-suggested maximum speed during its daily operation, a "service speed" has to be defined for commercial reasons. This service speed is traditionally calculated by adding 15% to the power curve and subtracting 15% from the engine power line. The 15% in the power curve increase is attributed as per below:

- 5% for weather losses and
- 10% for losses due to hull and propeller condition degradation due to marine growth and corrosion.

The final graph produced (Figure 3.6) is considered as the benchmark reference data against any measurements & data acquired during the operational days of the vessel.

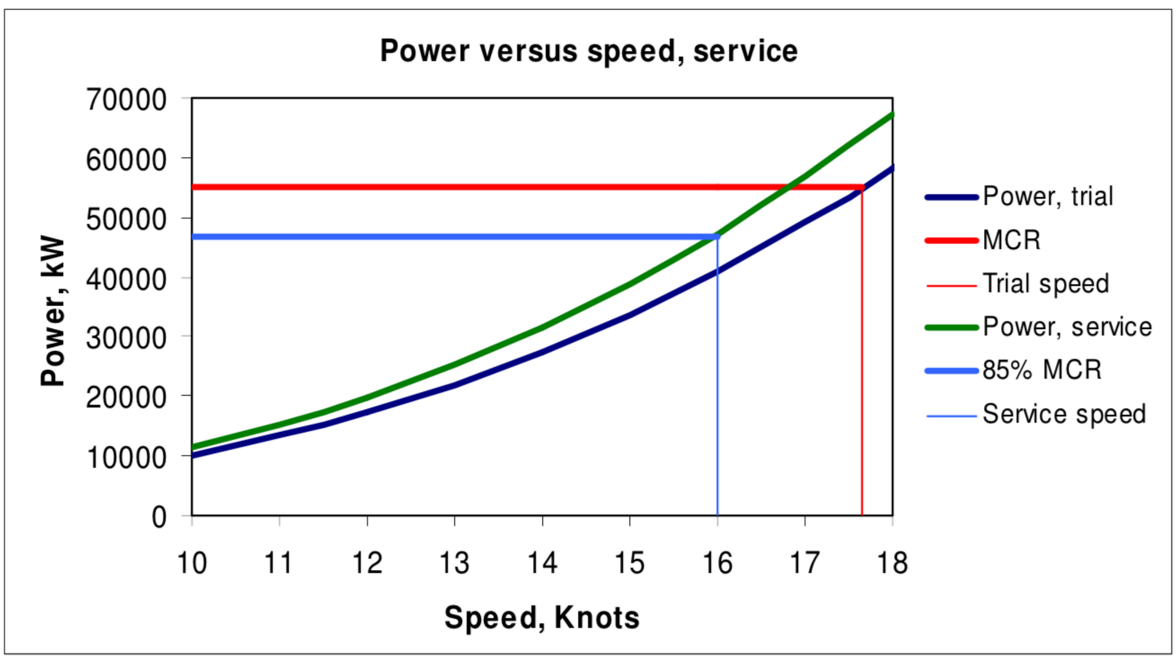


Figure 3.6: Service line and weather margin lines incorporated in a typical power vs speed diagram [33]

The actual situation for any particular ship may be worse if the marine fouling is significant.

3.1.4 Vessel's resistance

A vessel's resistance is a very complicated and wide topic, which has been studied thoroughly during the past years. The scope of this thesis is far from the analysis of the processes involved in order to calculate a ship's resistance, however a short reference will be made.

There are many different models developed in order to calculate a ship's resistance (theoretically). One of the most well-known and widely used is the ITTC approach (established by the International Towing Tank Conference).

As per the ITTC 2011 model [35], the total resistance of a vessel is calculated by the formula below:

$$R_T = \frac{1}{2}\rho S C_T V^2$$

Where:

R_T is the total resistance

ϱ is the density of the water

S is the wetted surface area

C_T is the total resistance coefficient

V is the speed

Now the most important element of the above equation and the most difficult to attain is the total resistance coefficient $C_{T.}$

As per ITTC 2011, the ship's total resistance coefficient is calculated using the formula below:

$$C_T = (1 + k)C_{FS} + \Delta C_F + C_A + C_R + C_{AAS}$$

Where:

k is the form factor of the surface

C_{FS} is the smooth frictional resistance coefficient

ΔC_F is the frictional resistance increase due to roughness

C_R is the residual resistance coefficient

C_A is the correlation allowance

C_{AAS} is the air resistance coefficient in full scale

As it can be easily identified from the above definition, the main concern, when it comes to discuss about fouling and antifouling, is the so called "frictional resistance increase due to roughness" (ΔC_F). However, calculating this variable is far from easy when it comes to a real vessel. The fouling, which is attached to the vessel's hull, affect the roughness of the surface. Especially hard-shelled fouling can cause a considerable rise in the ship's frictional resistance and hence increase the fuel consumption. Hard shelled barnacles can also deteriorate the paint and cause other problems, such as corrosion, which have a significant effect on the vessel's surface roughness and may cause problems to the vessel's watertight integrity in extreme cases.

The remaining resistance terms can be calculated using the below formulas, which are hereby stated for reference only:

$$C_{FS} = \frac{0.075}{(logRe - 2)^2}$$

$$C_A = (5.68 - 0.61 logRe)10^{-3}$$

Finally, and since air resistance can be ignored, C_R is determined from the total and frictional resistance coefficients of the model using the formula below (where subscript "m" indicates the model terms):

$$C_R = C_{Tm} - C_{Fm}(1 + k)$$

The parenthesis of the necessary equations, in order to evaluate the effect of fouling on a vessel's ship, closes with the formula which calculates the effective power (which is the power needed for a ship to be dragged through the sea):

$$P_E = R_T V$$

The conclusions drawn from all the above are the following:

- The effective power is directly related to the total resistance.
- The total resistance consists of many terms which include different types of resistances.
- The fouling of the vessel affects the ΔC_F.
- The calculation of the fouling effect on the total resistance of a vessel is a very difficult task.

What is also interesting to investigate is the fuel consumption compared to speed for various stages of added resistance. In Figure 3.7, this is presented by a fleet performance of 7 sister ships due to fouling [33].

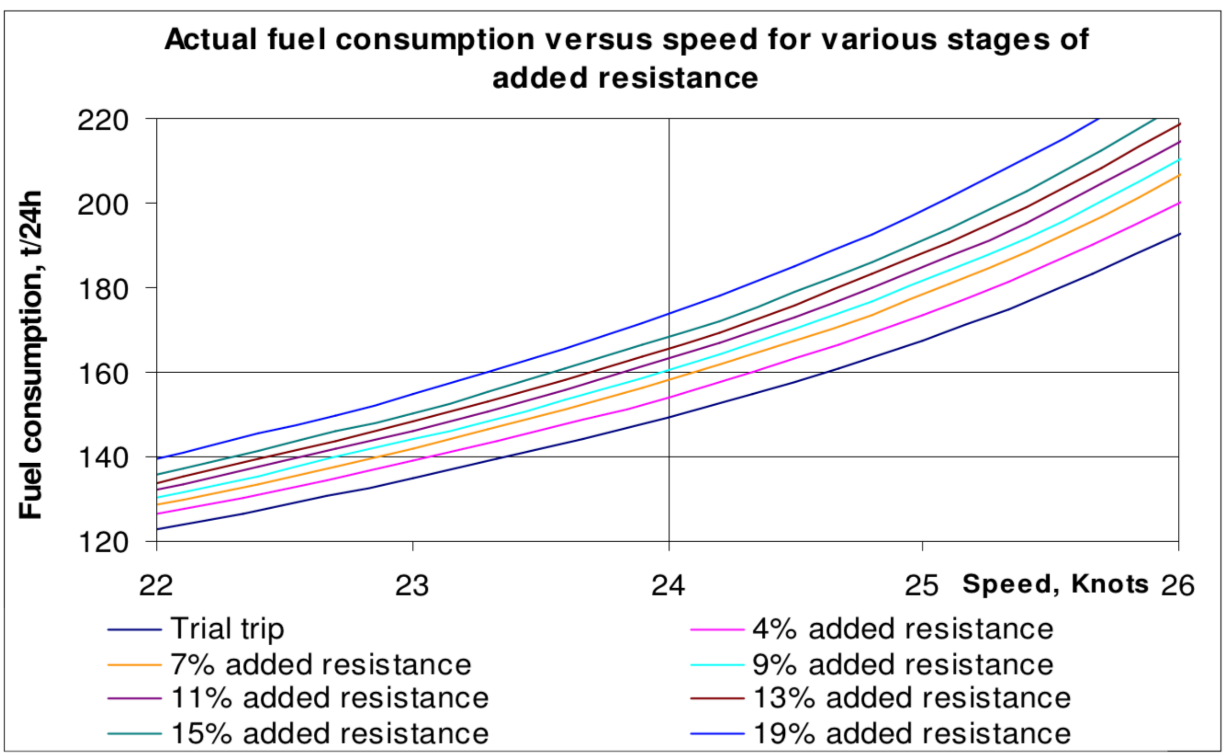


Figure 3.7: Actual fuel consumption vs speed for various stages of added resistance [33]

The above plot shows the performance of 7 sister ships compared to the trial performance. Each vessel is suffering from a different percentage of added resistance. The effect of the added resistance (with all other variables corrected) is demonstrated accordingly and as one can note there is a difference of roughly 20tons between the consumption of the "best" and "worst" performing vessels at a speed of 24knots.

3.2 Marine fouling on a vessel's performance (case studies)

It is estimated that approximately 300 million tonnes of fuel are consumed on an annual basis by waterborne transportation, while the International Maritime Organization (IMO) estimates that air emissions, which are directly related to the aforementioned fuel consumption, are bound to increase between 38% and 72% by 2020 unless corrective measures are taken and new technologies are introduced. [4]

Fouling is an unwanted phenomenon in marine transportation (Figure 3.8), given that the vessels consume less fuel when they are foul-free and with their hulls smooth and clean. This is one of the main reasons why people have been trying to cope with the fouling problem and introduce new technologies since the very first days of the shipping history.

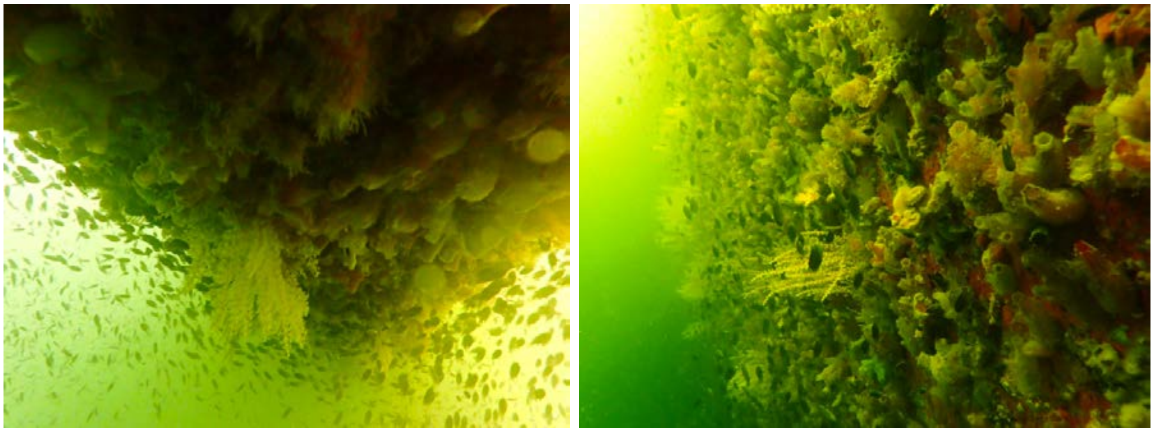


Figure 3.8: Marine growth on vessel's (a) bottom and (b) sides following lay-up period [36]

The biggest effect of marine fouling on a ship's performance is regarding the increase of the vessel's resistance and thus the total power needed in order to attain a certain speed.

'Fouling' can take many different forms, each having a different effect on the performance of a vessel. When the coating is just deteriorated or has thin slime, the effect is not the same as when it has heavy slime. Just the same, the result differs a lot when one refers to small, medium or heavy calcareous fouling.

Hull cleaning technologies have advanced greatly in the past years, however it should be pointed out that sometimes a "badly" performed hull cleaning operation (which is performed using hard brushes and by incompetent divers) may have a worse final result than not cleaning the hull at all. A poor cleaning technique may lead to removal of the actual antifouling coating, leaving the metal of the hull exposed, something that will subsequently lead to faster fouling growth (due to the lack of antifouling coating), as well as hull corrosion.

Another important issue for a vessel's performance is the occurring fouling on the propeller. The fouling growth on the propeller is quite similar (or potential slightly smaller) to the fouling growth on the hull for a sea-going vessel. In cases where the vessel is stationary (idle periods or cold/hot lay-up), the propeller area is more exposed to fouling growth, as the most of the times it is not protected by antifouling coatings.

The sea environment (temperature / salinity) has also an effect on the analysis of the results, even if it is not the most crucial criterion for the vessel's performance.

In order to point out the effect of fouling and its countermeasures on a vessel's resistance (thus performance), many measurements, experiments and simulations have been conducted by different ship companies, associations and scientists. Hereafter, a set of examples of different case studies that relate the vessel's performance with all the above elements, derived from real life, will be presented. Subsequently, some simulation results using computational fluid dynamics will be displayed.

3.2.1 Case studies / Real life

(1) Effects of various fouling conditions [37]

During the last decades, a big amount of experiments to determine the effects of fouling on ship performance were carried out by the naval forces, since having a combat ready and efficient ship was of vital importance. Experiments carried out included towing of combat ships in various fouling conditions in order to determine the towing force needed and thus reduce it to speed loss or increase in shaft horsepower needed. Some of the results acquired are presented in Figures 3.9-3.12.

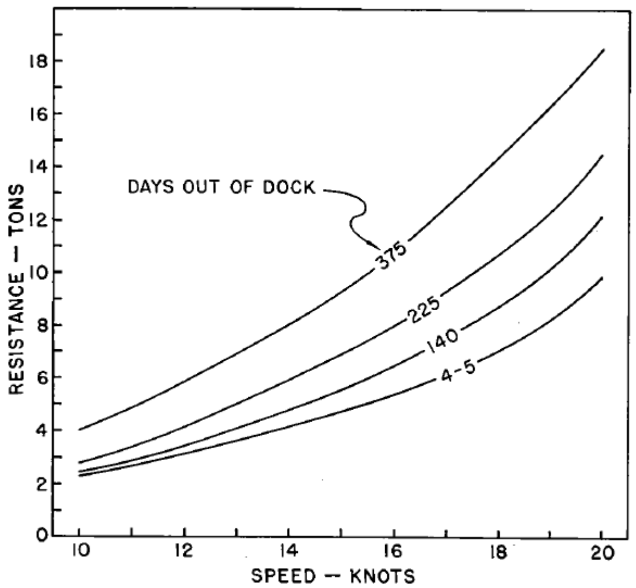


Figure 3.9: Resistance of destroyer Yudachi towed at different speeds after various periods out of dock [37]

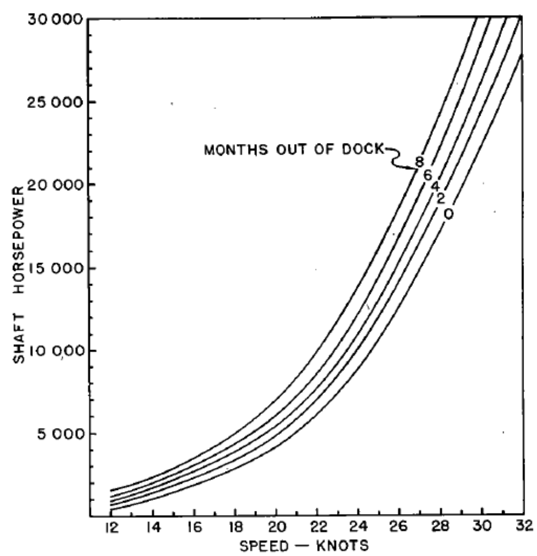


Figure 3.10: Shaft horsepower required to propel the destroyer Pulman.11 at different speeds after various periods out of dock [37]

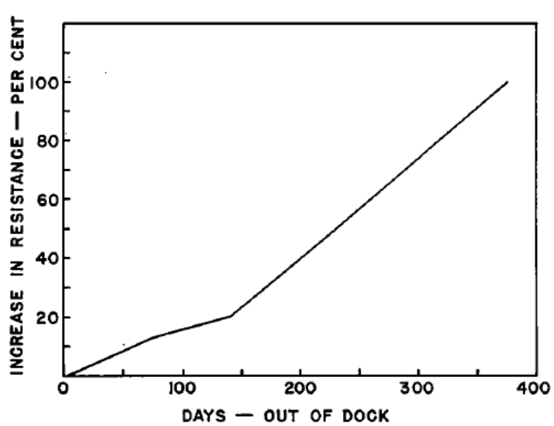


Figure 3.11 Percentage increase in resistance of destroyer Yudachi when towed at 16knots after various periods out of dock [37]

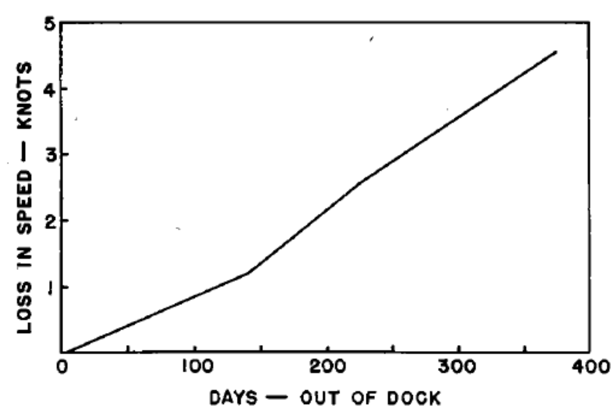


Figure 3.12: Loss in speed of destroyer Yudachi when towed with a force of 10tons after various periods out of dock. Initial speed: 20 knots [37]

(2) Coating conditions

An interesting case study has been presented during the SNAME meeting in Athens (Greece) in December 2013 [38], where "A practical way to evaluate the in-service performance of antifouling coatings" was presented by HPS in cooperation with Jotun Coating Manufacturers and SeaStar alliance.

Once again the study focused on the issue of the propulsion efficiency loss due to bio-fouling and mechanical damages on a ship's hull, due to the increase in frictional resistance. The vast importance of such an efficiency loss was presented using a reference from the MEPC 60/4/21 (2010), presented in Table 3.1.

Coating Condition	**Additional Shaft Power (%)**
Freshly applied coating	0
Deteriorated coating or thin slime	9
Heavy slime	19
Small calcareous fouling or macro-algae	33
Medium calcareous fouling	52
Heavy calcareous fouling	84

Table 3.1: Effect of the coating condition as % of the additional shaft power [39]

It is obvious that power demands can grow up to 84% on a poorly maintained hull, which will of course ultimately lead to a much higher fuel consumption, as well as to higher CO_2 emissions.

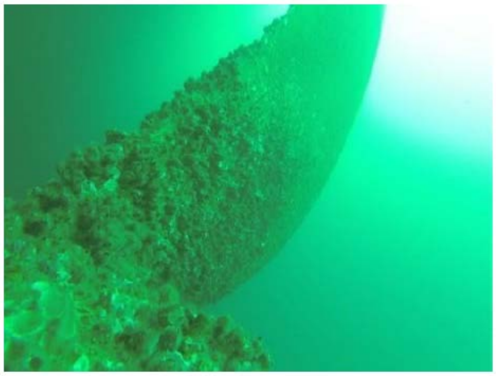
(3) Sea trials for different hull's & propeller's conditions / Energy models obtained [40]

Another interesting case study has been carried out by Technology Development section of Bureau Veritas Brazil along with Petrobras Shipping Company. Petrobras manages fleet of vessels with much diversity in their operating profiles, with many of the vessels performing short voyages with extended idle periods at ports making them extremely prone to fouling development.

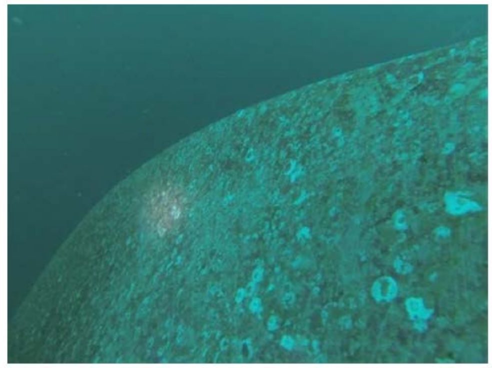
The experiment was carried out on a 264m crude oil carrier which performed a series of sea trials after an 8month idle period at port. The sea trials were performed under three conditions, which are listed below:

a. With the ship in completely fouled condition (***Condition 1***)
b. After propeller's cleaning (***Condition 2***)
c. After cleaning the hull and polishing the propeller (***Condition 3***)

Some indicative photos of the hull's and propeller's condition before and after cleaning are presented in Figures 3.13 and 3.14 respectively.



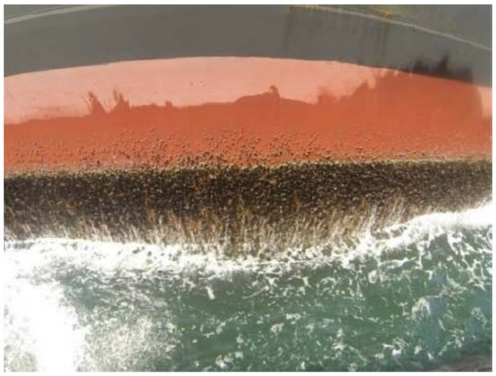
(a)



(b)

(c)

Figure 3.13: Propeller (a) before cleaning, (b) after cleaning and (c) after polishing [40]



(a)

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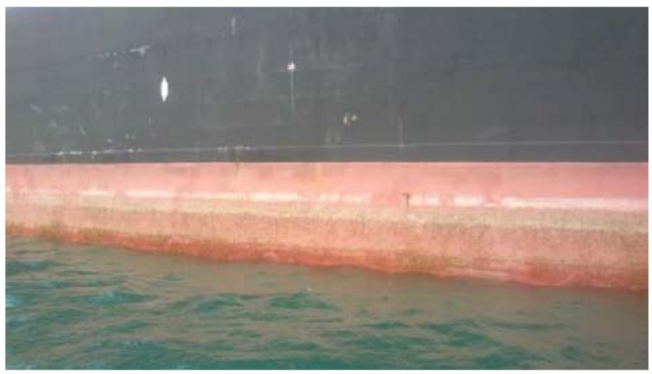


(c)

Figure 3.14: (a) Hull before cleaning, (b) Submerged hull before cleaning and (c) Hull after cleaning [40]

A comprehensive set of measurements were taken throughout the sea trials and relevant corrections were then made for different displacement, trim, water depth, weather and sea conditions. The results of the sea trials are presented in Figure 3.15.

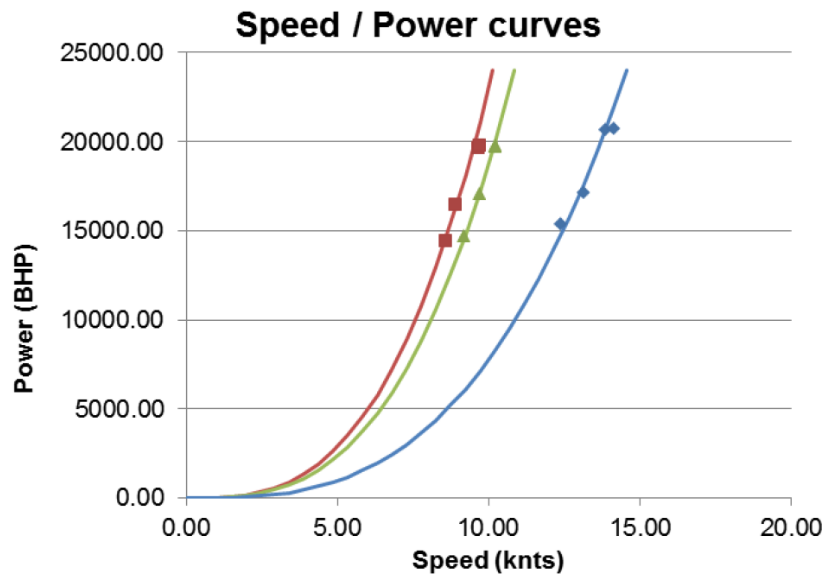


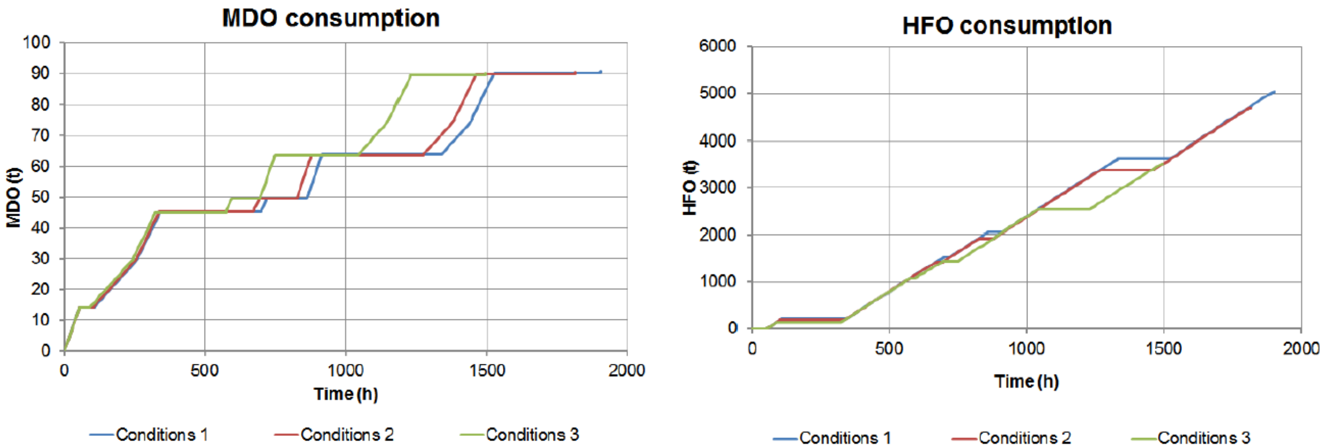
Figure 3.15: Speed/Power curves for the three sea trials carried out [40]

The red curve corresponds to Condition 1 (ship completely fouled), the green curve corresponds to Condition 2 (after propeller cleaning) and the blue curve corresponds to Condition 3 (after hull cleaning and propeller polishing)

The results obtained show a 7% improvement in performance between initial condition and condition after propeller cleaning and a gain of 35% after carrying out the hull cleaning and propeller polishing, summing up to a final gain of around 45% from the completely fouled condition.

The findings of the sea trials were then put in test in an actual operational scenario with the vessel sailing between Tramandai (Brazil), Angra dos Reis (Brazil), Tenerife (Spain), Fos (France), Agbami (Nigeria) and back to Tramandai (Brazil) corresponding to a voyage of around 13500 nautical miles. Three energy models were performed taking into consideration the three different hull's and propeller's states. Figure 3.16

shows the difference between HFO (Heavy Fuel Oil) and MGO (Marine Gas Oil) consumption for the three different states.



Conditions	MDO (t)	HFO (t)
1	90.74	5036.13
2	90.56	4698.45
3	90.25	3522.91

Figure 3.16: Total HFO and MGO consumption for the three hull and propeller states [40]

A 30% decrease in fuel consumption is observed for the clean hull and polished propeller state. In addition, the total voyage duration, which is highly increased for the fouled condition (Table 3.2), must be also taken into consideration.

Conditions	Time			
	Days	Hours	Minutes	Seconds
1	79	7	46	10.67
2	75	15	16	41.63
3	62	7	5	55.56

Table 3.2: Time needed for a round voyage for the three hull and propeller states [40]

The results of this case study demonstrate in the most obvious way:

(a) the importance of retaining a foul free hull,

(b) the impact of the increased fouling in the vessel's performance, with all relevant financial consequences that arise due to the increased bunker consumption,

(c) the potential need for additional bunkering operation, and

(d) the low profit margin from a spot charter due to increased days needed in order to complete the roundtrip voyage.

(4) <u>Propeller polishing and hull cleaning</u> [33]

The below graph includes an example of an operational vessel undergoing various operations of propeller polishing and hull brushing, and the effect of those operations in terms of added hull resistance.

In this case, a rather fast increase of added resistance occurs (Figure 3.17). After the 3 first months, a propeller polishing takes place with no visible results. After 6 more months, a second propeller polishing takes place but this time also the results are not particularly prominent. The next step is a full hull brushing which is carried out with more satisfactory results. However, the added resistance growth is still fast (around 1% per month).

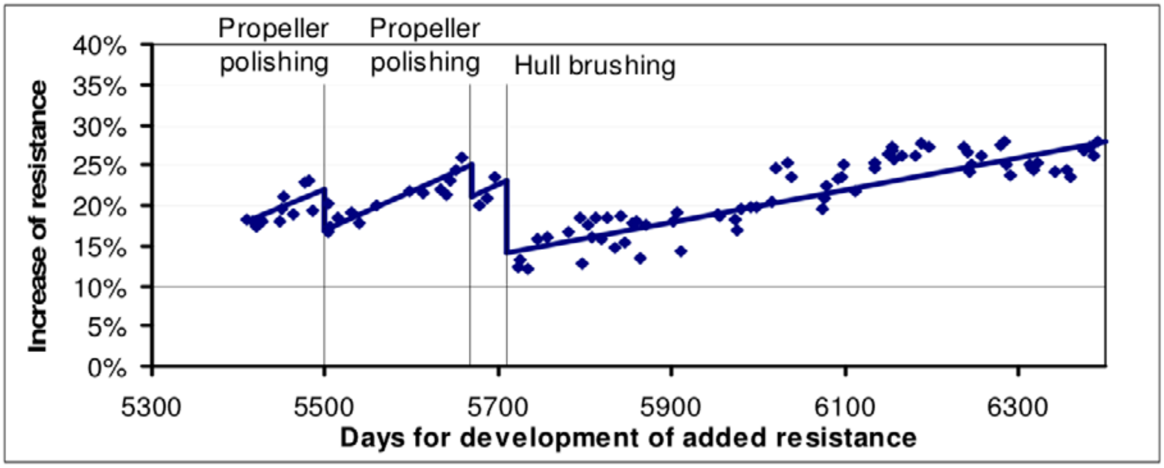


Figure 3.17: Increase of resistance vs days for development of added resistance [33]

(5) Depleted antifouling paint after hull cleaning [33]

On the following graph, one can observe the relevant increase of resistance overtime and the effect of various hull cleaning operations, as well as propeller polishing and full dry-docking, on the actual hull condition and frictional resistance.

As shown in Figure 3.18, the vessel has initially a very big added resistance. Propeller polishing and ship side cleaning is carried out, however the results are marginal. Then the operator decided to perform a full hull cleaning which had great results. However, it is noted that the added resistance increase rate is very big following the full cleaning, meaning that the antifouling coating was damaged/depleted. After the dry-docking, the added resistance was significantly reduced and the growth rate resumed to normal figures.

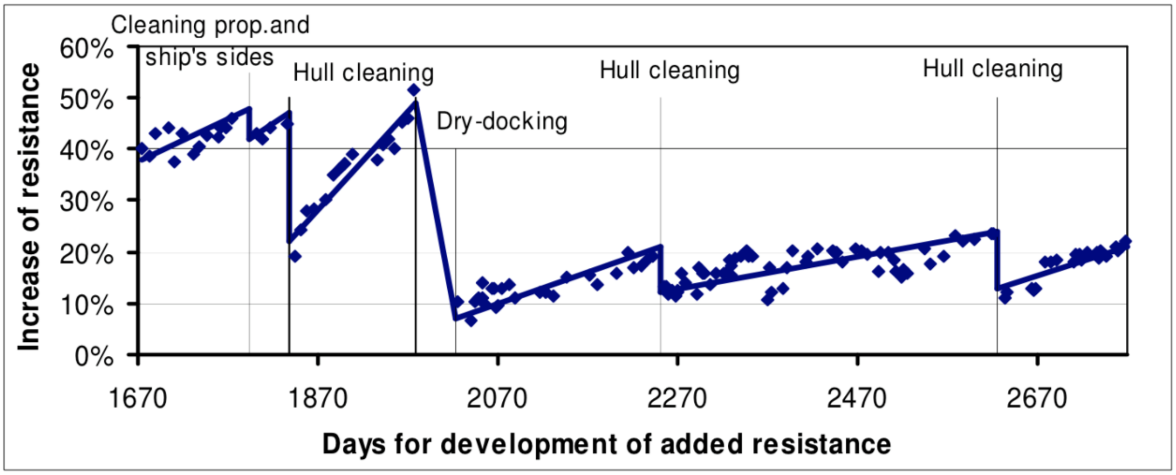


Figure 3.18: Increase of resistance vs days for development of added resistance [33]

(6) Badly performed hull cleaning [41]

An example of a "badly performed hull cleaning" is presented in Figure 3.19. On January, the vessel's hull was washed and the hull friction percentage increase dropped to about 1.5%. However, the cleaning obviously damaged the hull coating, leading in a rapid increase of fouling just after the cleaning, which also resulted to a hull friction increase of about 4% in a 3 month period.

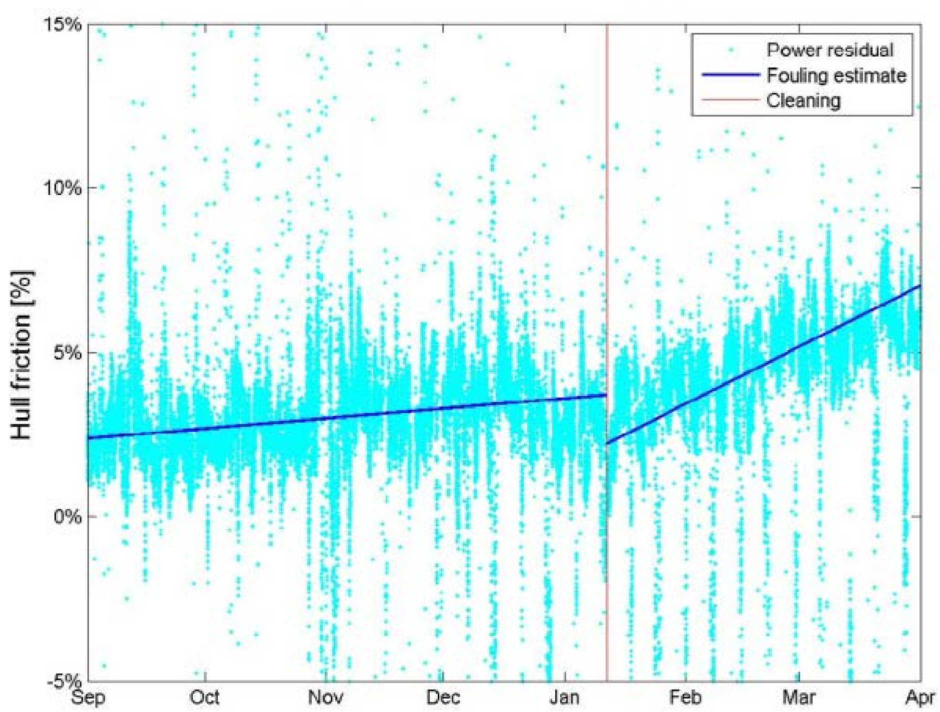


Figure 3.19: Effect of poor hull cleaning on hull friction [41]

(7) Poor dry-docking [33]

In this case-study, one can observe the development of added resistance due to fouling, following a full dry-docking on which the hull treatment was performed poorly.

The vessel left the dry-docking with a measured added resistance of around 40%. Then, following an unknown event, the added resistance fell to 20% (Figure 3.20). This was probably caused by an object adhering to the vessel's hull before docking out. Subsequently, the resistance growth resumed a normal development line. What should be pointed out is that taking into consideration the "normal development" line as it progressed after the "unknown event" the vessel left the dry-docking with an approximate estimated 16% added resistance, showing that poor treatment was carried out during the docking period.

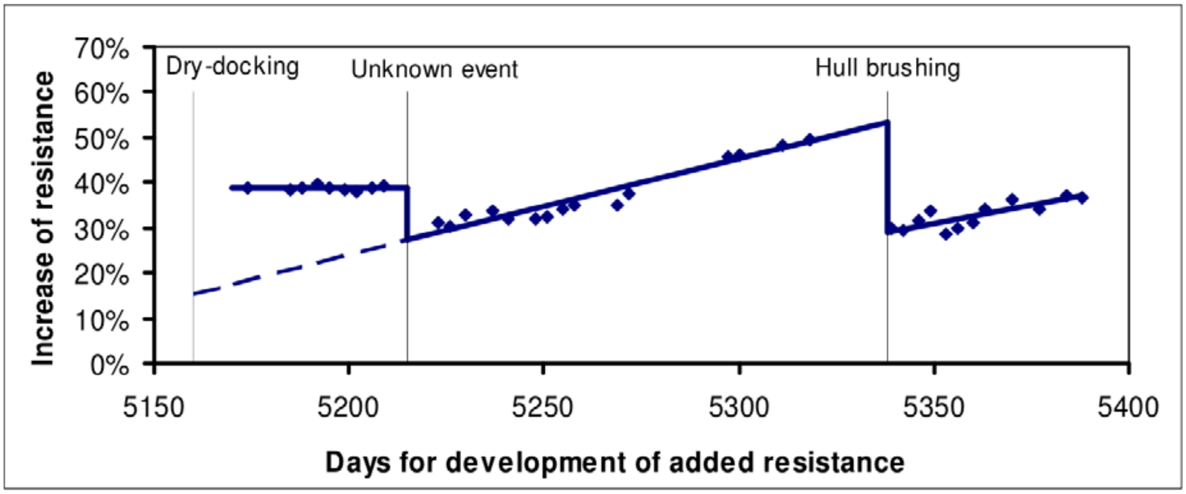


Figure 3.20: Increase of resistance vs days for development of added resistance [33]

(8) Dry-docking (full coating renewal) [33]

Another interesting case is presented below, showing the results of a full dry-docking in terms of hull frictional resistance, while demonstrating the before and after docking condition.

Figure 3.21 consists of a typical example of the development of the hull added resistance due to fouling. The effect of dry-docking – with a simultaneously full coating renewal – is significant, as it decreases the resistance by around 23%. As one can notice, the development of the added resistance, following a well-performed coating renewal, occurs at a rate of around 0.5% per month.

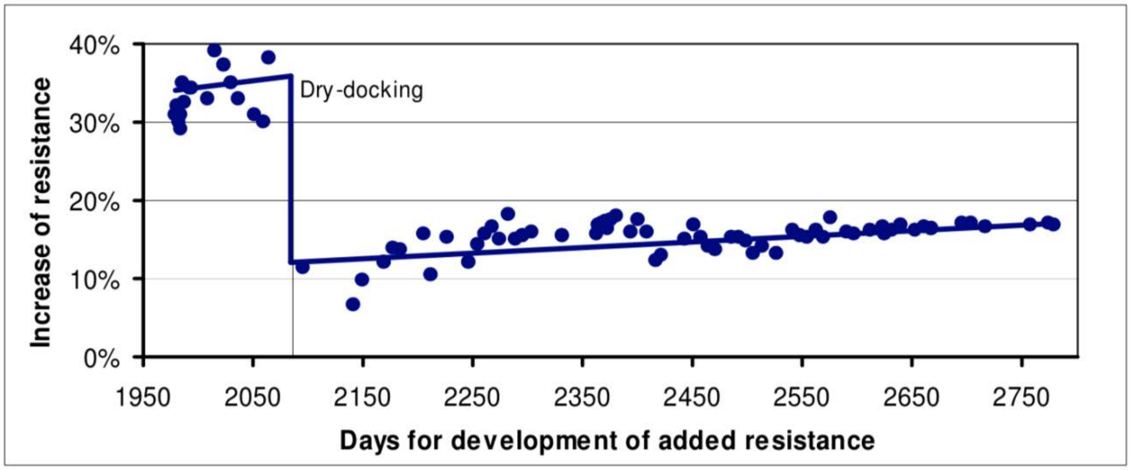


Figure 3.21: Increase of resistance vs days for development of added resistance [33]

Notation: Case studies No (4), (5), (7) and (8), presented above, are real-life cases that summarize the operational data of vessels using the "CASPER" software (Computerized Analysis of Ship Performance) for performance analysis and monitoring [33]. The individual analysis results are demonstrated as "dots" and then a 1st order curve (a straight line) is drawn through the points in order to show the trend of development.

(9) Effects depending on the sea area [41]

As already stated, fouling development is affected by numerous different factors. ENIRAM[41] has used data from cruise vessels sailing in the areas of Alaska, California, Caribbean, Mediterranean and other areas in order to monitor the fouling development in different aquatic environments. The study lasted for a period of 9months, over which the effect of changing sea areas on the power consumptions was monitored. The results of the study are presented in Figure 3.22 and Table 3.3.

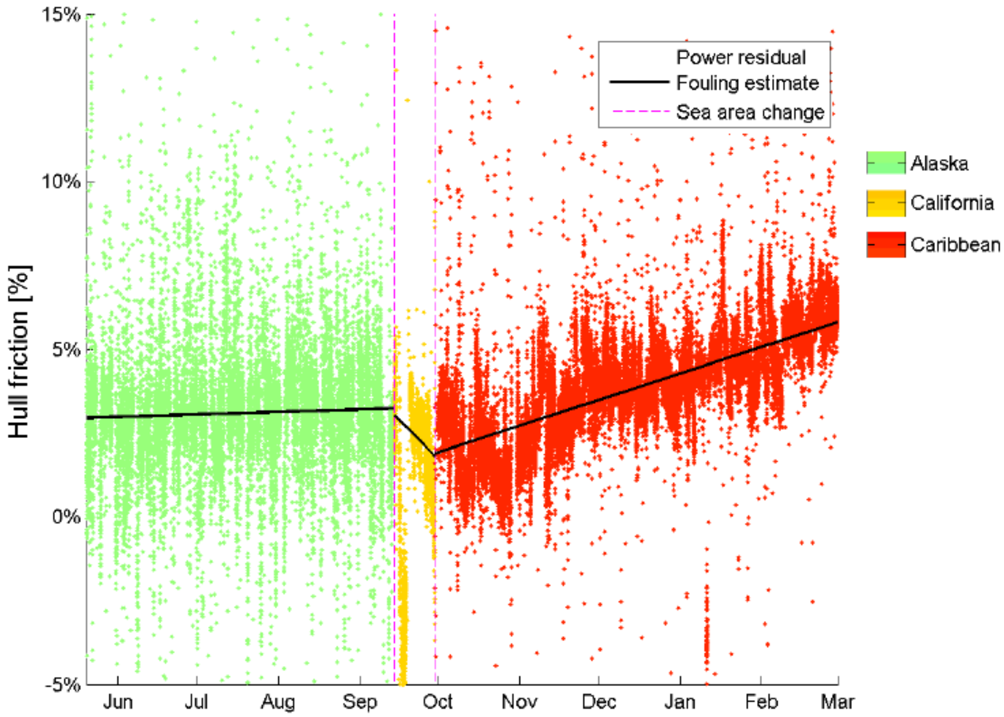


Figure 3.22: Fouling development in different sea areas [41]

Area	Average	Standard deviation	Time in area (days)	Samples	% in-crease in fouling in 90 days
Alaska	2.00	1.35	3 371	25	0.9
California	2.47	1.56	1 405	14	1.1
Caribbean	3.35	3.55	9 228	74	1.5
Mediterranean	2.59	3.87	2 938	22	1.2

Table 3.3: Average fouling of cruise ships across different sea areas [41]

The conclusion drawn is that the fouling development differs significantly from one area to another. The fouling growth while sailing within the Caribbean is the largest, while the fouling growth within Alaska waters is the smallest. This is attributed to a number of factors including salinity, water temperature, etc.

(10) Reproducibility of performance measurements [38]

In order to check the reproducibility of results the average speed drop of three sister bulk carrier vessels has been monitored. The hulls of all three sister vessels have been coated with the same Tin-free antifouling coating.

All three vessels showed a comparable performance over their dry-docking periods, with an average speed drop of 6.2% up to 7.1% which confirms the reproducibility of the tests carried out (Figure 3.23).

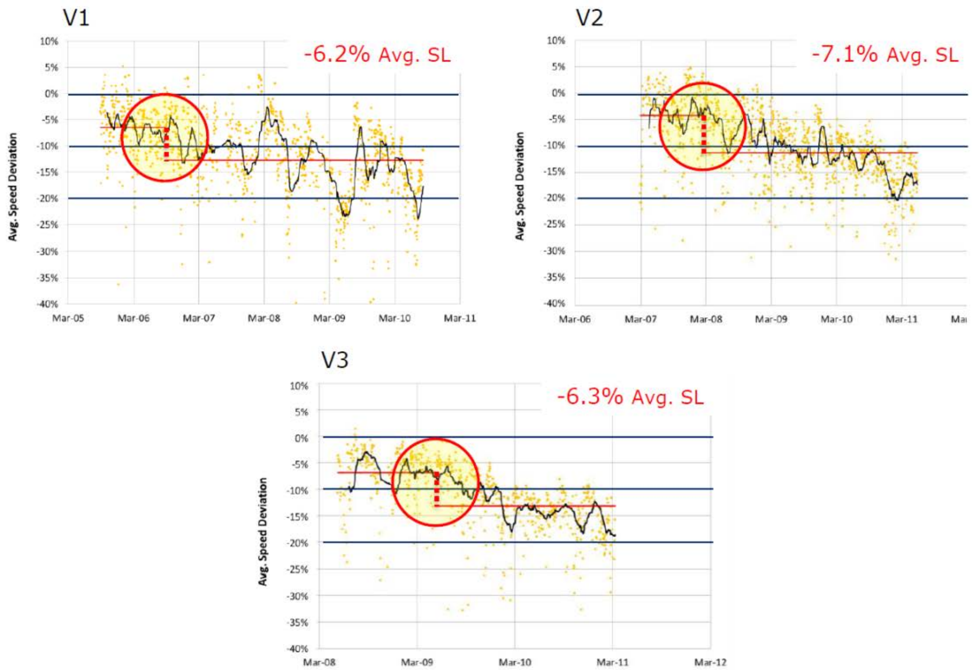


Figure 3.23: Average speed deviation over time [38]

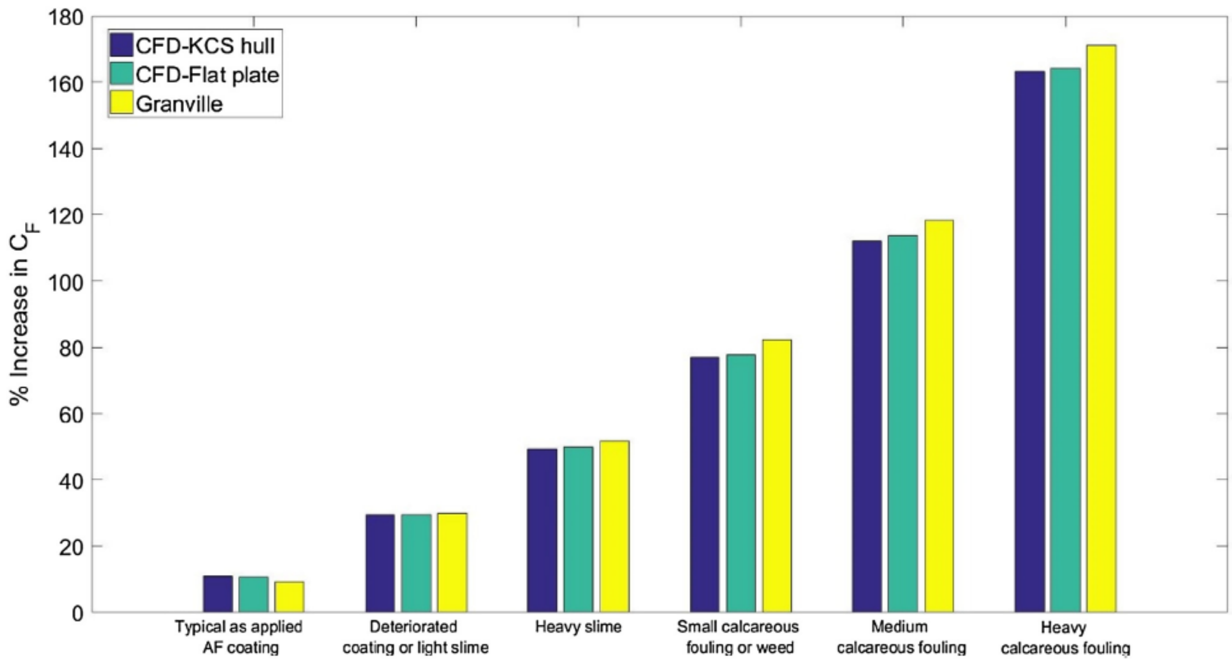
The experience gained from the above monitoring of sea-going vessels shows that the added resistance, due to roughness and fouling of the hull and the propeller, varies significantly and can reach extreme figures. In average, the added resistance is 30%, if no special attention is paid on the ship condition. However, a 30% added resistance in an aframax tanker would lead to a 1.0knot penalty or a fuel increase of 12tonnes/day at design speed of about 18 knots. In a scaled-up example of a high-speed container vessel, the same 30% added resistance would equate a speed loss of 1.8knots or an increase of 70tonnes/day in fuel, at a design speed of 25knots.

3.2.2 Computational Fluid Dynamics simulation

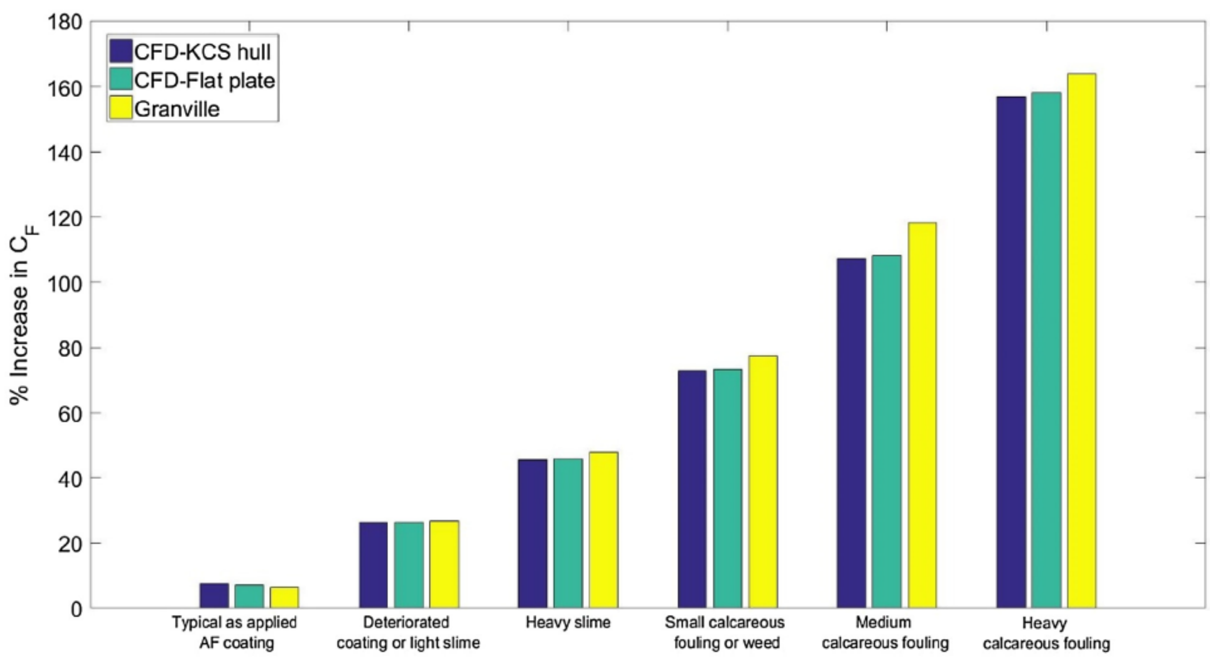
While all the above consist of real-life examples on how bio-fouling affects a ship's performance, it should be pointed out that there are also computational models by which such effects can be predicted using CFD (Computational Fluid Dynamics) simulation.

In order to take advantage of such models, one should first create the roughness function models of the typical coating and of the different fouling conditions. As soon as the roughness models are in place the data can be employed in the CFD software and used on a real ship model to make predictions of the effects of the different fouling conditions.

One such experiment was carried out in the University of Strathclyde [46]. Researchers created roughness models for flat plate in its original state, in a coated condition and in various fouled conditions. The flat plate was tested using CFD software for the effects of the different roughness functions on two different speeds of 19 and 24knots on the frictional resistance. The flat plate shared similar dimensions to an existing vessel, the Kriso Container Ship, for which various experimental data was already available for comparison purposes. The two set of results were also compared with a third set of results gained using the similarity law analysis of Granville. All results acquired are presented in Figure 3.24.



(a)



(b)

Figure 3.24: % Increase in CF in different fouling conditions for a speed of: (a) 24knots and (b) 19knots [42]

The initial observation that can be made is that all results between the three different methods used are in full agreement with an observed deviation of less than 7%. Results also indicate that a typical coating application leads to an increase of the frictional resistance coefficient in the area of 10%, while increase of the frictional resistance coefficient under heavy calcareous fouling may reach up to 160%. The relevant increase in the resistance and effective power under the same fouling conditions for both tested speeds are presented in Figure 3.25.

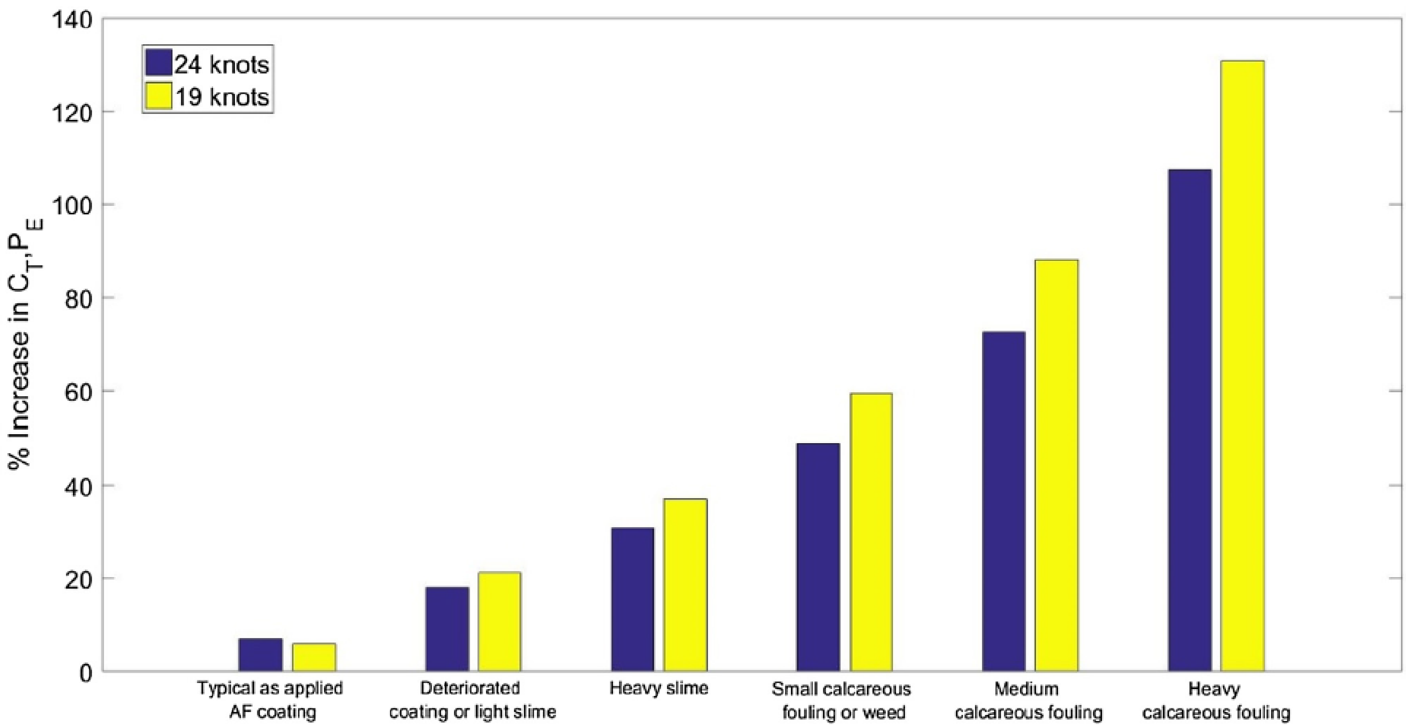


Figure 3.25: % Increase in resistance and effective power due to surface conditions [42]

3.3 Antifouling coatings on a vessel's performance (case studies)

The role of antifouling coatings on a well-performing vessel, especially in low sailing speeds, is very important.

Antifouling coatings are the primary protective measure against marine bio-fouling and surface roughness of a ship's hull. It is estimated that through the application of antifouling coatings $60 billion worth of fuel is saved, as well as 384 million tonnes of carbon dioxide and 3.6 million tonnes of sulphur dioxide are not emitted to the environment on an annual basis. [4]

As it has already been stated, there have been many developments in the field of antifouling coatings. The main purpose of all these developments is to create an antifouling coating that will be efficient enough to protect the vessel's hull and, in the same time, will not affect the marine environment and its biodiversity.

A new and novel antifouling coating should reduce the fouling accumulation on the hull and thus decrease the ship's resistance. This is very important, as it was previously shown, because the resistance is directly affecting the effective power needed consecutively and therefore the fuel consumption.

(1) Fouling on different antifouling coatings [4]

The best way to demonstrate the above is a study carried out for a LNG carrier of 270mtrs length. A service speed of 12.5 knots was selected and the increase in frictional resistance and effective power, due to different levels of fouling, was evaluated. Three different types of antifouling coatings were selected: a **SPC TBT coating**, an **Ablative copper coating** and a **SPC copper coating**.

The SPC TBT coating has proven to be the most effective against bio-fouling, however for reasons that have already been explained in Chapter 1, its use has been banned. Nevertheless, this type of coating was also studied and compared to the other two types as a good demonstration of the importance to develop an effective antifouling coating.

Firstly, the increase of the frictional resistance coefficient (ΔC_F) was predicted and, on a second stage, the total resistance coefficient was estimated taking into account the ΔC_F.

In order to examine the frictional resistance coefficient of a vessel with a certain "roughness" (e.g. fouling), the same frictional resistance coefficient on a flat plate with the same particular roughness was first examined. Subsequently, "Granville's boundary layer similarity law analysis" permits to scale the experiment to the actual vessel and calculate the frictional resistance coefficient (Schultz, 2007).

The boundary layer (or friction belt) is a layer of water around the vessel which is created by the hull friction while the vessel is moving (Figure 3.26). In this friction belt, the velocity of the water on the surface of the hull is equal to the vessel's speed (meaning that the water is moved by the vessel at an equal speed) and it is getting reduced with the distance from the surface of the hull. At a certain distance from the hull (the outer surface of the friction belt) the water velocity is equal to zero.

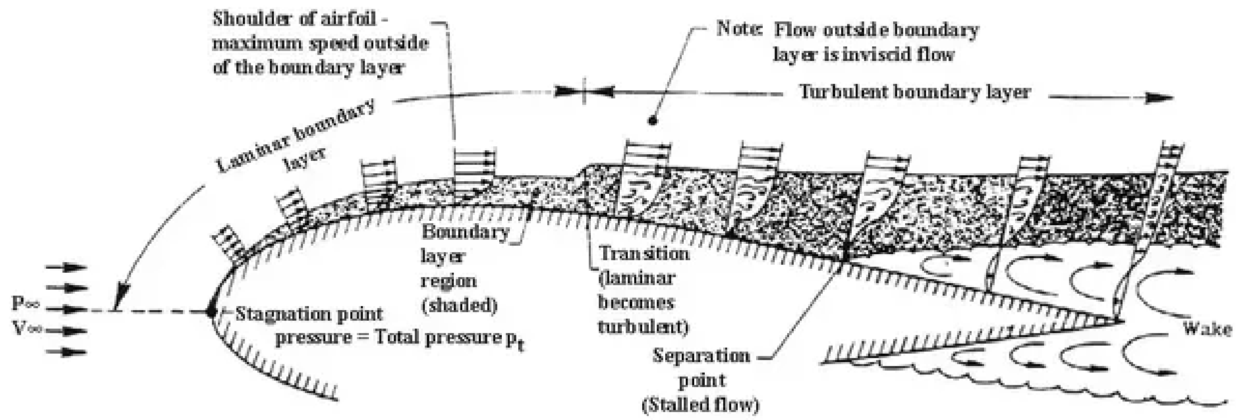


Figure 3.26: Formation of the boundary layer [4]

Schultz conducted flat plate experiments during which three different flat plates of identical dimensions, material and initial roughness were used and coated with the three different types of coatings. The three plates were then left exposed to water for 287days. Fouling coverage on the three plates after the exposure is demonstrated in Table 3.4.

Coating Type	Exposure Time (days)	Total fouling coverage (%)	Slime (%)	Hydroids (%)	Barnacles (%)
SPC TBT	287	70	70	0	0
Ablative Copper	287	76	75	0	1
SPC Copper	287	73	65	3	4

Table 3.4: Fouling coverage on three flat plates following 287 days of marine exposure [4]

The experiment results presented in Table 3.4 reveal a total fouling coverage ranging from 70% (for the plate coated with the SPC TBT coating) up to 76% (for the plate coated with the Ablative Copper coating). The total fouling coverage is then split in slime, hydroids and barnacles coverage. While the SPC TBT coating has allowed only slime fouling to occur, the Ablative Copper and SPC Copper coatings show a barnacle growth (1% and 4% respectively). Moreover, the latter shows hydroids growth of 3% on the total fouling coverage.

The roughness functions of the three plates after the exposure were also analyzed by Schultz and are presented in Figure 3.27.

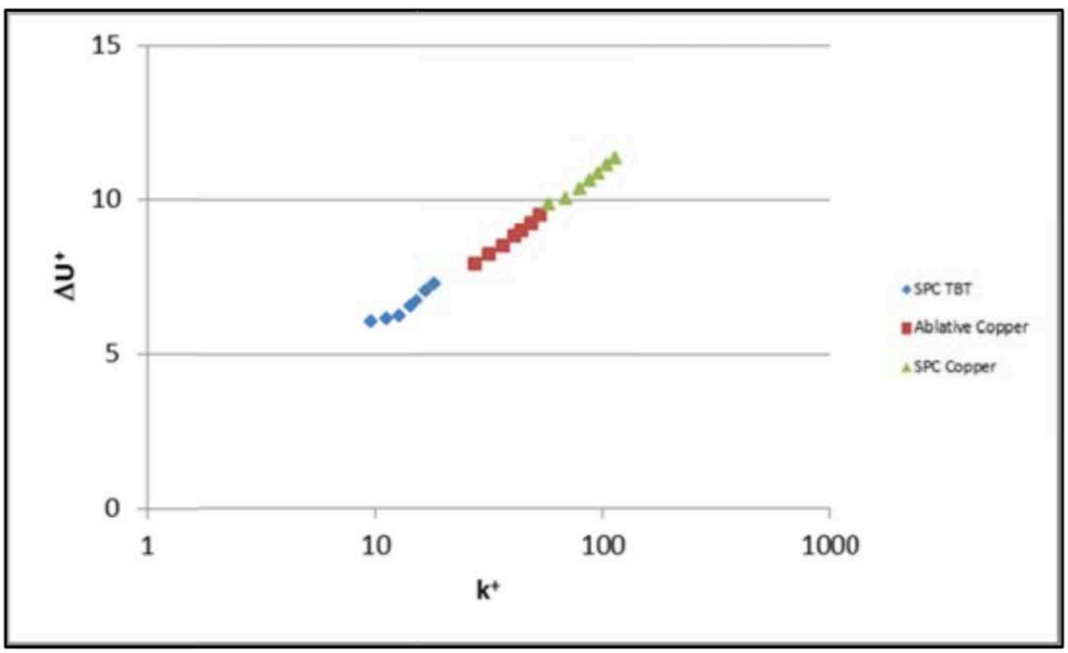


Figure 3.27: Roughness functions of the three plates after exposure of 287 days in marine environment [4]

ΔU^+ expresses a downward shift of the velocity profile of the log-law region and is directly related to the increase in the frictional drag of the surface, while k^+ represents the Reynolds roughness number.

Since the roughness function is now known for each of the plates for the same exposure time, it is now possible to jump to the calculation of the C_F of the actual ship for the same roughness conditions. The "scale-up" proposition extracted, using Granville's "home-made" tool, is demonstrated in Figure 3.28.

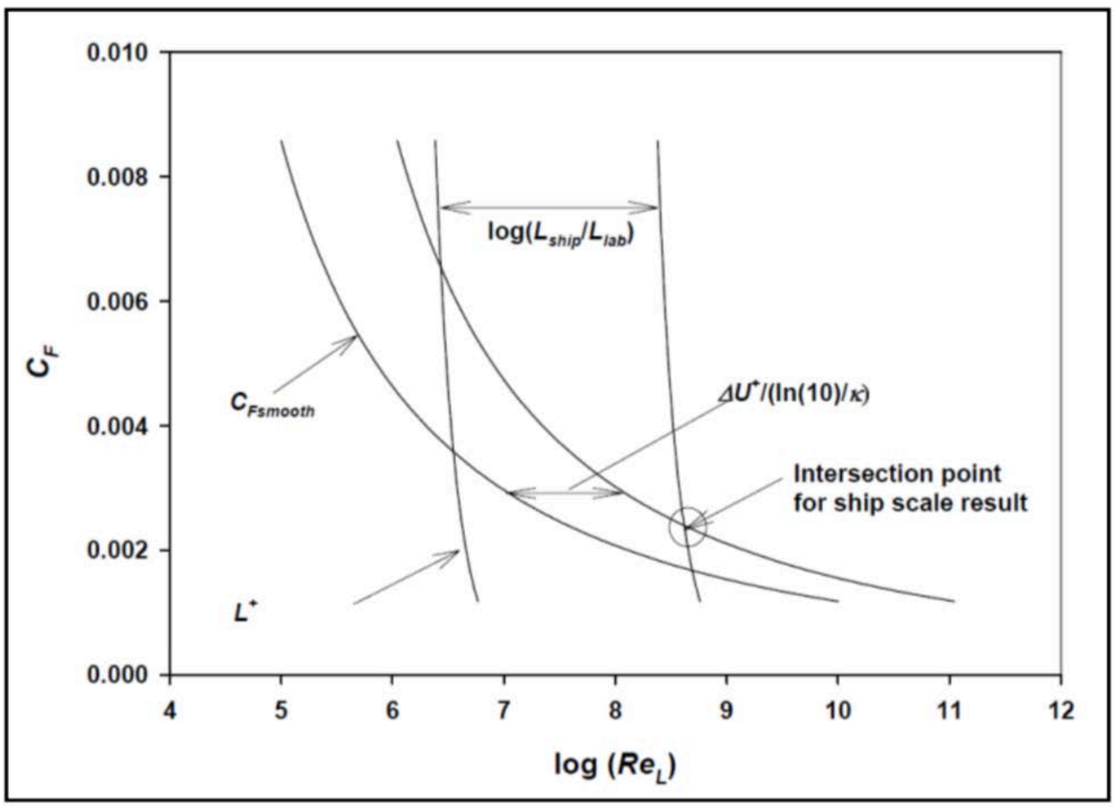


Figure 3.28: Granville's scale up proposition diagram [4]

It should be pointed out that the prediction tool of Granville has proven to be extremely accurate in way of predictions made for powering a naval ship (tests between model and sea trials were in excellent agreement). However, modern technology offers alternatives to Granville's prediction model by using complex computational fluid dynamics (CFD) software suites.

By using the above suggested model(s), the increase in frictional resistance coefficient (ΔC_F) can now be calculated and the results for a vessel at a speed of 12.5knots are demonstrated in Table 3.5. The final surface condition (of the plates coated with the three different coating types) can be comprehended by the relative increase in the frictional resistance coefficient. Now that the ΔC_F is known, the frictional resistance and the total resistance can be also calculated by using the formulas provided in the earlier sections of this chapter.

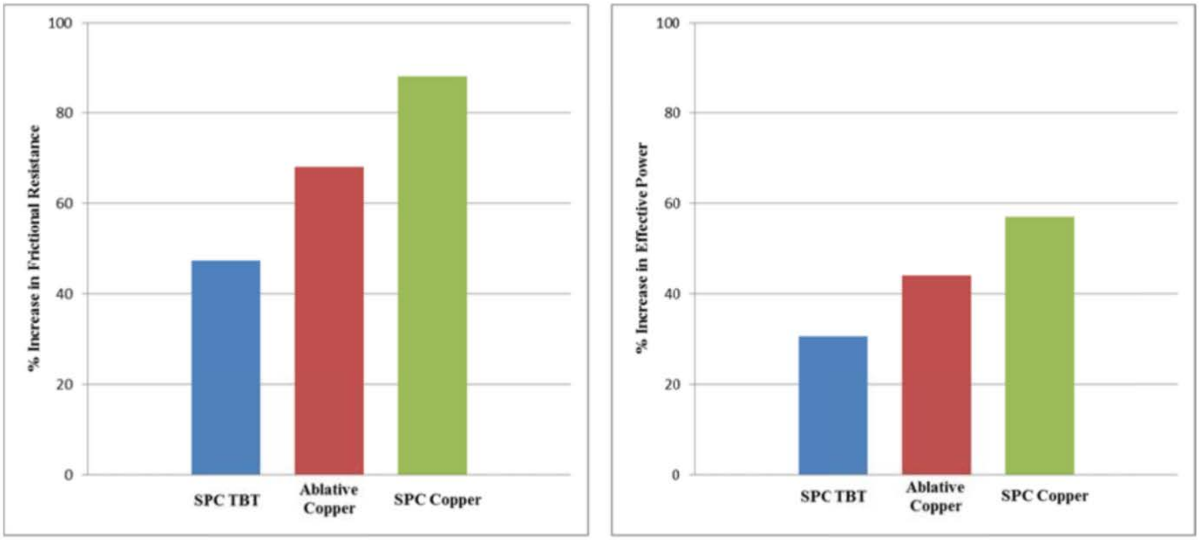
Coating Type	SPC TBT	Ablative Copper	SPC Copper
Sea Exposure Period	287 days	287 days	287 days
ΔC_F	0.0006904	0.0009929	0.0012851

Table 3.5: Increase in frictional resistance coefficient for three different coatings [4]

As expected, the SPC TBT coating has the smallest increase on the frictional resistance coefficient, since it has long been proved to be by far the most efficient antifouling technology due to its' high toxic nature. On the contrary, the SPC copper coating is the one with the poorest performance out of the three selected coatings, while the Ablative copper coating's performance is in between. It is, also, easily understood that the coating type directly affects the increase in frictional (thus total) resistance, since it is so directly related to the fouling accumulation over time.

It should be mentioned that it is highly unlike for a vessel to remain stationary for such a long period, i.e. a whole year (since the experiment examines the fouling growth on a still plate). However, for the scope of the experiment, such conditions can be accepted.

The increase in the frictional resistance is in the area of 47% for the SPC TBT coating, 68% for the Ablative copper coating and 88% (almost double from the TBT) for the SPC copper coating. The relative increase in effective power for each case is 30%, 44% and 57% respectively for the SPC TBT, Ablative copper and SPC copper coatings which consists a dramatic increase in all three cases, showing the tremendous effect of fouling in a vessel's performance. The aforementioned results are depicted in Figure 3.29.



(a) (b)

Figure 3.29: Increase % in (a) frictional resistance and (b) effective power due to fouling for three different coating types [4]

The relative contribution of added resistance to total resistance due to fouling leads to a result of 23% contribution for the SPC TBT coating, against 31% and 36% for the Ablative copper and SPC copper coatings respectively, as presented in Figure 3.30.

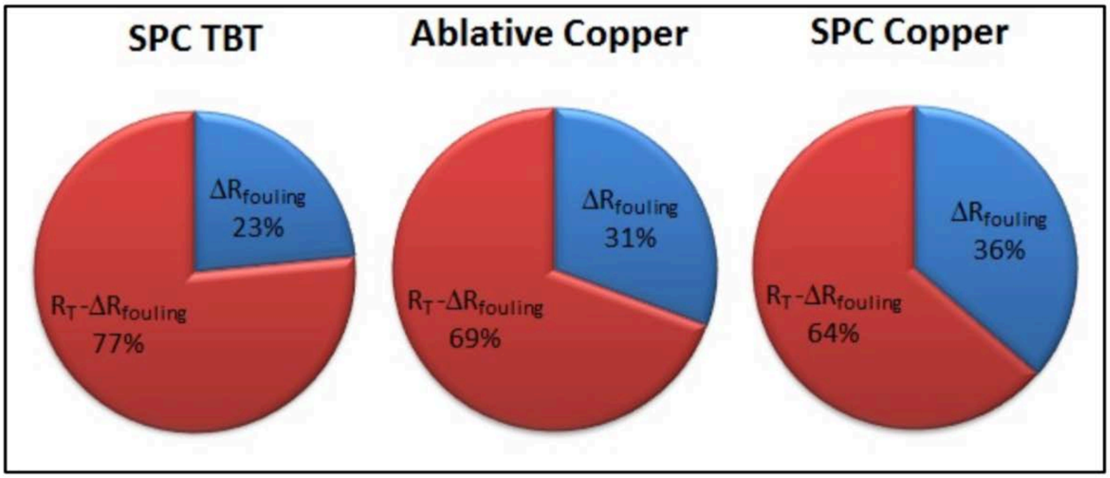


Figure 3.30: % relative contribution of added resistance to total resistance for three different coating types [4]

(2) Speed deviation for different antifouling coatings [38]

The case study presented previously, which was carried out by HPS in cooperation with Jotun Coating Manufacturers and SeaStar alliance and was presented during the SNAME meeting in Athens (Greece) in December 2013, also included the results on the performance monitoring of a certain Bulk Carrier vessel. A different type of antifouling coating was applied on this vessel's hull during 4 interval periods. The results are presented in Figure 3.31.

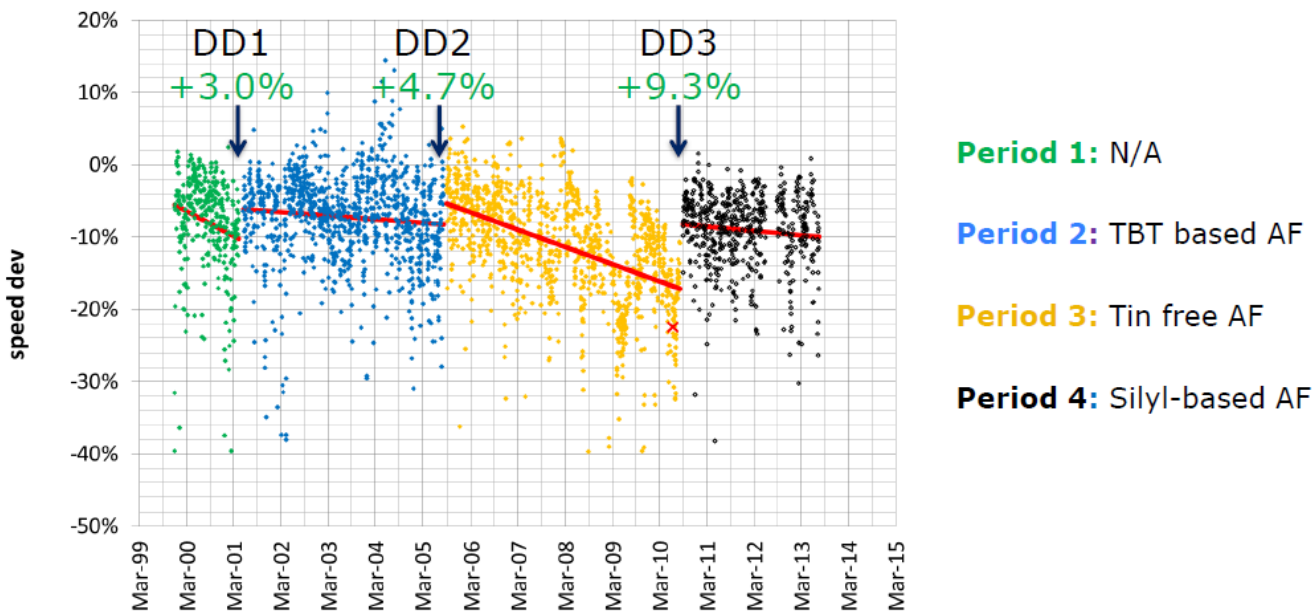


Figure 3.31: Speed deviation over time [38]

Figure 3.31 presents the speed deviation observed over 4 different docking periods using different types of antifouling coatings.

For the first period the antifouling coating used is unknown, while the coatings used for the second, third and fourth period are TBT based, Tin free and Silyl-based respectively.

During the initial period (which is one year long), a speed deviation of about 5% is observed. After the TBT free coating application and over a 5-year period a speed deviation of roughly 2% is observed. On the third period, by using a tin-free coating, a stunning 10% speed deviation is observed (also, over a 5-year period). The Silyl-based AF showcases a similar performance to the TBT coating resulting in a 2% drop, however the data for the fourth period is limited only to 3 years.

(3) <u>Added resistance for different antifouling coatings</u> [33]

This case study presents a real comparison between two sister vessels, using a different brand of antifouling coatings.

The different coating leads to a different added resistance development line (Figure 3.32). Ship A has about 5% bigger added resistance before being dry-docked and the development growth after docking is shown to be faster. Therefore, the brand Y coating is better than the brand X.

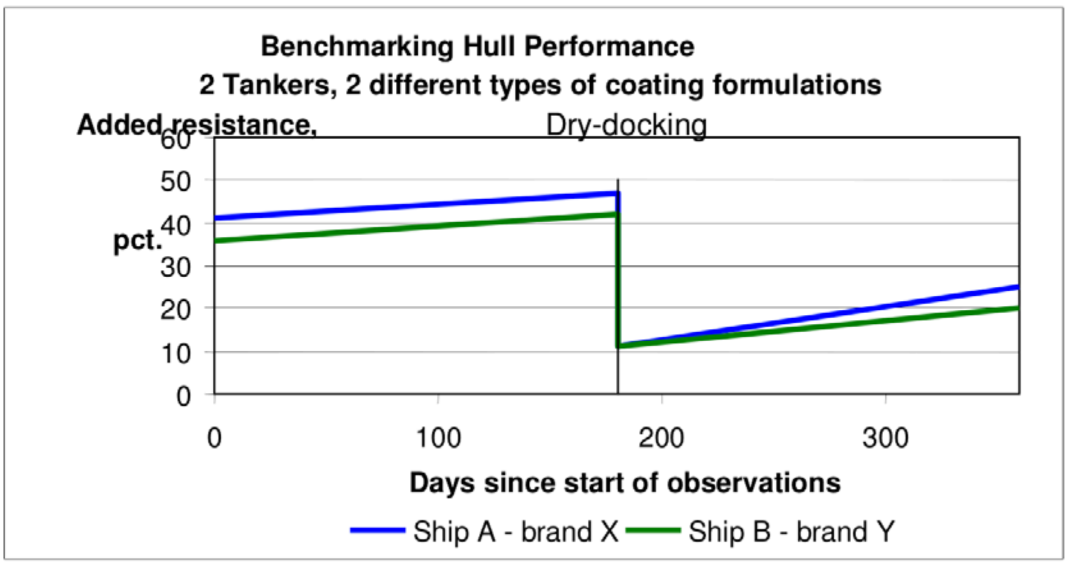


Figure 3.32: Added resistance vs days since start of observations [33]

(4) <u>Performance of an antifouling coating over time</u> [38]

In order to measure the hull and propeller performance in terms of their actual fouling condition, a change of speed deviation over docking period was used as KPI for performance of the antifouling coating applied. Data was collected over long periods and plotted (after being normalized and corrected for variations in environmental and operational conditions) in order to draw conclusions on the actual hull condition as well as for the performance of various antifouling coatings between various vessels. Some of the results of the performance analysis of the case study will be presented below.

Anonymous data LNG

The average speed deviation is monitored throughout yearly intervals (Figure 3.33). The monitoring period commences on June 2005 for a base year, where an average speed drop of 7.6% is observed, following all measurements taken. At the end of the monitoring period, on December 2008, the average speed drop has reached 20.2%, showing a big aggravation of the coating condition and increase of the hull frictional resistance.

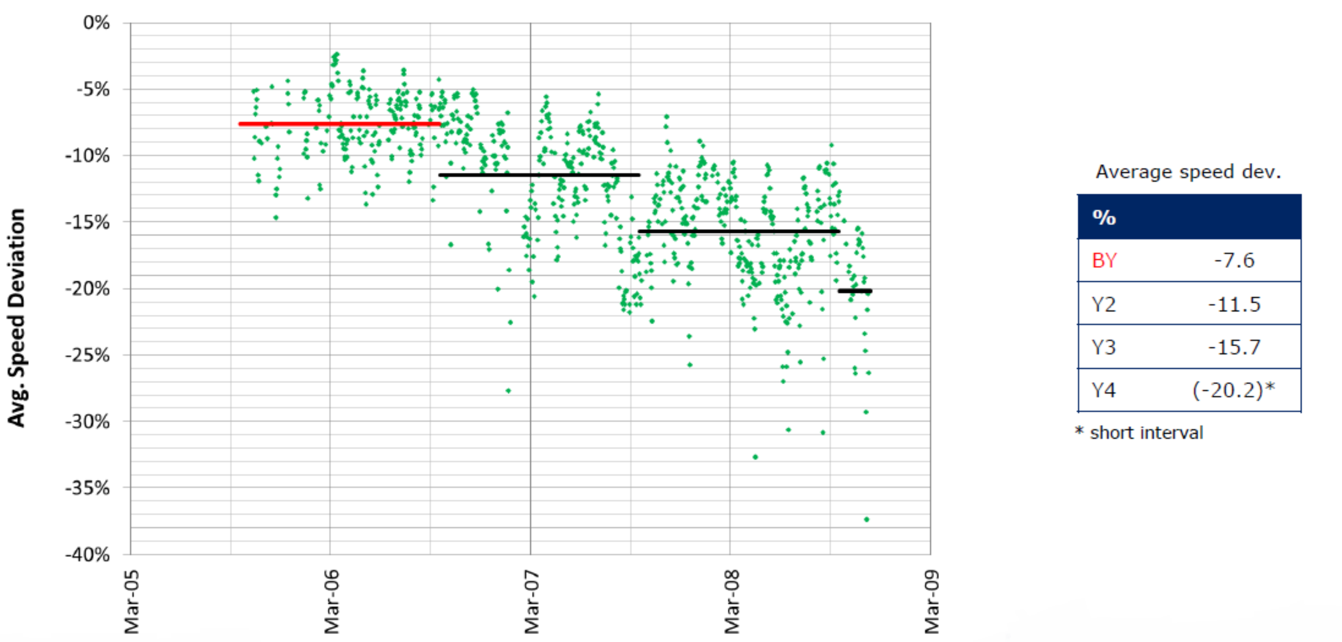


Figure 3.33: Average speed deviation over time [38]

Anonymous data 135.000 m^3 LNG

Figure 3.34 showcases the observed speed deviation on a 135.000m^3 LNG vessel coating over a 10-yearly period. The graph is segregated into clearly separated periods, over which the vessel is dry-docked and the antifouling coating is renewed. The performance losses observed in between the dry-docking periods are significant and reaching even 20% at the end of the 3rd observable period. What is also clearly demonstrated is that the hull performance is fully restored following a proper hull treatment during docking.

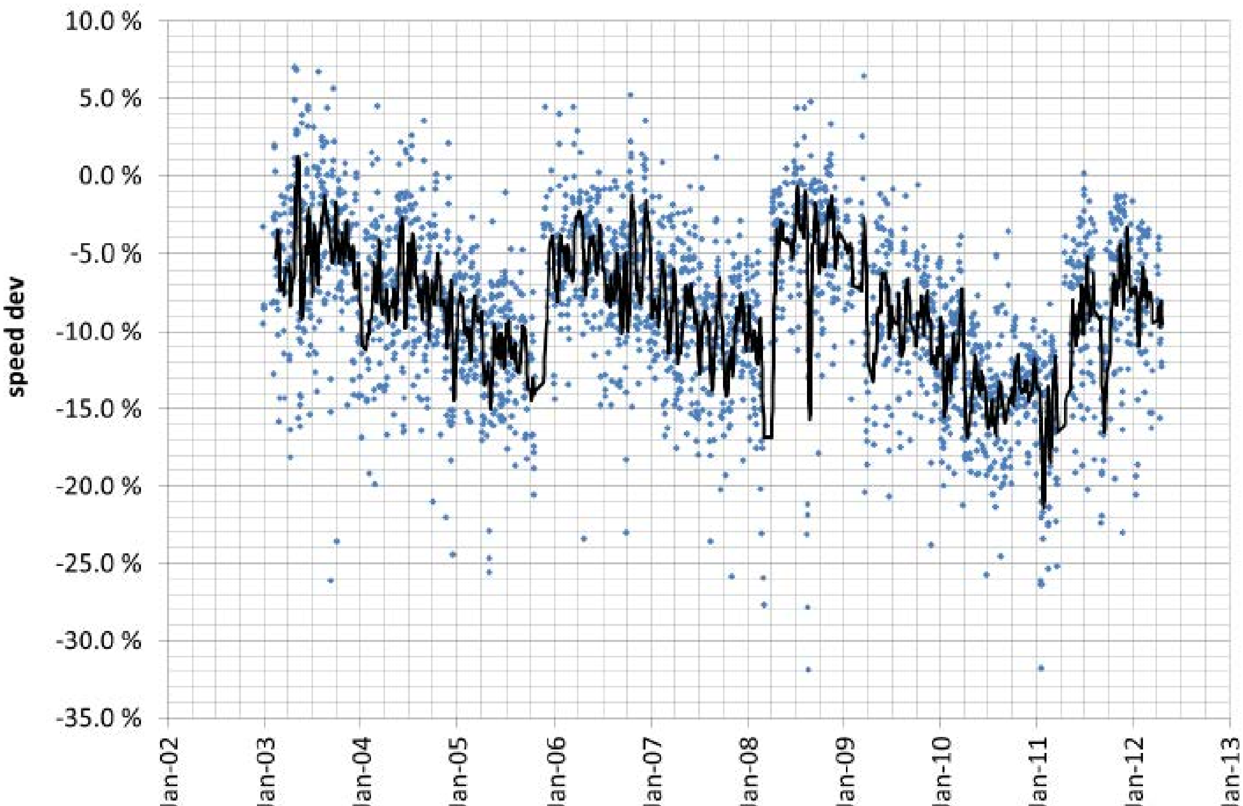


Figure 3.34: Speed deviation over time [38]

It should be pointed out that for this last example the same SPC coating is applied on all periods.

Chapter 4 – New trends in the antifouling industry

Throughout the previous chapters, the antifouling technology has been presented thoroughly, as well as the fouling/antifouling effect on the vessels' performance by stating many different case studies.

The fouling problem is an ongoing issue and the related technology still faces challenges towards more efficient and cost-effective solutions, than those currently available in the market worldwide. Continuous developments are made and new breakthroughs are achieved by using different approaches to the "fouling problem" and new technologies emerge in a constant rate.

While those innovative technologies are not still widespread or sufficiently cost-effective due to their "early stage" being, one cannot ignore their existence. In the following paragraphs a few of those technologies, which have emerged both in the antifouling coating industry, as well as in the whole antifouling industry sector, will be presented.

4.1 New antifouling systems

Even today no existing coating can meet the needs in terms of performance in durability so as to replace the biocide based antifouling coatings. The research in the maritime coating industry is still ongoing but one would assume that there will not be any significant change in the near future and that the existing (already improved) coatings, along with the binder antifouling systems containing boost biocides, are likely to maintain their domination of the market for the years to come.

However, there are various fields and aspects of the coatings that are open for further investigation and are likely to lead to the invention of new antifouling systems since many of the basic ingredients that are used in the composition of a marine coating have very promiscuous characteristics that render them extremely effective and adhere promising properties to the end product.

Some research has been made on **<u>non-stick fouling release coatings</u>**. It revealed that the adhesion of bio-fouling organisms can be prevented by creating an ultra-low friction and ultra-soft surface coating, on which the fouling organisms have great difficulty to inhabit. The function mechanism of such coatings is very close to the one of the self- polishing copolymer coatings.

Furthermore, ongoing research and studies have revealed the main characteristics, a coating ought to have, in order to resist adhesion of micro- and macro-fouling organisms. Those characteristics can be summed up as below [5]:

- A supple linear matrix that brings forward no undesirable interactions
- An adequate number of surface vibrant cluster of ingredients that are free to move to the surface and transmit the energy in the desired range
- Low elastic modulus
- Smooth surface at the molecular level so as to avert penetration of biological adhesives that could lead to mechanical interlocking
- Provide mobility to molecules in the backbone and surface-active side-chains
- A thickness that can control the fracture mechanics of the interface

4.1.1 Fluoropolymers and silicones

The molecules which gather together all the previously mentioned factors are physically and chemically changeless and remain stable for a sustained period of time in the aquatic environment. These properties are mainly possessed by two families of materials: **fluoropolymers** and **silicones**.

Fluoropolymers create non-porous, noticeably low energy surfaces with profound non-adhesive characteristics, creating a surface that is highly difficult for the marine organisms to attach on to. The drawback of these materials is the restricted mobility regarding the rigidness that is put on by the molecular elements. A superior critical stress is also required so as to make the adhesive – underlayment joint weaken due to a much higher bulk modulus compared to elastomers.

On the other hand, ***silicones*** that are applied in a thick layer of about 6mm can improve the non-adhesive aptness of fluoropolymers. Today, the most common used coating is the poly-based *(dimethyl-siloxane)* fouling release system, because of its low level of energy on the surface, low roughness and good elastic modulus.

The key features and benefits of foul release coatings are summed up in Table 4.1.

Poly-siloxanes surrogated by fluorine seem to be a category of appealing compounds for surfaces with minimum bio-adhesion and further research should be focused on them.

Feature	Asset
Non-biocidal	▪ There is no release of biocides into the water ▪ No toxic waste *(during dry-dock)* ▪ There is no regulatory restrictions
Soft and glossy surface	▪ max speed ▪ min fuel consumption / energy
Expansive fouling control	▪ Long operation services *(approximately 5 years)* ▪ Low maintenance costs
Chemically substantive	▪ The surface remains soft
Copper-free	▪ They have low weight comparing to traditional antifouling coatings ▪ They are safe to use on aluminum
High-solid	▪ They have low solvent content *(for 2–coat system there is a durability of about 5 years)*

Table 4.1: Key features and benefits of foul release coatings [5]

4.1.2 Control of biocide release

For the past years development around the antifouling coating industry insisted on the "biocide" approach, meaning that biocide agents were added in the mixture in order to eliminate the fouling at its early stages of development. This of course has proven harmful towards the aquatic environment throughout the ages, hence the need to adopt a different approach emerged.

Given the new extended knowledge on the topic of human interaction with the environment and the harm done through the industrialization and the technologies introduced, the need for a new approach is now more important than ever. Except of the widespread "global warming" phenomenon, there are other less known catastrophic effects of the human activity which are just now starting to emerge and must be immediately stopped.

In order to turn towards more "environmental-friendly" products in the antifouling coating industry, researchers have had to radicalize their mindset and look at the fouling problem from an entirely different perspective. Quite a few novel ideas immerged, some of which will be presented below.

As stated above the problem of biocides being released in an uncontrolled way in the aquatic environment through marine coatings has been a red flag in the antifouling industry since the recent past. In addition to this issue, the biocide-based coatings usually tend to release their biocide agents very fast in their early days of application resulting in a very poor antifouling performance very soon. But what if the release of the biocide agents could be controlled?

A novel technology named "AntiGuard®" promises exactly the above, by combining and using a unique fusion of biocide and hydrogel technologies offering immense control of the biocide-release mechanism, while minimizing the biocide agent content.

The AntiGuard® works by forming a biocide activated hydrogel on the surface of the Fouling Defense coating. The hydrogel effectively traps the biocide during diffusion out of the film, thereby increasing the surface concentration of the biocide while prolonging the retention time of biocide in the coating matrix and on the surface. This effectively means that a lower amount of biocide is needed to effectively prevent the settlement of biofouling species. The working mechanism of AntiGuard® is illustrated in Figure 4.1 [43]

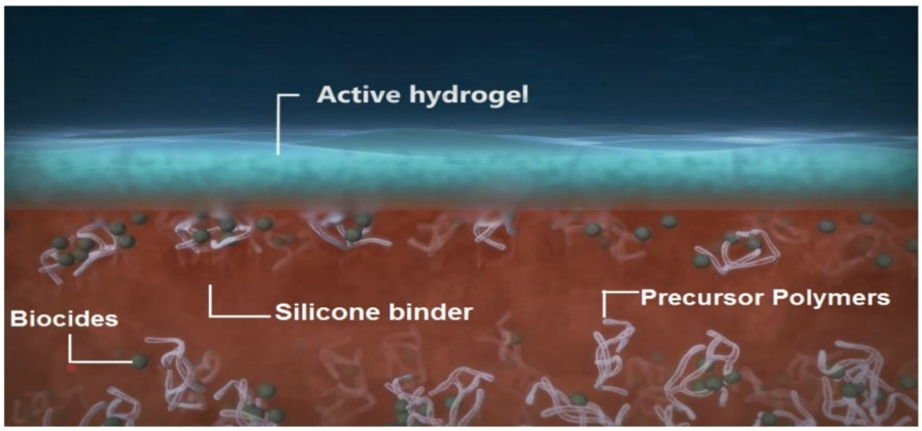


Figure 4.1: Illustration of AntiGuard® mechanism [43]

Figure 4.1 indicates that the biocide concentration of the AntiGuard® is higher than that of a conventional fouling release coating containing biocides since the agents are trapped in the hydrogel on its way out of the coating. In terms of biocide concentration, AntiGuard® needs only a very limited amount of biocide to work effectively for prolonged immersion. Figure 4.2 compares two AntiGuard® systems (Hemaguard X5 and X7) with a conventional silyl acrylate antifouling coating in terms of actual biocide content [43].

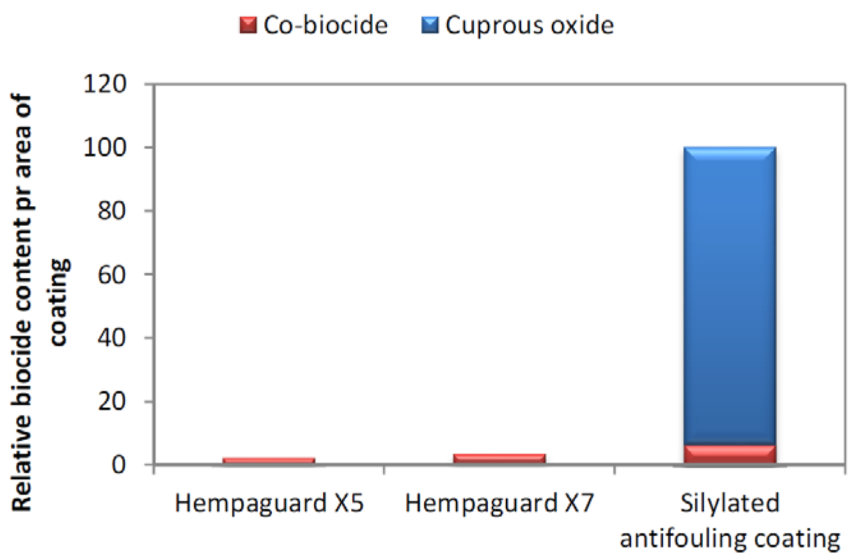


Figure 4.2: Biocide content of AntiGuard® coatings and conventional silyl acrylate coating [43]

Finally, and in terms of biocide release rate the AntiGuard® coatings have the advantage of releasing their agents in a very stable rate. This is exactly the opposite of the conventional biocide release coatings, which have a very high initial release rate. This initial high release rate falls dramatically soon after and ends up being less than the minimum effective release rate. The relevant comparison is presented in Figure 4.3[43].

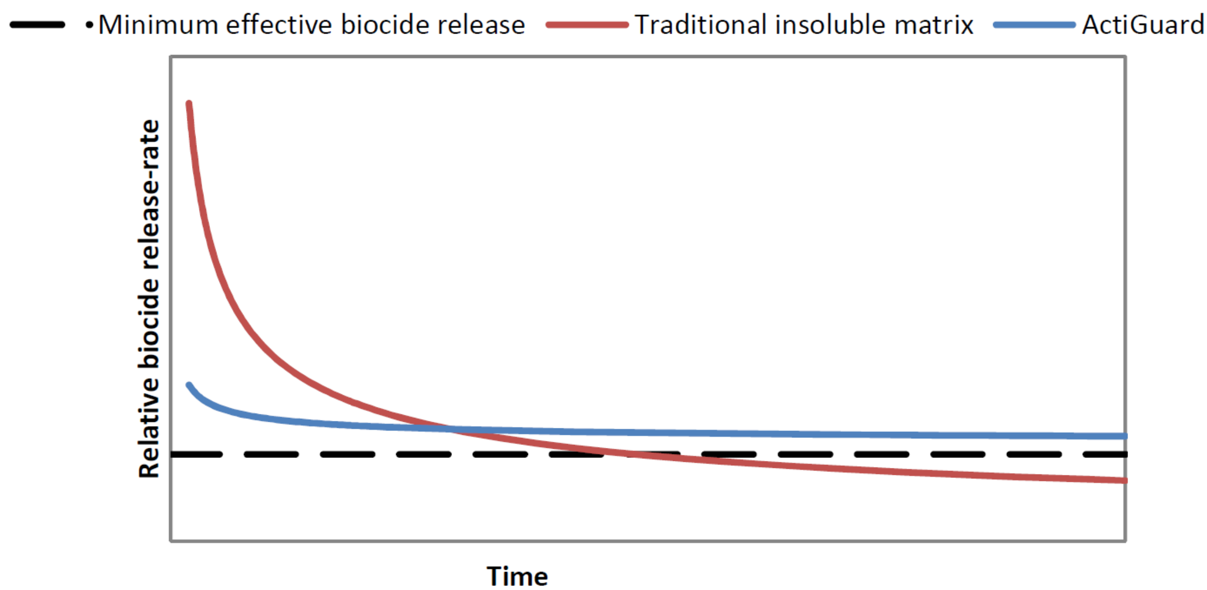


Figure 4.3: Release rate of AntiGuard® coating vs traditional insoluble matrix coatings [43]

4.1.3 Anti-adhesive agents

Antifouling coatings are necessary in order to avoid the colonization of surfaces by bio-foulers. The antifouling coatings are based on antifouling agents and, as discussed, there is a continuous need on development of new non-toxic antifouling formulations, permitting a long-lasting life cycle control, while being durable, resistant to damage, repairable, of low maintenance, easy to apply, compatible with anti-corrosive agents and cost effective.

All marine fouling organisms use an adhesive mechanism to attach to surfaces. Controlling such attachment could be achieved by physically preventing adhesion through certain anti-adhesion mechanisms and agents which can be used in antifouling coatings affecting the settlement pattern of specific bio-foulers. Until now, the best anti-adhesive properties have been found in silicon and polymer based anti-fouling coatings, which also happen to be extremely durable. On the other hand, those technologies suffer from persisting colonization by slime adhering on ships at speeds even over 50knots [44].

In the battle towards inventing new anti-adhesive agents, various technologies have emerged and are presented below:

Novel Acylamino Compounds

Researchers have synthesized two novel acylamino compounds containing gramine groups. The structure of target compounds was established using 1HNMR, 13CNMR, IR spectra, and elemental analysis. The antibacterial activity of the synthesized compounds against Escherichia coli and Staphylococcus aureus, as well as their antifouling activity was studied. The results showed that these compounds possessed high antibacterial activity and a minimal inhibitory concentration value of 0.03mg/mL against bacteria. Moreover, their antifouling properties are superior to cuprous oxide and chlorothalonil, which are widely used as antifoulants. Furthermore, quantitative structure activity relationship studies with antibacterial activity of the nine gramine compounds were established. These provide theoretical and technical bases for preparing environmental-friendly antifouling coatings with the compounds as antifouling agents [45].

Heterocyclic Compounds

Research on the topic has revealed that simple heterocyclic compounds disrupt cell-cell communication (quorum sensing) and interfere with the formation of biofilms such as those that cause fouling on ships' hulls. Such heterocyclic novel compounds have been discovered and used on an experimental stage, with tests having been carried out for two months in submerged plates in the marina in Haifa Bay and showing great promise in the battle against fouling [46].

The key features of such compounds are summarized below:

- Technology has proven to be successfully incorporated into acrylic polymers
- No antibacterial or antifungal effect, avoids development of resistant strains
- Environmental-safe non-leaching coating
- Effective against both fungal and bacterial biofilms
- Inhibit and reverse biofilm formation

Zinc Oxide Nanostructures

Tests have shown that zinc oxide (ZnO) nanostructures can photocatalytically inhibit growth of bacterial and fungal strains under solar irradiation. Studies have been carried out in order to investigate the potential prevention of the formation of marine biofilms by ZnO infused nanorod coatings. ZnO nanorod coatings were fabricated on microscope glass substrates by a simple hydrothermal technique using equimolar solutions of 10 mM zinc nitrate and hexamethyltetramine. In a continuous 5 days out-door experiment with sea water collected from the Sea of Oman, the nanorod coatings significantly reduced density of bacteria in comparison to the control subject (no coatings) under the sunlight conditions. However, in the absence of sunlight, test and control slides were equally colonized by bacteria. Most of bacteria on the coatings under sunlight were dead, while bacteria in the absence of sunlight were alive, as shown using live and dead stating, suggesting that ZnO nanorod coatings effectively prevent biofilm formation and can be used as a novel green antifouling technology, subject to enough sunlight being available [47].

Sulphated Polysaccharides from Algae

The specific activity of surfaces by biocidal molecules, active against biofilms, is a great challenge, leading to the development of materials with antimicrobial barriers. Research projects focused on preventing the growth of microorganisms by using natural biocides or anti-biofilm molecules have been carried out. Algae have the ability to produce a large variety of chemical defenses which prevent over-predation, defense against competition from foreign microorganisms or changes in environmental conditions. Tests were performed on the antifouling and antimicrobial activities of sulphated polysaccharides extracted from algae against 12 strains of bacteria and 4 strains of marine microalgae involved in surface colonization process. Nine extracts have shown promising results by inhibiting the growth of bacteria with a Minimum Inhibition Concentration (MIC) value $\leq 0.01 \mu g/ml$. The most promising compounds were subsequently combined and both antifouling and antibacterial activities were re-assessed. One of the mixture of compounds displayed remarkable results by inhibiting the growth of five bacteria and two microalgae strains with MIC value $\leq 0.01 \mu g/ml$. The relevant research has led to the discovery of new compounds with antimicrobial and antifouling properties which could be used in the shipping industry in order to combat the fouling problem in an efficient and environmentally friendly way [47].

Bioactive Marine Natural Products

Some of the best antifouling compounds can be found in marine natural products such as sponges, corals and macroalgae and/or their associated microflora and/or symbionts. To date, purification of active products from marine organisms has yielded to around 200 molecules with various degrees of antifouling activities against a wide range of marine fouling organisms. Discovery of new compounds has improved through the continuous advances in technological innovation (increased NMR magnetic field strength, probe technology, soft ionization etc.). Moreover, the marine environment is rich in unexplored species (estimated around 1-2 million) that may prove to have novel antifouling capabilities. Very promising compounds have been purified from microorganisms, macroalgae and sponges. For example, new triterpene glycosides were obtained from the sponge Erylus formosus and did exhibit high and broad-spectrum activities towards bacteria, fungi, macroalgae and invertebrates. Many other compounds have been purified from sponges but displayed activities against invertebrates' settlement or microbial growth only. Regarding the investigation of macroalgal secondary metabolites for new AF compounds, most of the research has been focused towards Rhodophyceae and Phaeophyceae. Species of the genus Laurencia have been extensively investigated for the production of secondary metabolites and are known to produce around 700 natural products, particularly bioactive halogenated compounds. Regarding AF activity, the best compound obtained from this genus is the elatol, which is potent against marine bacteria, and invertebrates at low concentration. Concerning Phaeophyceae, the most promising extracts are Bifurcaria and Sargassum. Diterpenes displaying large spectra AF activities were isolated from Bifurcaria bifurcata. Interesting compounds from Sargassum tennerimum were shown to interfere with larval settlement of Hydroides elegans and biofilm formation. This only shows the vast opportunities that many natural organisms can offer towards an effective and efficient battle against the fouling problem [44].

The various natural marine products specified above are presented in Figures 4.4 - 4.8.

Figure 4.4: Rhodophyceae [48]

Figure 4.5: Erylus Formosus Sponge [49]

Figure 4.6: Phaeophyceae [50]

Figure 4.7: Sargassum [51]

Figure 4.8: Bifurcaria Bifurcata [52]

4.1.4 Modification of the surface topography

The surface topography has been an important development in the battle against fouling in recent years. Controlling bio-adhesion and growth of fouling organisms, using either static, or dynamically modified, surface chemistry and topography, is an attractive option for developing novel antifouling systems.

The fact that there are many adhesion strategies and different organisms competing for space on exposed surfaces, means that developing a surface that is an effective non-biocidal antifouling material or coating against all, or even most, organisms remains challenging. Careful control of surface chemistry or release/delivery of biocidal compounds or materials are approaches commonly used for control of biofouling. However, appropriate scaling and engineered control of surface topography at nano- and micro-scale can also affect initial cell settlement, attachment, adhesion strength and the required shear forces for removal of organisms. Determining the topographic parameters that influence settlement is however difficult, especially where different competing organisms of different length scales are involved [47].

An interesting approach in the field of surface topography is the biomimetic approach of antifouling surfaces.

Biomimetics is defined as the study of the structure and function of biological systems and processes as models or inspiration for the sustainable design and engineering of materials and machines. One of the interesting developments in the area of green tribology over the past 10 years is the recognition that nature has developed many highly optimized tribological surfaces that are: (i) typically multifunctional, (ii) reactive to their environment, and (iii) using a combination of physical and biological design strategies.

Such natural surfaces are self-healing and self-cleaning and possess the ability to produce cell-to-cell communication signals to prevent colonization. In this context, tribology includes the interfacial science of a fluid's flow over a solid surface and the friction induced by this flow.

In order to study this topic, we must focus on the below important aspects:

Surface physical features

The hydrodynamic interactions of biological systems are quite common to those of man-made structures. Reynolds number is a measure of the ration of the inertial forces to viscous forces and quantifies the importance of these forces for given flow conditions. Figure 4.9 illustrates the Reynolds number variation for various biological systems compared to a large vessel.

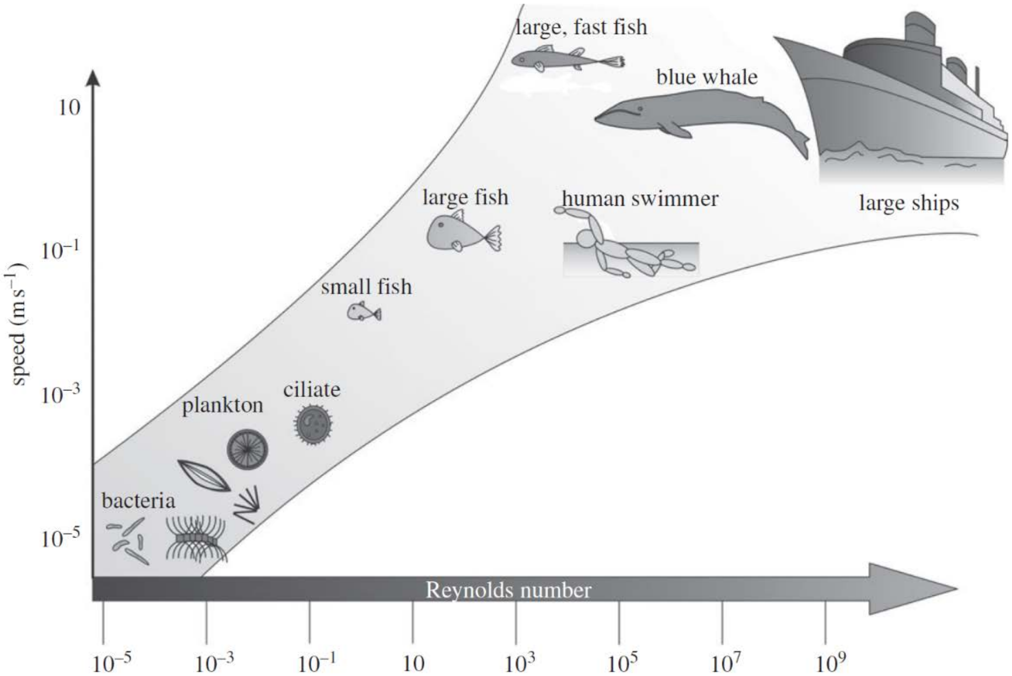


Figure 4.9: Hydrodynamic interactions – Reynolds number variation for biological systems in respect to speed [53]

The movement of different organisms involves Reynolds numbers spanning a huge range of order of magnitude. Micro-organisms at Reynolds numbers around 10^{-5} are in an environment where viscous forces significantly dominate over inertial forces. These viscous hydrodynamic interactions almost completely influence the settlement processes, allowing the micro-organism to identify an appropriate substratum surface. This contrasts with engineered underwater structures, where Reynolds numbers are usually between 10^3 and 10^9. A challenge to biomimicry is to adapt natural systems that are effective at relatively low Reynolds numbers over small surfaces to man-made systems that operate under parameters orders of magnitude greater [53].

Topography/Textures

Many organisms have evolved surface topographies that deter settlement, for example, pilot whale skin, mussel/bivalve surfaces, crabs and eggshell casings. The roughness scale of a coating significantly influences its wettability. Notably, the AMBIO project (Advanced Nanostructured Surfaces for the Control of Biofouling) has developed a range of nanostructured surfaces, including sol-gel coatings with nanoparticle inclusions, and nano-scaled self-assembled surfaces. Customized surface nano-architecture has yielded a commercial product, Sharklet, inspired by the overlapping, ridged platelet structures of sharkskin (Carman et al. 2006). The topography of this structure, which features a gradient of microscale change in three dimensions, offers a more hydrophobic surface compared with isolated topography gradients. Among other applications, Sharklet is undergoing development as an AF coating [53]. In Figures 4.10 and 4.11, the skin near the gills of a bonnet head shark and different scale patterns of various species of fast sharks are presented respectively.

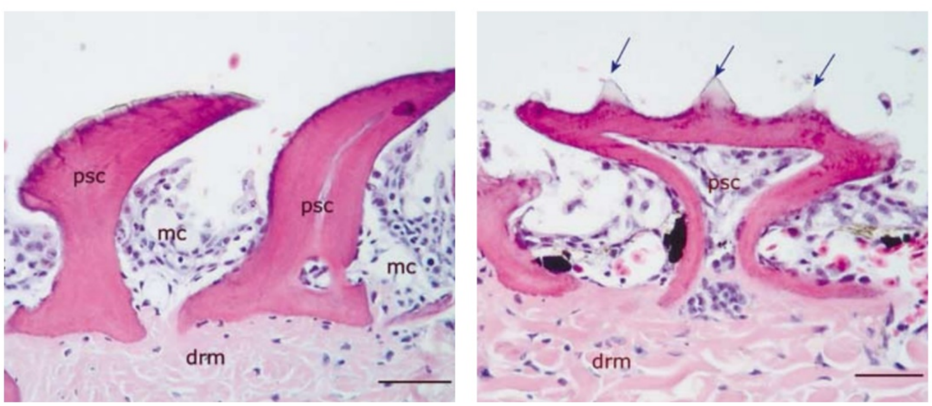


Figure 4.10: Skin near the gills of bonnet head shark (Sphyrna tiburo) and transversal section [54]

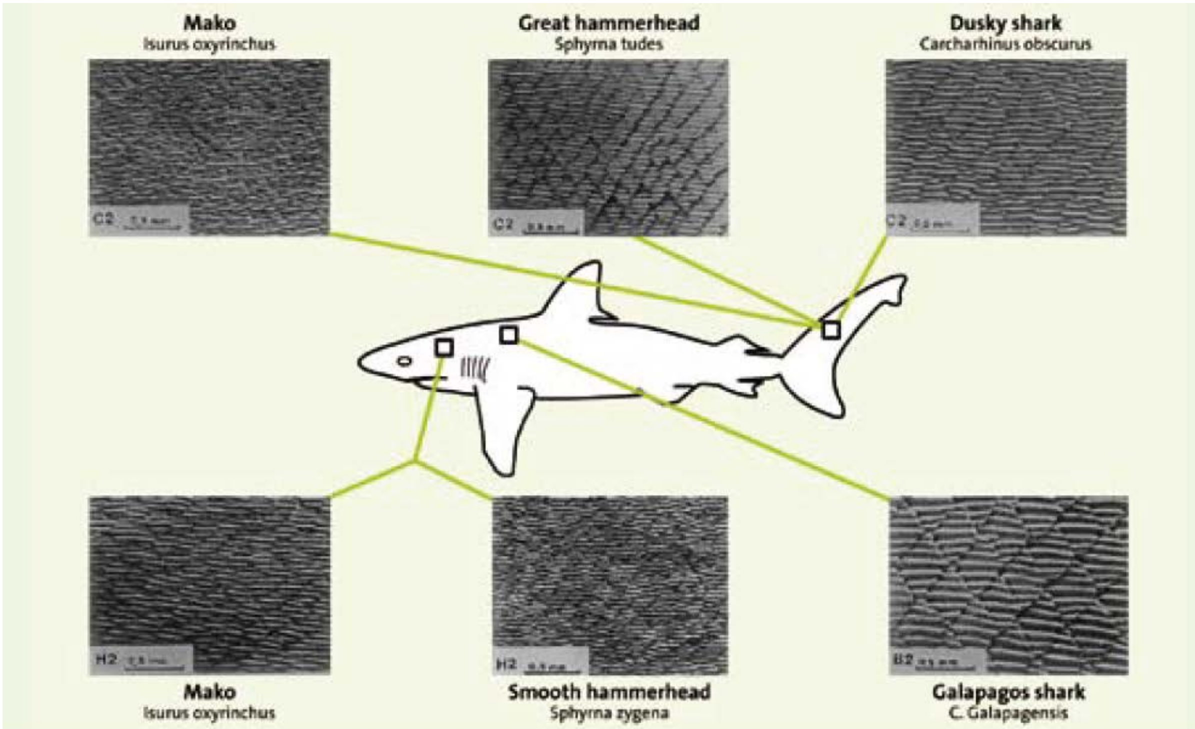


Figure 4.11: Scale patterns of various species of fast sharks [54]

Summing up what has been presented above, a wide range of antifouling coatings using novel technologies are already available in the market and are presented in Table 4.2.

Product	Company	Type
Devclear	Devoe Coatings	Silicone Polymer
Sigma LSE	Sigma Shinto Coatings	Silicone Polymer
Nipple Sleek	Nippon Paint Company	Silicone Polymer
Epco-Tek 2000	Hi Tek Company	Epoxy-Cu Powder
Luminore	Luminore	Cold Spray/Metal-Cu
Copper Metal	Multiple companies	Metal
Brass Metal	Multiple companies	Metal
Copper-Nickel Alloy (90:10)	Multiple companies	Metal
Copper Thermal Spray	Multiple companies	Metal
Brass Thermal Spray	Multiple companies	Metal Thermal Spray
Bronze Thermal Spray	Multiple companies	Metal Thermal Spray
Zinc Galvanising	Multiple companies	Metal Thermal Spray
Polyshield Aqualastic	Cynet Enterprises	Hot-Dip or Electrocoat-Zn
SeaLion	Juton Group	Polyurea Elastomer
Rilsan	Arkema Inc	Silicone Foul-Release
Kynar 500	Arkema Inc	PVDF Resin
Fluon ETDE	Asahi Glass	Thermoplastic Fluoropolymer
Neoflon	Daikin Industries	Perfluoroalkoxy Resin
Teflon-FEP	DuPont	Fluorinated Ethylene Propylene
Sylgard 184	DowCorning	Silicone Elastomer
Mille Light	Hempel	Non-Toxic Ablative
Micron Eco	International	Non-Toxic Ablative
SSC-44	US Gloss	Non-Toxic Ablative
Lefant H2000	Lotrec AB	Physical Growth Repellent
Hempasil X3	Hempel	Hydrogel Silicone Foul-Release
Ecolosilk	Nippon Paint	Biocide-free Antifouling
SigmaGlide	Sigma Coatings	Silicone Foul-release

Table 4.2: List of novel antifouling coating products available in the market [55]

4.2 Novel technologies

The technology in order to battle the fouling problem goes beyond the antifouling coatings themselves and as years pass and the technology around the antifouling industry grows, new and innovative ways to battle the "fouling problem" emerge.

4.2.1 Ultrasonic transducers

One such novel technology consists of the installation of various ultrasonic transducers on the inner hull (hull protection) and on the forward seal area (propeller protection). The ultrasonic transducers produce a specific set of ultrasonic signals through the metallic surfaces which are subsequently diffused in the liquid surrounding them and prevent the biofilm from being created.

As previously discussed, the biofilm consists of micro-organisms in which cells are sticking to each other. These micro-organisms are able to multiply under favorable conditions and as a result the biofilm will eventually be created and will form the base for every further fouling (algea, barnacles, shells).

Conclusively, this technology is eliminating the fouling problem from the root of it and from its initial stage. Some indicative photos of this system are presented in Figures 4.12 and 4.13.

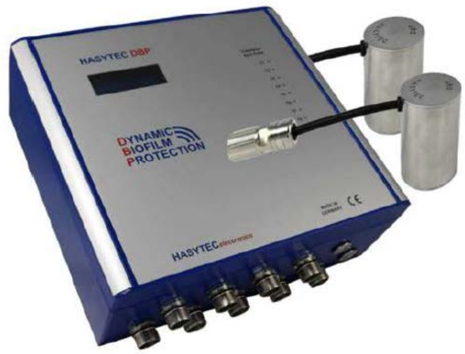


Figure 4.12: Ultrasonic Transducer System [56]

Figure 4.13: Typical forward seal installation of ultrasonic system for propeller protection [57]

4.2.2 UV light

In the same line of thought an interesting technology has been emerged integrating the advantages of UV spectrum against fouling.

AkzoNobel is the first company to introduce such an innovative technology integrating UV LEDs from Royal Philips (Dutch Healthcare and lighting company) into a marine coating system developed by the company itself. UV light is emitted from the coating surface, preventing organisms from being collected on the surface (Figure 4.14). The UV-based approach eschews the use of biocides, which have been effective in preventing fouling but have come up against health and environmental concerns.

The project of incorporating the LED technology into coatings on ship hulls and other structures is obviously a difficult one in terms of initial effort. According to AkzoNobel, this new technology will overcome the early challenges and will "revolutionize the fouling control industry." The company intends to focus initially on using the new coating technology to protect ships, yachts and offshore assets.

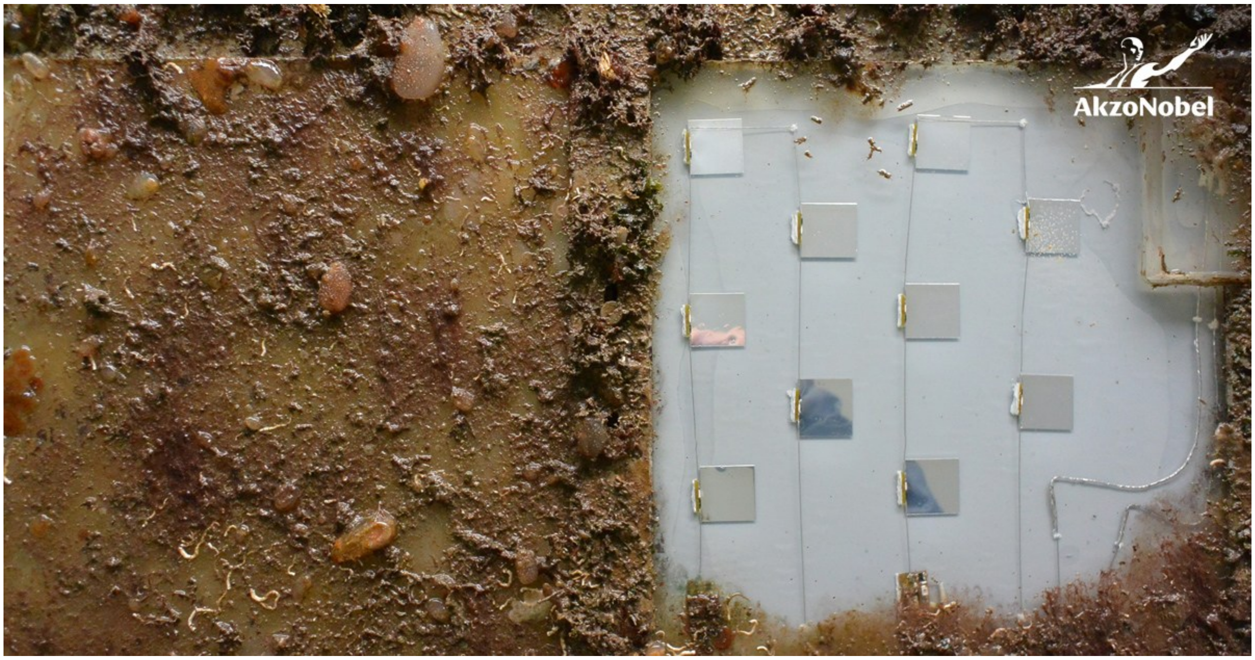


Figure 4.14: UV Panel introduced by Akzonobel [58]

4.3 ROVs in hull cleaning

Finally, an honorable mention should be made to the industry behind the in-water cleaning operations of vessels' hulls and polishing of their propellers.

The hull-cleaning industry is facing now more challenges than ever with new regulations regarding hull cleaning and propeller polishing coming in place and forcing many changes and developments in their operational practices and equipment used.

While in the recent years the hull cleaning operations were done by engaging divers with handheld brushes and relevant equipment, regulatory developments have led to the invention of ROVs (remotely operated vehicles) which are carrying out the relevant works as well as other innovative technologies (Figures 4.15 - 4.17).

Figure 4.15: Underwater propeller polishing performed by diver [59]

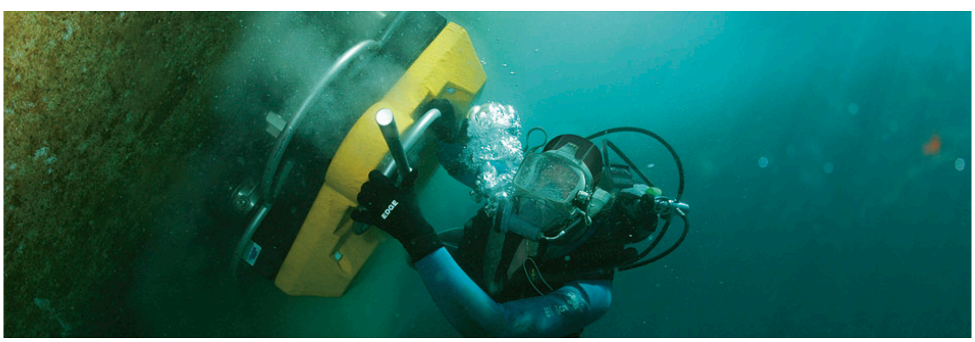


Figure 4.16: Underwater hull cleaning performed by diver [60]

(a) (b)

Figure 4.17: (a) Typical example of brushes used for underwater hull cleaning [61] and (b) ROV machine from GAC marine [62]

Table 4.3 illustrates the current list of robotic equipment currently available for the hull cleaning of marine vessels.

Robots	Operating Type	Filter	Holding System	Cleaning System
CleanHull	Semiautonomous	Yes	Turbines	High pressure water
Fleet Cleaner	Manual	Yes	Magnets	High pressure water jets
GreenSea Robotic Hull Cleaner	Autonomous	Yes	Neodymium magnet track System	Brushes using ultrasonic action
Hull Surface Treatment	Manual	Not needed	Magnets	Thermal Shock
Hullbot	Manual	No	3 thrusters	Rotating cleaning disks
HullBUG	Autonomous and Semiautonomous	Yes	Magnetic, or negative pressure	Brushes, and jet based operatic modeler
Hulltimo	Manual	Yes	Suction system	Brushes, roller of polyamide
HullWiper	Manual	Yes	Negative Pressure system	Cleaning discs that pump saltwater
KeelCrab Sail One	Manual	Yes	Turbine	Turbine vacuum, rubber, and nylon brushes
M6 sub sea Cleaning Tool	Manual	Unknown	Magnets	High pressure water nozzles
Magnetic Hull Cleaner	Manual	No	Magnets	Pressure washer
Remora	Autonomous	Unknown	Magnets	Unknown
RovingBAT	Semiautonomous	Unknown	Thrusters, motorized tracks	Uses either hydro-jetting or a brushing system
Underwater Hull Cleaning Robot	Proprietary	Yes	Proprietary	Proprietary
Underwater Robot	Autonomous	Unknown	Propeller	Unknown
(No Name)	Unknown	Unknown	Unknown	Unknown

Table 4.3: List of available robots for hull cleaning operations [21]

4.4 Coatings for propellers

While most of the cases and developments have referred to technologies related to the hull of commercial vessels, one should not forget that the propeller condition, also, plays an important role towards an efficient vessel.

The propeller's fouling is quite similar to the fouling of the hull, since it also refers to a submerged metallic surface in a bio-accumulating marine environment, and while one would say that due to the high speed of the propeller (directional speed of the vessel and rotational speed coming from the vessel's engine through the intermediate and propeller shaft) the fouling phenomenon would be minimal (since it is also vastly speed dependent), it should be pointed out that the propeller (most of the times at least for commercial vessels) is a cast outfitting equipment piece made out of copper alloys and is not protected by any antifouling coating. The effect of high speed on the fouling growth is almost cancelled by the lack of antifouling coating, thus the fouling growth on the propeller is quite similar (or potential slightly smaller) to the fouling growth on the hull for a sea-going vessel. In cases where the vessel is stationary (idle periods or cold/hot lay-up), the propeller area is more exposed to fouling growth.

While traditionally the propeller is left coat-free, recent technologies have emerged, offering anti-fouling coatings for propellers, and have proven way promising for potential application, of course with the relevant costs included. Two examples are demonstrated in Figure 4.18.

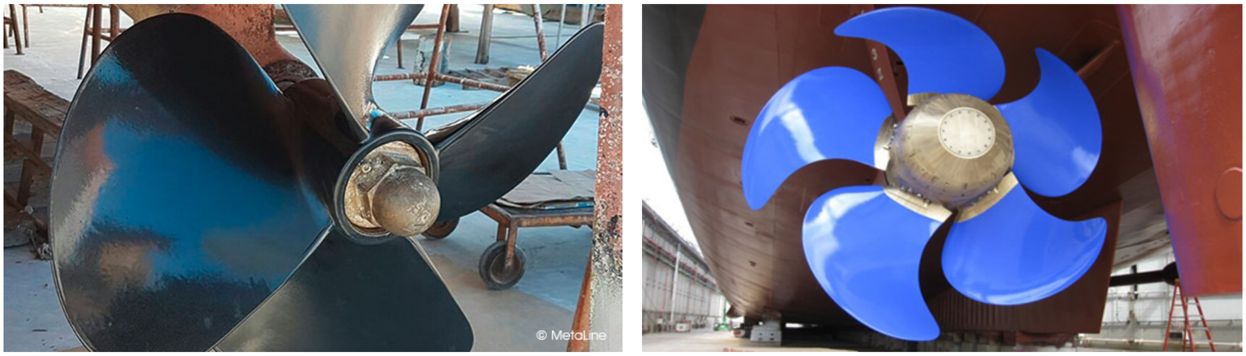


Figure 4.18: Antifouling coating application on marine type propellers [63]

Chapter 5 – Conclusions

The "fouling problem" has been extensively presented throughout this thesis. The fundamental properties of fouling organisms, the chemistry involved, as well as the various types of foulers have been presented.

Furthermore, the readers have had a chance to assess the various types of antifouling coatings used since the early stages of shipping. For a long time ships' hulls were protected by the use of arsenical or mercurial coatings and other pesticides, which were replaced by TBT compounds. All these antifouling coatings turned out to be highly toxic and remained in the marine environment for years creating the so called "aquatic pollution". So, the need for environmentally friendly coatings turned the market towards viable non-toxic biocide free technologies, known as "foul release coatings".

The different properties, standards and specifications of antifouling coatings as well as their inherent differences have also been reviewed, while taking into consideration the development of the regulatory framework around the antifouling industry. When choosing an antifouling coating, various factors have to be taken into consideration such as the temperature, the salinity, the trim of the vessel, the presence of silt and the marine environment. These factors can affect the vessel in numerous ways such as speed, fuel efficiency, emission augmentation and, generally, compromise the ship owner's investment.

The importance of antifouling coatings regarding ship resistance and performance as well as the performance of different coating systems have been highlighted and established using various real case studies carried out from various organizations within the shipping industry. What has been clearly proved through all the examples provided, is that ship resistance is directly related to the fouling condition of a vessel's hull. That same increase of frictional resistance whether it originates from bad application, poor maintenance or bad selection of antifouling coating can have detrimental effects on the fuel oil consumption and on the effective propulsion power needed, leading to increased operational costs. In addition, it has been proven through the provided examples that the operation profile of the vessel (sea temperature, salinity, days idle) can also differentiate significantly the rate of growth of marine fouling even when the comparison is made between sister vessels.

Moreover, the performance between the most widespread and long used antifouling coating types has been compared showing that, while TBT has proven to be the most effective antifouling means, new technologies show promise of reaching similar effectiveness. Theoretical models exist in order to study the fouling effects on a vessel's performance and shipowners shall take advantage of them during their decision making.

In order to have a minimum increase in the surface roughness of an operating vessel during its lifetime and between coating renewals, the most necessary steps that should take place are summarized below:

- The correct antifouling coating shall be selected according to the operational profile of the vessel.

- The hull surface shall be prepared correctly prior to the application of any coating.
- The environmental conditions (humidity, temperature, etc.) shall be suitable during the application of the coating.
- The application shall be done following the coating's specification.
- Each coating shall be allowed to dry sufficiently following the producer's recommendations.
- After application and resuming operation of the vessel, the coating condition shall be evaluated and the hull shall be treated accordingly.
- Any hull treatment shall be performed carefully without removing the coating itself.

All the above are of detrimental importance for the ship's efficiency, not only towards the potential bunker savings that will occur, as a result of a properly maintained and foul-free hull, but also towards a "greener" vessel and an "environmentally friendly" shipping industry as a whole.

Looming on the horizon are higher bunker fuel prices as well as greater demand to reduce emissions and the antifouling industry will always play a key-role towards achieving the relevant targets set by the responsible committees.

Finally, the horizon remains open for the development and/or discovery of new technologies within the anti-fouling industry, which will prove both more efficient compared to the existing technologies, as well as more environmentally friendly. The new antifouling systems include: fluoropolymers & silicones, control of biocide release, anti-adhesive agents and modification of the surface topography. As displayed, some novel technologies (ultrasonic transducers, UV light) with a completely different approach towards the fouling problem are already in place and while not relatively widespread for the time being, they might prove to be the mainstream practice in the near future.

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