

## A Review on Marine Bio-fouling and Progresses in Antifouling Coatings

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### Abstract

*Marine environment is the storehouse of all the aggressive corrosion factors along with wide variety of the marine micro- and macro organisms responsible for biofouling. Biofouling is a problem for the ship's hull, pipelines and submerged parts in seawater. For inhibiting, the fouling by marine organisms, earlier people were using plates of zinc, lead, copper etc. in wooden ship hulls, then mercury, lead, arsenic in coating as antifouling agent, and now a days organochemical compounds, copper compounds (Cu<sub>2</sub>O and its salts) and organotin compounds as the most effective antifouling agent. Due to their toxic effects and negative impact on non target marine organisms, most of them have been banned and rests are under consideration. As an alternative, nontoxic antifouling coatings and paints have been developed by modifying some physico-chemical parameters of polymers like surface energy, critical surface tension, elastic modulus, functional groups and polymer structure etc., which influences by repelling (weakening the adhesion between organism and surface) the foulant on polymer surface. Most recently antifouling agents from marine organisms like coral, red algae, bryozoans, sea grass, species of sea pansy etc and from their metabolites have been extracted. Synthetic fibers and enzymes (Alcalase, Pulpzyme, etc), which are eco-friendly; with antifouling property; membrane biofouling of (bio) sensors and its remedies have been reviewed.*

**Keywords:** Marine environment, biofouling, antifouling agent, physico-chemical parameters, Marine organisms, enzymes, (bio) sensor.

### 1. Introduction

The corrosion of metallic structures submerged in seawater and their fouling by marine organisms attached necessitate periodic cleaning and maintenance of the ships' hulls, etc. Fouling by plant and animal organisms lead to the deterioration of the organic coatings, accelerating the corrosion process and increasing the frequency of repair or material replacement, and reducing the efficiency of the operation. The adhesion of marine organisms to the hulls of ships is a problem from the date of its operation in marine environment. Marine environment is a vast and diverse ecosystem. The types and number of the native fouling organisms are distinct in different zones of the vast ocean. The temperature, salinity, clarity and micronutrients in the water control the nature and number of the foulers. Shell fouling (barnacles, mussels, bryozoans) and soft foulings (algae, slime, diatoms, bacteria and hydroids) occur in many forms, and the adhesives used by these organisms are equally varied. Fouling decreases the speed, raises the fuel consumption and lowers the efficiency. The necessity of solving this

problem in the most effective way is the development of long life antifouling products, paints or coatings. An efficient paint must prevent the attachment of fouling organisms over a prolonged period. In a soluble matrix product, toxicant leaching rate, which defines the biocidal power, can be controlled both by the content of the toxic material in the film as well as by the rate of dissolution of the binder, but efficiency of fouling elimination solely depend on toxicant concentration. The biocides for antifouling coatings should provide high efficiency, low mammalian toxicity, low impact, and it should be ecofriendly and economically preferable. The most important factors are its effectiveness in controlling fouling and its potential to meet existing and anticipated standards. Additional factors include ease of application and removal, adhesive qualities, ability to overcoat, material cost, maintenance requirements, performance underflow wear rate, and anticipated performance life. A new coating system is desirable only if it either equals or outperforms the previous state-of-the-art on many of these labels.

## 2. Biofouling

Fouling is the undesirable accumulation of the deposits on the equipment surface that reduces its utility and service life. Generally fouling is classified into four types: biological, corrosion, particulate and precipitation fouling. Microorganisms adhered to metal surfaces or embedded in a gelatinous organic matrix called biofilm, catalyze biological and corrosion type of fouling. Biofilm affects the interaction between metal surfaces and the environment not only in biodeterioration processes/ corrosion but also in material recovery / bioleaching.

Biofilm accumulation is the final result of several physical, chemical and biological process that occur sequentially, (i) Organic molecules are transported from bulk liquid to the substratum where some of them get adsorbed on the surface, (ii) free floating cells (planktons) are transported from bulk water to the surface conditioned by organic adsorption, (iii) the permanently (irreversibly) adsorbed cells start to grow by using the nutrient in the bulk environment and at the metal surface, increasing biofilm thickness and sessile (adsorbed) cell number. So many natural and industrial biofilm consists of a large fraction of adsorbed and entrapped materials such as corrosion products and debris. Immobilized cells grow, reproduce and produce extracellular polymers, provide structure to the assemblage, called Biofilm [1]. It consists of water [2] (ca. 95% of its weight) and are very adsorptive and porous. The Extracellular polymeric substances (EPS) can be considered as a set of substances secreted by the cell during metabolic activities and latter accumulated in its vicinity. EPS also referred as slime, mucilage or glycocalyx, plays a relevant role in bacterial adhesion to surfaces and are one of the main components of microbial biofilm causing biofouling and biocorrosion of industrial system [3,4]. Generally these polymers are homo- or heteropolysaccharides and in some cases they are proteins and glycoproteins. Biofilm behave as structured assemblages of microorganisms embedded in exopolymers. They are also complex communities consisting of colonies, consortia, newly arrived cells, drying cells, extra cellular products, polymers, and trapped inorganic materials. The microorganisms can attach to the surface, with growth occurring through the assimilation of the nutrients. All surfaces in aquatic environment are under the influence of fouling by the bacteria, protozoan, algae and invertebrates. The most fouling marine organisms belong to the group of crustacean organisms referred as Barnacles [5] and belong to the Cirripedia subgroup. In the adult stage they are sessile and attached to the solid surface by secretion of a cement gland on their first antenna. The Cirripedia subclass includes

four orders: Thoracia, Acrothoracia, Ascothoracia and Rhizocephala and are mostly involved in fouling. Eventually, some of the biofilm is sheared away and reentered in the solution to repeat the process of biofilm development.

Characklis [6] studied the following effects of biofilm on the interface and consequently on corrosion: (i) Influence of microbial activity and metabolites on the substratum, if the film is patchy, the influence is higher, (ii) Alternation of the passage of charged entities through the polymer matrix of the biofilm, (iii) The chelation of metal ion by the polymer matrix, and (iv) A drastic modification to the resistance to biocides and destabilization to the corrosion inhibitors.

The role of microbiota in the interfacial chemistry of metal/ metal oxide in biocorrosion is a responsible factor. It involves the physical attachment of the organisms to the solid substrate and formation of biofilm communities. The growth of bacteria within adherent biofilm, facilitate the development of structured consortia that enhance the effect of microbial metabolic activities. The microbial mode of action that initiate corrosion are- production of acidic metabolites (production of metabolites having ability to counteract the protective characteristics of an inorganic film), increasing the redox potential inducing favorable corrosion conditions, creating differential aeration cells, selectively attacking at the welded areas of the metal, facilitating the pitting initiation by microbial adhesion effects, microbial consumption of corrosion inhibitors, and microbial degradation of protecting coating on the metal surface.

## 2.1. Biofouling in Seawater

### 2.1.1. Effects of Medium

The marine environment is the storehouse of all kind of corrosive factors. Besides its 3.4 % salt content, seawater is a living medium of wide variety of organisms that range from the smallest bacteria to the largest mammals. Biofouling accumulation in marine environment involves deposition of biological species including protozoa, fungi, micro algae and finally macroscopic organisms. This macrofouling is divided [8] as soft fouling (algae, soft corals, sponges tunicates and hydroids), and hard fouling (crustose algae, barnacle, mussels, tubeworms and other organisms). A metal surface undergoes a biological and chemical change may leads to metal deterioration or metal protection after its immersion in seawater. Biofouling formation is the accumulation of biofilm, corrosion products and diverse debris. Both biological and inorganic processes take place in aqueous medium simultaneously. Corrosion and subsequent passivation are directed from the metal surface towards the solution whereas; biofouling is due to the arrival of the planktonic cells, which became sessile organisms remaining attached to the metal surface and increasing biofilm thickness by microbial growth and extracellular polymeric substances (EPS) production. Biofilm are influenced by both the substratum and the bulk liquid phase. The interactive effects between three phases–metallic substratum, biofilm, and liquid medium create concentration gradient and localized heterogeneity favorable to corrosion.

### 2.1.2. Effects of Metal

The nature of metal surface plays a vital role in microbial attachment and facilitating or hindering biofilm formation. A corrosion resistant metal such as titanium or stainless steel

presents a good substratum for microbial colonization due to homogenous oxide layers present in those metal surfaces but on a nonpassive metal surface like various copper-nickel alloys, microbial adhesion is hindered by various types of corrosion products and by the toxic effects of the cupric ions leaching from the surface. The chemistry of the liquid medium can also facilitate microbial colonization and reduces the time needed to form microbial biofilm.

### 2.1.3. Effects of Biocidal Additives

Microbial colonization can be inhibited with the help of film forming biocides. The mobile nature of the biocide can help to migrate from the interior to the film surface and to the cell membrane to destroy the microbe. Duration of the antifouling paint depends on the regular biocide migration from inside to the coating surface. Generally the migration occurs –through the porous paint film / water makes the matrix partially soluble and leaches out the biocide; -through full matrix solubilization arises due to bio-chemico-physical interactions with marine environment. These should be resistant to water leaching in the humid environment otherwise the paint formulator will incorporate initially enough biocide to compensate the loss arises due to leaching. Loss of biocides due to leaching creates problem since biocides are fundamentally toxic to the environment and risk to the surrounding ecosystem. Significant progress and toxicity minimization can be achieved [9] if (a) distribution of the biocides could be concentrated at or near the exposed surface, (b) the minimum inhibitory concentration of biocide could be sustained at an optimal level for extended period, (c) the biocides could be immobilized and released only on demand, and (d) the biocides could be shielded from any bad effects of environmental exposure during service condition.

The activity of the biocides in paints and coatings can be enhanced by the encapsulation of the biocides in a suitable matrix. Mostly the biocides release, drug release and fragrance delivery have based upon micro encapsulation: the application of a thin, uniform polymeric coating to micro particles of solids, liquids, solutions or dispersions and inclosing and release of organic molecules within an inorganic framework (carrier)[9] is also possible. The controlled release of isothiazolinone biocides from siliceous framework has been discussed by Allen *et al* [9]. Here the biocides retain their antimicrobial properties, while controlled delivery facilitates a dynamic equilibrium to maintain a minimum inhibitory concentration at the coating interface for a long service.

### 3. Antifouling Materials

An antifouling coating is paint or other coating used to interrupt the life cycle of the marine organisms (i.e. barnacles, mussels) by preventing and eliminating their settlement and growth on the hulls of the ship or any submerged article in seawater. In addition to the ship hulls, antifouling coatings can be used on any stationary structures. These materials typically contain a substance, which is toxic to the developing organism.

These are applied directly over the top of anticorrosive marine coating systems and are designed to be compatible with these materials. Generally antifoulants are not designed to protect vessels from corrosion. Antifouling coating are processed and designed taking several factors into consideration such as physical and chemical processes [7] that may occur under certain

environmental condition. Efficiency of any antifoulant is seized by the complex physico-chemical and biological events; conditions of paint film surface, seawater pollution and marine environmental factors such as temperature, salinity, pH, microorganisms and water current etc. Efficiency, duration over time and environmental compatibility requirements in antifouling products depend on the performance mechanism of the antifoulant present in coating. Navigations under strong dynamic conditions, long stops in port with eutrophic water and regions with different climate conditions, are the elements affect maritime transport economy. To meet the above challenges and to counter the aggressive factors, innovative and effective antifouling coatings are necessary.

### 3.1. Bioactive Material for Antifouling Coating

All commercial antifouling processes are based on the leaching of biocides from the surface. Most of the biocides used in past linked with metallic and organometallic origin. The most frequently used biocides were tin, copper, arsenic, mercury, lead and their compounds along with oxides of zinc, antimony, lead, and strychnine. Antifouling coatings containing a mixture of cuprous oxide and triorganotin compounds in combination with sophisticated release mechanism were considered the most efficient system. Due to their toxic nature, the development of nontoxic novel environment friendly antifouling coating is the focus of paint technology.

The four basic categories include the major marine antifouling coatings may be classified [10,11] as-

- a. Conventional, soluble matrix-type antifouling
- b. Advanced, insoluble matrix antifouling
- c. Self polishing antifouling
- d. Polishing / Ablative antifouling.

#### a. Conventional, Soluble Matrix-Type Antifouling

During the early 30s, this conventional, soluble matrix type antifouling was the mainstream coating and providing protection for 12-15 months. The relatively short life is due to the result of their low mechanical strength. The binder was mainly composed of gum rosin or resin derivatives, which confer poor mechanical properties and allow the build-up of only relative thin systems. This coating worked by the dissolution of the acidic resin in seawater, exposing the biocidal particles, which are subsequently dissolved. Release of the toxin into the water occurs at a controlled rate, which is dependent on the ratio of the soluble to the insoluble binder. The release of biocides remains constant until the paint has completely dissolved. High build soluble matrix antifouling paint, thixotropic samples<sup>12</sup> were formulated with WW rosin and Grade 10 chlorinated rubber as a binder using red cuprous oxide as the main toxicant and zinc oxide as the reinforcing toxicant and non-thixotropic samples with Grade 20 chlorinated rubber as binder keeping other concentrations same. It was observed that both the rosin: chlorinated rubber ratio and cuprous oxide content influence significantly on the antifouling behavior of the paint.

### **b. Advanced, Insoluble Matrix Antifouling**

The development of the advanced, insoluble matrix types of antifouling coating became popular in 50s due to the availability of the new polymers such as chlorinated rubbers, vinylic resins. The high mechanical strength obtained with these polymers permits the application of thicker systems with a higher loading of biocides in the polymer matrix, provides effective protection for 18-30 months in normal to severe fouling conditions. Unlike conventional antifouling coating, the binder in advanced insoluble matrix type of antifouling coating is no longer soluble in seawater. Biocides (i.e. TBT) and other soluble ingredients dissolve from the surface layers and underlying soluble ingredients, including biocides are exposed.

### **c. Self-Polishing Antifouling**

The revolutionary self-polishing antifouling coating were launched during 70s containing an organotin copolymer with high mechanical strength and allows the build up of very thick systems with an effective service period of around 5 years. The organotin is chemically bound to the acrylic backbone of the organotin copolymer and is released in contact with seawater by a combination of hydrolysis and ion exchange. The remaining backbone is then dissolved and washed away by the movement of the ship exposing a new fresh surface. By this dissolution / erosion process a constant release of biocide obtained and the surface remains smooth. The self-polishing rate of the antifouling coating complying with ship's sailing speeds, seawater temperature, salinity etc

### **d. Polishing / Ablative Antifouling**

Like the self-polishing antifouling type coating, the ablative antifouling coatings utilize a dissolution / erosion process. They contain a large proportion of seawater soluble binder combined with high performance polymeric ingredients, which are able to control the dissolution rate by a physical process. When in contact with seawater, the biocides dissolve together with the soluble binder. The ingredients controlling dissolution are then washed away in the form of micro-lumps and provide a constant polishing / ablation rate. Tin free and tin based antifouling paints are operating in this category.

## **3.2. Organotin Based Antifouling Coating**

In the early half of the 20<sup>th</sup> century, compounds of copper, mercury and arsenic were the well-known and primary antifouling agents. But due to toxic and ecological factors, mercury and arsenic used no more. At the mean time organotin compounds were evaluated as antifouling agent and widely accepted due to its non-influence to galvanic corrosion [13], wide range of its biological activity, lower mammalian toxicity than the organomercuric and arsenic compounds; and requiring lower dose of active ingredient than the copper compounds to be effective for antifouling. Mostly organotin antifouling paint belongs to the TBT group. Widely used antifouling TBT compounds are bis (tributyltin) oxide, tributyltin fluoride, organotin copolymers i.e. tributyl tin methacrylate and triphenyltin formulations. TBT can have a single active ingredient or two/more active ingredient or a combination of TBT and Cu compounds. But these TBT based antifouling coatings are responsible for some marine environmental problems due its

toxic nature. The worldwide legislature on antifouling coatings containing TBT compounds has been effective. Some countries i.e. Japan, Britain banned the use of TBT as antifouling agent and other laid some restriction towards its concentration and the release rate less than  $4\mu\text{g TBT cm}^{-2}\text{ d}^{-1}$  in USA, New Zealand and Canada, and  $5\mu\text{g TBT cm}^{-2}\text{ d}^{-1}$  in Australia.

### 3.3. Copper Based Marine Antifoulants

Marine fouling is a long-standing problem for vessels that spend part or all of their time in salt water. The earliest method of repelling marine organisms consisted of attaching plates of zinc, copper, or leads to the wooden ship hulls. Today's antifouling coatings incorporate copper or copper salts into a paint coating. Copper oxide is recognized as the best broad-spectrum antifouling biocide available worldwide. Other products using tin, mercury and arsenic biocide compounds are not environmentally sound. Soluble antifoulants includes cuprous oxide into a water-soluble matrix. Release of the toxin into the water occurs at a controlled rate, which is dependent on the ratio of the soluble to insoluble binder. Other antifoulants rely on the diffusion or leaching of the cuprous oxide biocide from the coating. These materials form an oxide layer, which must be mechanically cleaned every 1 to 2 year to reactivate the coating. Similar to the leaching antifoulants, the new free association antifoulants, which use metallic copper dust as a freely mixed component of the coating. These coatings must also be reactivated at least every other year in order to restore their antifouling property. The use of copper and copper salt containing antifoulant is recommended on a trial basis for control of zebra mussels on steel and concrete components that are critical to facilitate operation and are susceptible to infestation.

Copper ablative Antifouling coatings are generally rosin filled, acrylic resin systems [14] that contain 40-55% cuprous oxide and 20% Zn. These have been used in the US Navy since 1980s. Many paint company have marketed the coatings containing organic booster biocides or co-biocides. Research in the area of environmentally friendly biocides has led to the development of new organic booster or co-biocides. Addition of co-biocides will reduce the amount of copper needed to control fouling and are degradable in marine environment. Virtually all copper self-polishing coatings are used in combination with co-biocide technology in order to achieve the desired AF performance. Yonehara *et al* [15] presented the release rate of the copper oxide, the biocide from the paints formulated with zinc acrylate copolymers. They developed a series of novel acrylic copolymers, which contains zinc atom in the form of polymeric salt, and undergo ion exchange reaction with the sodium ions in seawater. As the ion exchange reaction proceeds, the polymers become soluble and leach out by flow of seawater. The dissolved zinc doesn't act as a biocide [16] but the presence of biocidal ingredient, such as copper acts. The erosion rate (self polishing rate) of the paint samples were closely related to the leaching of the polymers [17] i.e. to control the erosion rate of the paints by controlling the leaching out of the polymers, depends upon the molecular weight, content of zinc acrylate and hydrophilicity of the co-monomer.

According to The Pesticide Act 1990, apart from copper and organotin compounds, the biocides that have been registered in UK for use in antifouling coating are given in the **Table 1**.

**Table 1. Biocides Registered for Antifouling Coating in the UK [18]**Carbamates

Manganese ethylene-1, 2-bis (dithiocarbamate)	(Maneb)
Zinc ethyle-1, 2-bis (dithiocarbamate)	(Zineb)
Bis (dimethylthiocarbamyl) disulfide	(Thiram)
Zinc bis (dimethylthiocarbamate)	(Ziram)

Others

Dichlofluanid

2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine

2-(Thiocyanomethylthio) benzothiazole

2,3,5,6-tetrachloro-4- (methyl sulphonyl) pyridine

1-(3-chloroally)-3,5,7-triaza-1-azoniaadamantane chloride

Dichlorophenyl dimethylurea

Fluorinated zinc pyrithione

2,4,5,6-Tetrachloro isophthalonitrile.

4,5-dichloro-2-N-octyl-4-isothiazolin-3-one

Methyl bis-thiocyanate

Parachloromethacresol

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**3.4. Bactericides and Bactericidal Polymeric Coating**

Bactericides are the chemicals that kill or control microorganisms by inhibiting their growth and reproductive cycles. Wide range of different biocides such as mercury based biocides, tin based biocides, PCPs, and PCBs etc are mostly effective towards microorganisms but are almost banned for their toxic and ecological effects. Many of the chemicals are the surface-active cationic materials and must be used with care relative to the compatibility with anionic chemicals, such as scale inhibitors. The most common surface-active bactericides [19] are dimethyl coco amine quarternised with methyl chloride; coco diamine acetate, benzoate or adipate; 3-alkoxy-2-hydroxy-n-propyl trimethylammonium chloride; and dimethyl coco amine quarternized with 2,2-dichloro-diethyl ether. The most common nonsurface active bactericides are formaldehyde, glutaraldehyde, acrolien, chlorine dioxide (ClO<sub>2</sub>), chlorine, sodium hypochlorite (NaClO), Calcium hypochlorite (Ca (ClO)<sub>2</sub>). The organosulphur compounds [20] such as sodium dimethyl dithiocarbamate, methylene bis thiocyanate, bis trichloromethylsulfone and tetrahydro-3, 5-dimethyl-2H-1, 3,5-thiadiazine-2-thione dibromonitrile propionamide; isothiazolinone [21]-CIT (5-Chloro-2-methyl-4-isothiazolin-3-one), MIT (2-methyl-4-isothiazolin-3-one), OIT (2-octyl-4-isothiazolin-3-one) and DCOIT (4,5-Dichloro-2-octyl-4-isothiazolin-3-one); and Benzothiazol-2-ylthiomethylthiocyanate; 2,2-dibromo-3-nitropropionamide (DBNPA), are the most effective biocides. Biocides can be oxidizing or nonoxidising toxicants [21] and have been used in the cooling water system to prevent biofouling as given in



Table-2

Biocides	Effectiveness			Properties
	Bacteria	Fungi	Algae	
Chlorine	E	S	E	Oxidizing, reacts with –NH group, effective at neutral pH, loses effectiveness at high pH use concentration: 0.1- 0.2mg/L, free radical.
Chlorine dioxide	E	G	G	Oxidizing, pH insensitive, can be used in presence of –NH <sub>2</sub> groups, Use concentration: 0.1-1mg / L, Intermittent free radical.
Bromine	E	S	E	Oxidizing, substitute for Cl <sub>2</sub> and ClO <sub>2</sub> , effective over broad pH range, use concentration: 0.05-0.1 mg / L , intermittent free radical.
Organobromide	E	NA	S	Nonoxidising pH range 6-8.5, use concentration: 0.5-24 mg / L
Methylene bis thiocyanate	E	S	S	Non –oxidizing, hydrolyze above pH 8, use Concentration : 1.58mg/L.
Isothiazolinone	E	G	E	Non-oxidizing pH insensitive, deactivated by –HS and –NH <sub>2</sub> groups, use concentration, 0.9-13 mg/L.
Quaternary ammonium	E	G	E	Nonoxidising, tendency to foam, surface active, ineffective salt in highly oil or organic fouled systems, use concentration: 8-35 mg/L
Glutaraldehyde	E	E	E	Nonoxidising, deactivated by –NH <sub>2</sub> groups, effective over broad pH range, use concentration: 10-75 mg/L

**E. Excellent; G. Good; S. Slight; NA. Not Applicable.**

Bactericidal coating is a polymeric coating whose main purpose is to produce an antimicrobial-promoting surface through the use of a bactericidal preparation contained within the coating film and protects from the corrosive action of the environment [22]. Compositions for producing coating with bactericidal properties containing substances with elements such as copper,

mercury, lead or arsenic exist, but are too toxic to be used in medicine, in the food industry, in water purification, storage equipments, and in the agriculture [23].

Ulberg *et al* [24] suggested that polymeric coating possessing bactericidal properties might be used in the above fields. But selecting antimicrobial agents and polymeric components possessing bactericidal activity relative to microorganisms of the type is the main problem along with the effect of the mechanism of coating formation i.e. electrophoresis, diffusiohoresis, electrodiffusiohoresis etc as far as the physicochemical properties of the coatings are concerned. The polymers used in coating are polystyrene, polyurethane, poly (butadiene/styrene) lattices, epoxy oligomer, polycapraamides, polyethylene, and mixture of these polymers. The antimicrobial agents were N, N-dimethyl- N, N, N', N'-tetramethyldiamine (I), hexamethylene-1, 6-bis (dimethylcarbodesoxyammonium) dichloride (II), decamethylene-1, 10-bis (dimethylcarbomethoxymethylammonium) dichloride (III) and organotin compound  $(C_2H_5)_3Sn(OH)$  (IV). Diquaternary ammonium compounds are efficient over other antimicrobial agents in the absence of any toxicity. The bacterial action of coatings has been studied with respect to 13 strains of microorganisms, including *E. coli* St. 316,356; *Pseudomonas aeruginosa* St. 136, 137; *Micrococcus lysodeixiticus* St. 440, *Sarcina* St. 116, 118 and others. The activity of the individual coatings was determined by the disc methods estimated by measurement of the diameter of the inhibition zone for microorganism growth. The bacterial selectivity of the diquaternary ammonium compounds towards various bacterial strains is determined by the specific action of these compounds on the biochemical processes occurring in the cell. According to the existing concepts<sup>25</sup>, the death of a microbial cell arises from the activation of the specific enzymes by the antimicrobial agents and form deterioration in the permeability of the cell membrane.

Antimicrobial coatings must have a homogenous structure, which can be generated by simultaneous deposition of polymer and antimicrobial agents dispersions on to a substrate and carried out in an alternating electrical field by the electrodiffusiohoresis method. The introduction of the water-soluble diquaternary ammonium compounds I, II and III into the deposit was achieved through their adsorption on to the surface of the latex and oligomer particles. The service life of a given coating is extended by increasing the concentration of an antimicrobial agent in the film assuming that the latter leaches into solution at a constant rate. The coating prepared from the solution containing antimicrobial agents whose concentration corresponds to the critical micelle concentration (CMC), i.e. the antimicrobial agents are introduced into a given coating in a micellar state. The introduction of these substances is achieved via the electrophoretic or electrodiffusiohoresis deposition of the micelles themselves. The enhanced bonding of the molecules of the antimicrobial agents reduces the rate of extraction of these agents from the coating and hence increases the service life of later.

### 3.5. Nonbiocidal Concept for Antifouling

New polymers and resin systems and more restrictive legislation on air or water quality at the local, national, and international level have led to the development of several emerging coating technology. It involves a surface with no inherent power to interact with other materials, especially biological polymers used by marine organisms to bind themselves to objects in the sea. The most promising non-biocidal concept described to date for preventing the attachment of fouling organism is the use of low surface energy surfaces. The relationship between surface

energy and adhesion of fouling organisms has been intensively studied [26,27]. Fletcher *et al* [28] showed that a reduction in the critical surface tension produced a corresponding increase in the size of the basal attachment systems of selected algal sporelings. The disc like attachment base produced on the high-energy surfaces was strongly adherent and difficult to remove by gentle brushing, while the more filamentous attachment base produced on the low energy surface was more loosely adhered and quite easily detached. The two main types of low energy non-biocidal materials under consideration are fluoropolymers and silicone polymers. Antifouling coatings have been made from polytetrafluoroethylene (PTFE) and related fluoropolymers, though these surfaces do accumulate fouling, the attachment is weak [29]. Nontoxic silicone easy release coatings are designed to minimize the strength of adhesion between the fouling organism and the slick silicone surface. The coating may allow fouling to settle, but under flow i.e. motion of ship through the water or its own weight, the fouling will release (hull will self clean). Silicone coatings contain no biocide and are effective through a nontoxic mechanism.

Conventional coatings suffer from lack of adhesion to the substrate and lack of mechanical strength, which is overcome by the use of two-coat system: A base coating acting as adhesive, providing mechanical strength and reacts with the top coat i.e. polybutadiene, polyurethane; and a top coat acting i.e. silicone, hydrocarbon as a non toxic and non adhesive surface eliminating the adhesion of marine microorganisms. Generally used two coat systems [30] are polyurethane-silicone-hydrocarbon coating, acrylate-silicone coating, 1,2-polybutadiene-silicone coating, silicone-urethane coatings, urethane- hydrocarbon coating, silicon oil-filled urethane coating etc.

### 3.5.1. Biofouling and Critical Surface Tension

Brandy [31-33] discussed the requirements for the structure and dynamics of the polymers, which refuse or resist strong bond to other materials. The polymer surface property which has been correlated with bioadhesion / biofouling is the critical surface tension ( $\gamma_c$ ). A generalized relationship between the  $\gamma_c$  of the polymer surface and the relative amount of bioadhesion is known as Baier Curve [34]. Its reproducibility has been tested in variety of the marine exposure studies and in biomedical applications like vascular prostheses and dental implants. It only shows the relative adhesion as a function of the critical surface tension of one adherend while both surfaces and interfacial energy at their interface must be considered. The Good-Girifalco equation, Eq. (1) states that the interfacial energy  $\gamma_{sw}$  between a surface and water is equal to the sum of the critical surface tensions of each surface reduced by the geometric mean of these values times an interfacial constant  $\Phi$ .

$$\gamma_{sw} = \gamma_s + \gamma_w - 2 \Phi_{sw} (\gamma_s \gamma_w)^{1/2} \dots\dots\dots(1)$$

- $\Phi = 1$ , if the intermolecular forces across the interface are of same type as they are within the liquid and solid;
- $\Phi < 1$ , if these forces are different;
- $\Phi > 1$ , if an interaction such as solubility or interdiffusion occurs.

The interfacial energy may be minimized by matching the critical surface tensions of polymer and adherend, and by reducing the interactions of the biological adhesive with the surface and with water.

### 3.5.2. Elastic Modulus and Bioadhesion

Brandy studied the influence of the bulk property of the polymer like elastic modulus to bioadhesion. The minimum bioadhesion coincides with the lowest value of elastic modulus. He proposed the low values for bioadhesion on poly (dimethylsiloxane), the most elastic polymer tested, are a consequence of the ability of the adhesive to slip on the polymer surface. Again he interpreted the Baier Curve from the viewpoint of elastic modulus is that; bioadhesion correlates directly with elastic modulus. Low bioadhesion coincides with low elastic modulus because the mobility of the low modulus surface allows the adhesive to slip during interfacial failure, reducing the energy input needed to achieve failure.

### 3.5.3. Polymer Structure and Bioadhesion

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Surface energy of a polymer is related to the reactive groups i.e. functional groups [35] at the polymer surface. Generally the poly (ethylene) and poly (propylene) have the lowest surface energies and when hydrogen is replaced by fluorine the surface energy is reduced further and surface energy decreases [36] in the order  $-\text{CH}_2- > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_3$ . The fluorinated polymers and the polysiloxane polymers possess a critical surface tension lower than most other polymers while they differ substantially in their resistance to bioadhesion with respect to their structure and property. Substituents in a polymer backbone greatly influence its property. More bulkier the substituents, more the activation energy required for rotation i.e. the activation energy for rotation about a backbone bond is 43% greater in poly (tetrafluoroethylene) than in poly (ethylene). Poly (siloxanes) substituted with fluorine might seem to be attractive for surfaces with low bioadhesion than the poly (siloxane) itself. To attach a fluorocarbon group with low surface energy, to a polysiloxane backbone with highest mobility is the way of introduction of the most active group to the surface of the polymer. Poly (nonafluorohexylmethylsiloxane) and poly (trifluoropropylmethylsiloxane) are the commercial fluorosilicones used as antifouling coating.

#### The Factors Highly Desirable in Polymer Surface to Resist Adhesion Includes:

- A flexible, linear backbone, which introduces no undesirable interactions,
- A sufficient number of surface-active groups, which are free to move to the surface to impart a surface energy in a desirable range,
- Low elastic modulus,
- High molecular mobility in the backbone and surface-active side chain,
- A smooth molecular surface to avoid infiltration of a biological adhesive leading to mechanical interlinking, and
- Physically and chemically stable for a long period in marine environment.

### 3.6. Synthetic Fibers as Environment-Friendly Antifouling Coating

All surfaces that are submerged in water are immediately subjected to various type of fouling. Ever since humans began to sail, these floral and faunal growth have hindered speed and maneuverability, and many methods have been called on to prevent such fouling. Solutions using environmentally hazardous substances have predominated for the past century, but their negative impact on the environment has encouraged the development of the alternative antifouling agent. One of these agents is SealCoat; a system consists of an epoxy surface, on top of which a pillow of synthetic fibers stands perpendicular to the surface whose practical testing on vessels in Danish waters began in spring 1999. The first stage of hard fouling starts with larvae colonizing on the surface. By nature, larvae will only colonize on a firm, stable surface. Since SealCoat consists of a thin layer of synthetic fibers, the larvae will find colonizing on the surface extremely difficult. In other words SealCoat works mechanically not chemically. The colonizing larvae will eventually drop off, as they become too big and loose their grip on the movable fiber surface.

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### 3.7. Fouling Control by Marine Organisms [37,38]

Many marine organisms are capable of staying free from fouling of other marine organisms. For some cases it can be explained by the production of the secondary metabolites, which prevent the organisms from being fouled. Extracts of these secondary metabolites and from their tissues may form the basis for the development of new biocides for antifouling coatings. The basic principle [37] involved in these works is extraction of active components from marine organisms and the extract is tested in selected bioassays. Then the bioactive extracts are subjected to chromatographic separation and the fractions derived are evaluated in the bioassays. By repeated column chromatography monitored by the biological assays, active compounds are purified and finally identified by means of selected analytical principles: nuclear magnetic resonance, ultraviolet analysis, infrared analysis, mass spectrometry etc. Going through this procedure, it has been possible to identify several chemical families, which may form the basis for the development of new bioactive material for antifouling coatings.

John Castlow and colleague at Duke University marine laboratory in North Carolina have isolated the natural antifouling agents such as diterpenoid lipids from the octacorals; lipids-pukalide and epoyukalide from the outer layer of the fleshy tissues of whip coral *Leptogorgia virgulata*; and a group of terpene compounds named as renillafoulins from a species of sea pansy *Renilla reniformis*. A crude extract of *Zostera marina*, a species of eelgrass, prevented settlement of some marine bacteria, algae, barnacles and tubeworms according to the study of Richard Zimmerman and colleagues at the Hupkins Marine Station in 1990s. This ingredient was an aromatic compound, zosteric acid. Wataru Miki isolated a number of active biofoulant called as tribrogramine (TBG), from the bryozoans *Zoobotryon pellucidum* at the Biotechnology Institute in Tokyo. TBG is only one-tenth as toxic as TBT, but is six to eight times potent in order to inhibit the settlement of larvae. A family of bromine containing furanones extracted from a red alga, *Delisea pulchra* by Peter Steinberg and colleagues in Sydney, which is used as antifouling agent to reduce the settlement of barnacles and to curb development of the fertilized eggs of the alga *Ulva*.

### 3.8. Enzyme as Antifouling Agent

The micro and macro organisms are involved in the fouling through a biological mechanism i.e. a form of glue to settle at ship hull. Barnacle larvae secrete a protein (glue) to settle as cypris larvae on a surface and can be hydrolyzed by enzymes. Similarly the polysaccharides secreted from the bacteria, give rise to slime layer, and hydrolyzed by enzymes. Enzymes are biological molecules (proteins) consist of amino acids and acts as a catalyst to hydrolyze or synthesize the substrate and can be degraded to amino acids.

Schneider *et al* [39] tested the enzymes, Alcalase, SP234 and SP 249 to prohibit the settlement of the cyprid barnacle larvae. They used 7 different binders (modified rosin dry matter, hydrogenated rosin dry matter, polyvinyl acetate emulsion dry matter, polyvinyl ether dry matter, polyvinyl chloride copolymer dry matter, Acrylic resin copolymer dry matter, and silicon dry matter) with enzymes Alcalase, SP234 and SP249 in the concentration ranges 0.25% 0.5%, 1.0% and 2.0% by weight. It was observed that the proteases were active at a dose as low as 50- $\mu\text{g/ml}$  compared to the control in seawater with the natural binders like modified rosin and hydrated rosin. The commercially available marine paints [40] BioB (solvent based) and BioS (water based) were tested by incorporating the enzymes: Alcalase (Alcalase 2.5 L type DX), AMG (AMG300L), Pulpzyme (Pulpzyme HC) and their combinations (Alcalase+AMG, Pulpzyme+Alcalase, Alcalase+AMG+Pulpzyme), in the concentration ranges 0.25%, 0.5%, 1.0% and 2.0% by weight. It is observed that the (BioB+ Alcalase + AMG) and (BioS+ Alcalase +AMG) coating resulted in complete inhibition of the barnacles, algae in compare to the coatings BioB and BioS only whose efficiency are compared with the commercially antifouling products containing Cu and the biocides Irgarol and Diuron which inhibits completely the attachment of barnacles.

### 3.9. Antifoulants for Prevention of Membrane Biofouling of Implanted (Bio) Sensor

Continuous monitoring of medical parameters, biological species, and industrial processes is gaining the ground. A major cause of concern, particularly in environmental, clinical or bioreactor monitoring, is the formation of protein layers or the adhesion of microorganisms and cells [41, 42]. Sensor biofouling makes long term monitoring difficult and require probe replacement. Sensor monitoring is common to every monitoring technique that operates in situ i.e. electrochemical, optical, electrical and thermal etc. Currently employed techniques to prevent or minimize membrane biofouling of implanted (bio) sensor are-novel polymeric materials and coatings [41,43] i.e. latex based, biodegradable, nitrogen monoxide releasing, tyrosine derivatives, star polymers, hydrogel overlays, stronger chitins, Nafions, etc.; anticoagulant heparin coating; phospholipid based biomimicry; physicochemical surface modifications (irradiation, plasma, corona, texturing, ozonisation, silanization, photocoupling, etc.); surfactant modified, natural and drug derived membranes; diamond like carbon coatings; and flow based systems combined with the *in vivo* sensors. Antifouling protection has been involved simple agitation of the sensor, polymer membranes containing biocides [44], piezoelectric actuators [45],  $\text{Cl}_2$  or biocide releasing mechanisms [46], and enzyme coatings. Antifouling polymers containing phosphorylcholine (PC) substituted methacrylate units have been prepared by copolymerisation with dodecyl methacrylate and used to coat luminescent oxygen sensors [47]. The novel biofouling resistant optosensors are superior to the commercial available oxygen

electrode and shown to response faster than the electrochemical devices for large oxygen concentration changes. The biomimetic coatings will be particularly useful for drift free long-term operation of environmental optosensor and *in vivo* fiber optic oxygen analyzers.

#### 4. Conclusion

Prevention of fouling by incorporation of biocides, antibacterial and antifungal agents into the polymeric matrix of paints and coatings doesn't impart a long-term protection to the biofouling problems of marine and naval structures. Biocidal efficiency of these antifouling paints and coatings is soon exhausted because of diffusion of biocides from coatings during the course of its interaction with the incoming fouling organisms. Further release of some hazardous biocides into the environment creates serious threat to the ecosystem. Antifouling agents derived from sea organisms may prove a better alternative to the present challenges. Also there is a need of development of nontoxic self-generating antibacterial coatings, which may prove its long life performance without loss in antifouling properties.

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