CHAPTER 1

GENERAL INTRODUCTION
Growth of marine organisms and plants on man-made structure is termed as biofouling. However, this phenomenon in marine environment is a sequential process, wherein it starts at microlevel and ends at macrolevel fouling. The microlevel fouling begins immediately after the immersion of objects into the seawater. First, organic macromolecules from seawater get adsorbed on to the surfaces, followed by bacteria, protozoans and diatoms, thereby constituting the slime film (Zobell, 1939, 1943, Daniel, 1955; Baier, 1972; Corpe, 1978; Loeb and Neihof, 1975; Baier, 1984; Mitchell and Kirchman, 1984). This is termed as microfouling. Thereafter, larvae of sedentary organisms invade onto the surface and start growing. This is called as macrofouling.

The adverse effects of fouling to the marine industries are well known. This was first noticed on the ship hull, when man started sailing in the sea. Micro as well as the macrofouling on ship hull cause increased frictional drag and enhance fuel consumption (Haderlie, 1984). It has been reported that the frictional resistance increases by 1/4% per day in temperate waters, whereas, it increases by 1/2% in tropical waters (Anon, 1952). Fouling of the condenser tubes of power plants affects the heat transfer efficiency (Haderlie, 1984). Fouling of sonar domes and naval acoustic devices results in their malfunctioning (Ganti, 1987). In addition, a number of marine instruments such as wave rider buoy, data buoy, current meter, tide gauze and the sensors which are used for monitoring of environmental parameters are also found to be affected by the fouling settlement (Padilla and Moraoka, 1972). Offshore oil platforms and Ocean Thermal Energy Conversion (OTEC) plants are also adversely affected in various ways by the
fouling growth (Corpe, 1979; Mitchell and Benson, 1980). Fouling increases the effective diameter of the platform legs leading to increased hydrodynamic loading (Freeman, 1978; Heaf, 1981).

In addition to the above effects, fouling is also known to cause destruction of metallic surfaces by accelerating the corrosion rate (Edyvean et al., 1988). Uneven fouling settlement results in the heterogeneity over the metal surface, thereby leading to formation of anodic and cathodic sites (LaQue, 1975). Secondly, the calcareous growth may cause physical damage to the protective paint film by penetrating into the film and exposing the bare metal to marine environment leading to corrosion. It has also been reported that a thick mat of calcareous growth may protect metal against corrosion by virtue of acting as a physical barrier for the entry of oxygen at the metal surface (LaQue, 1975). On the other hand, algal growth can enhance the corrosion rate by supplying oxygen to the metal surface through photosynthetic action. Besides these, some of the metabolites, particularly organic and inorganic acids produced by algae and microfoulers, result in higher metallic corrosion (Miller, 1970; Hardy, 1981; Moss, 1981; Dexter, 1986).

Fouling is considered as a site specific phenomenon and hence the nature and extent of fouling varies from place to place (Anon, 1952). This is thought to be mainly due to variation of different environmental factors which govern the fouling assemblage under a particular set of environmental parameters. It has been reported that fouling activity is more intense in tropical environment than in temperate. This
variation was attributed to the less temperature variations in tropical waters than that in the temperate waters (Anon, 1952). A wide range of fluctuation in temperature restricts the breeding of fouling organisms. As far as Indian water is concerned, some foulers have been reported to be breeding almost throughout the year (Ganapati et al., 1958; Nair, 1967; Karande, 1968; Sawant, 1985; Anil and Wagh, 1988).

It has also been observed that the extent and nature of fouling vary with time, depth and distance from the shore (Bascon et al., 1976; Wolfson et al., 1979; Hardy, 1981; Kinsbury, 1981; Forteath et al., 1982). In temperate waters, maximum fouling intensity was observed at 30 m, below which it decreases drastically (Anon, 1952). Similarly, in tropical waters, especially at Bombay High area in the Arabian sea, intense fouling was observed at 22 m depth, below which it decreased drastically (Venugopalan, 1987).

Seasonal as well as annual variations in the extent and nature of fouling have been reported in the literature. Seasonal variations in the fouling arise from the inability of any given species to reproduce except under a limited range of conditions (Anon, 1952). On the other hand, the cause of the annual variability of fouling is quite unknown.

There are numerous factors which determine the extent and nature of fouling at a given locality. The factors which determine the larval recruitment can be divided into two main groups. The first group includes the factors which determine the number of larvae coming into contact with the exposed surface, and the second group includes the
factors which control the attachment and growth of these larvae on to the surface. Some of the first group factors include movement of water, light penetration, water temperature, salinity, dissolved gases, nutrients, abundance of larvae etc., whereas the second group factors include type, texture, orientation and colour of the surfaces (Anon, 1952). The extent and nature of fouling also depends on the surface energy or hydrophobicity or degree of wettability of the given surface. It has been observed that paraffin, petrolatum and various waxes or greasy surfaces do not get fouled rapidly. The non-fouling action of these surfaces was attributed to the nonwettable nature or low surface energy. Subsequently, detailed studies on fouling of surfaces with low surface energy revealed that surfaces with low surface energies fouled less than the surfaces with high energies (Lindner, 1994). Some of these materials include coatings such as PTEF, silicon impregnated sulphur etc.

Exfoliation of surfaces has been found to affect fouling process. Corrosion and subsequent spalling of corrosion products from metal surface is considered as one of the exfoliation processes. In addition, numerous paints have been identified as exfoliating type. Thus, fouling organisms which attach on to these surfaces will be sloughed off because of the physical disintegration of the surface (Anon, 1952).

A vast range of methods has been suggested for controlling fouling process. The choice of preventive methods depends on the site and/or the structure to be protected. These methods can be classified as below.
1) Physical method

2) Electrolytical method

3) Ultrasonic and radiation method

4) Biological method

5) Chemical method

Physical method of combating fouling includes different techniques such as manual cleaning, hydraulic, compressed air, waterjets, sand blasting, high velocity ice particles etc. (Partridge 1981; Bain, 1981; Fisher et al., 1981; Fishcher et al., 1984).

A considerable amount of work could be done by hand tools. These include the divers knife, wire brushes, scrappers and chipping hammers. They offer virtually no hazard to divers. They are usually light in weight and small in size so they do not inhibit any difficulty to access to joints and crevice areas. This method is best suited for cleaning fixed offshore structures (Wilkens, 1981).

There are two types of hydraulically powered equipments viz., rotary brushes and rotary chippers. Rotary brushes do not damage the weld, and provide high cleaning standards. Rotary clipper which is comparatively a new device, provides only a lesser cleaning rate.
Hydraulically powered equipment does not need any physical effort from the operator and is less hazardous.

The compressed air needle gun has small chisel point "needles", which are impacted on the work surface in rapid succession. This tool cleans the surface well and does not pose problem for photographic observation. However, this method has some serious drawbacks. It is limited to shallow depths up to 30 m. Its performance drops off rapidly with increasing back pressure caused by the increasing depths. As regards to water jet, it is the most suitable technique for the underwater cleaning especially the soft growth. However, corrosion products and hard shelled growth are very difficult to remove when they are well bonded to the metal surface. In such cases addition of abrasives to water jet, use of cavitating water jets and use of much higher jet pressure proved to be more effective. However, the drawbacks of the use of abrasives in water jet include damage to the surface beneath the fouling growth, small fatigue cracks in the structure and the difficulty in supplying abrasives to the working site at greater depths.

In the cavitation jet, the growth of vapour within a water jet is stimulated using an appropriate nozzle design. With proper adjustment of nozzle stand from the surface, the vapour cavities grow and then collapse in the high pressure stagnation region where they get impacts on the solid surface. Extremely high local stresses can be produced by application of pressure due to the collapsing of vapour cavities. This method appears to be fast and efficient, but it has some drawbacks. The nozzle stand distance must be closely controlled and this can make the
operation difficult. It has been found that the performance of a cavitation jet reduces with increasing depth.

High pressure water jet can be used for fairly extensive cleaning programs. A typical machine may have a 200 bhp prime mover with an output of around 14000 psi (9820 kg/cm²). Though expensive, this method can be used for removing soft fouling growth. The major drawback in this method is that the water pressure is so powerful that it can be fatal to the divers and also produces high noise, which may have an effect on the eardrums of the divers.

Dry sand blasting is used for cleaning ship's hull in dry dock. This method gives a well cleaned surface and is relatively fast (7-8 m²/hr). However, this method is not widely used because of certain practical and economical reasons. It generates large amount of dust which creates bad working condition and poses danger to rubbing parts of ship as well as the dock machinery. However, the problem of dust is prevented in the wet sand blasting technique, where the machine is fed with sand and water simultaneously. The productivity of this method is 20% less than the dry sand-blasting. Bombarding of high velocity ice particles also works on the same principle as sand blasting. However, this does not cause surface pitting and hence has an advantage over sand blasting.

Electrical method includes placement of metal bars close to the structure to be cleaned for fouling. The metal bars are to be made as anodes and the structure as cathode in an electric circuit. When the current is impressed, large amount of hydrogen is liberated from the surface
under the corrosion products, breaking up rust and removing it from the surface. Thus, the fouling organisms along with the corrosion products will be removed. In another electrical method, the fouling can be prevented by generating electrolytic chlorine. In this method, platinum plate is made as anode and stainless steel as cathode. This electrolytic cells are mounted at close proximity to the surface to be protected from fouling in seawater. When the current is impressed, hypochlorite is generated, which prevents settlement of fouling larvae.

Recently ultrasonic and ultraviolet radiation methods have also been used for controlling fouling settlement (Plotner, 1968; Aras, 1980). Ultraviolet radiations interfere with the cellular components, causing the rupture of the cells.

The biological method of prevention of fouling includes release of marine organisms which feed on the sedentary organisms and algae on the surface to be cleaned. These organisms include crabs, star fishes, gastropods, some fishes etc. (Wahl, 1989). If these organisms are maintained in the vicinity of the structures to be protected, then, they can feed upon the fouling organisms resulting in the prevention of fouling. Secondly, bacterial film and soft bodied fouling organisms especially sponges, ascidians and algae once settled on the surface, will not allow the other forms to settle over them (Paul et. al., 1987; Porter and Targett, 1988; Maki et al., 1988 a, b; 1990). In view of this, if the underwater structure is allowed to be settled with these forms, then the hard growth can be controlled. Some oil companies have attempted biological control of fouling growth, but attained very limited success.
This type of antifouling method has advantages over others, as it is environmentally safe.

Besides all the methods described here, chemical method appears to be more effective in controlling fouling settlement, therefore it is used extensively. The method basically includes application of toxins or biocides to the marine fouling organisms. Application of biocides can be achieved in two ways. It can be added either directly into the environment (injectable biocides) or can be applied in the form of paint onto the surface to be protected from fouling.

Injectable biocides are advantageously used in places such as pipes of heat exchangers systems, flowing seawater systems etc. The most widely used biocide is hypochlorous acid. Other biocides include, aeroline, soluble copper salts, bromine, iodine, bromine chloride, ozone, chlorine dioxide and various trialkyl organometallic tin compounds (Fisher et al., 1981; Fishcher et al., 1984). Chlorine solution is very effective in controlling fouling inside pipes and conduits, which supplies seawater on board the ship or for cooling purposes in condensers of coastal installations. It has been demonstrated that a concentration of 10 parts per million in seawater is sufficient to kill any organisms, except sea anemones and mussels exposed for one hour per day. Residual chlorin concentration as small as 0.25 ppm was reported to be effective in preventing the fouling growth (Anon, 1952).

Antifouling paints generally contain copper, mercury or arsenic compounds in various combinations. The action of these materials
depends on the toxicity of their ions and its solubility in seawater which in turn prevents fouling. It is the toxicity of these materials which acts as poison to the organisms and either repel their larvae at the time of attachment or kill them before they can secure footing permanently.

Use of copper as antifoulant on boats dates back to 1763. The first authentic record of a patent issued for the inclusion of a toxin in a paint to prevent fouling is in 16th century and since then many patents have been filed for antifouling formulations (Anon, 1952). During 18th century some of the paint formulations worked well, but failed to last for long exposure. This problem was solved to some extent in 19th century by the introduction of resins which can control the leaching rate of the toxins from the paint and can last longer (Anon, 1952). Among the toxins such as copper, mercury and silver, both copper and mercury proved to be very effective in preventing fouling settlement. Silver has not been extensively tested probably due to its high cost. There are contradictory reports on the ratings of the toxicity of copper and mercury, however, in general these two metals and their salts have consistently given good results in antifouling paints. In addition to the above compounds, salts of zinc, iron, arsenic and lead have been reported to be toxic to marine organisms or to their larvae (Anon, 1952). The concentration at which they are lethal varies with respect to the metal and the organisms. Zinc was found to be 1/5th as toxic as copper or mercury and the rest were even less toxic than zinc. The probable reason behind this could be that the metallic lead when exposed to seawater gets deposited with a very insoluble compound on its surface, thereby not allowing the bare metal to come in contact with the fouling organisms.
As regards arsenic, there are contradictory reports about its action on fouling organisms. The investigations carried out by many investigators on the effects of these metallic toxins on the fouling organisms did not clearly show the synergistic effect.

Besides toxins of heavy metals and other inorganic compounds, organic compounds were also investigated for their antifouling activity. Till date 91 organic compounds were reported to be studied for toxicity (Anon, 1952). Though most of the organic compounds were found to be toxic to fouling organisms, many of them could not give satisfactory results in paint coatings. They were found to be specific in their toxic action to certain organisms rather than general toxicity showed by the heavy metals.

The effectiveness of toxins is found to be directly related to the leaching rate of the toxic ingredient from the paint film. For instance, the effectiveness of toxins such as metallic copper and cuprous oxide when incorporated into the antifouling paints was found to be optimum at the leaching rate of 10 µg/cm²/day (Banfield, 1980). Similarly, Barnes (1948) reported that about 2 µg/cm²/day leaching rate of mercury is adequate to prevent fouling. The leaching rate of toxins from the paint film depends upon factors such as their solubility, rate of dissolution and the way it is compounded in the paint matrix (Anon, 1952).

Generally antifouling paints can be grouped under two classes depending upon the mechanism of release of toxins into the seawater.
Class one include those paints from which toxin alone is released by diffusion through the paint matrix continuously while in contact with seawater whereas the class two include those paints from which the toxins are released along with the dissolution of the matrix. The matrix dissolution can be of inactive (self dissolution) or active, either by the bacterial action on the matrix or by the mechanical erosion. One of the new generation paints e.g. the self polishing copolymer (SPC) falls under this category of antifouling class of paints (Anon, 1952). Of these two classes of the antifouling paints, class two paints, i.e. matrix-soluble paints have higher utilization efficiencies than those of the class one i.e. continuous contact paints. The reasons are, better leaching of toxins to the surface and long lasting effectiveness.

The existing antifouling paints which are widely used, basically contain chemical biocides such as heavy metals and/or organometallic compounds. Among the various organometallic antifouling paints, self-polishing organotin copolymer formulations have the best toxin release rate characteristics and are capable of maintaining surface free from fouling up to five years (Christie and Dalley, 1987). However, in recent years it is evident that the Tributyltin (TBT) is a broad spectrum poison and harms many other forms of marine life besides the fouling organisms (Beaumont and Newman, 1986; Rexrode, 1987; Thain et al., 1987; Langston et al., 1990; Wester et al., 1990; Kelly et al., 1990 a, b). Reportedly, TBT was found to be responsible for high mortality of oysters larvae as well as deformation of shells of adult Oysters (Key et al., 1976; Alzieu et al., 1982; Champ and Lowenstein, 1986; Claisse and Alzieu, 1993) and dog Whelk snails (Bryan et al., 1986). Accumulation of
butyltin in mussels tissue of *Salmon* sold in the market was reported by Short and Thrower (1986). Occurrence of imposex and effects on reproductive system of gastropods and Oysters have also been reported (Champ and Lowenstein, 1986; Bright and Ellis, 1989; Alvarez and Ellis, 1990; Ellis and Pattisina, 1990; Spence et al., 1990 a, b; Smith and Mc Veagh, 1991; Oehlmann et al., 1991; Stewart et al., 1992; Foale, 1993; Nias et al., 1993; Wilson et al., 1993). In general, the use of such chemical toxins in marine environment pose great threat to the marine biota (Vrijhof, 1985). For this reason, restrictions are imposed on the use of these compounds in most of the advanced countries. A complete ban on the use of organo-metallic compounds especially TBT now, operates in Japan, while in Britain its use for small boats are outlawed since, 1988 (Clare, 1995).

Due to the existing and the expected future restrictions on the use of TBT (Dalley, 1987) and probably other polluting antifouling compounds, there is a growing need for other methods of the prevention of fouling. One of the probable methods presently being investigated all over the world includes formulation of antifouling paint based on natural compounds, which are generally believed to be easily biodegradable, causing no harm to the marine environment. The work on this aspect was initiated elsewhere during 1980s. Till date numerous marine organisms and algae have been screened for search of biogenic compounds which can serve as antifouling agents (Sieburth and Conover, 1985; Katsuoka et al., 1990). Reports show that several species of marine invertebrates especially, sponges, coelenterates, bryozoans and ascidians were found to contain some compounds which
could prevent settlement of macrofoulers in laboratory (Targett et al., 1983; Bakus and Kawaguchi, 1984; Bandurraga and Fenical, 1985; Rittschof et al., 1985, 1986; Gerehart et al., 1988; Wahl et al., 1989; Sears et al., 1990; Walls et al., 1993; Targett et al., 1994). The compounds include alkaloids, fatty acids (Goto et al., 1992), Terpenoids (Keifer et al., 1986; Sears et al., 1990) and bromopyrroles (Keifer et al., 1991). Though these groups of compounds have been identified, very few of them have been clarified with the structure and tried in the field.

In addition to marine organisms, terrestrial plants have also been screened for antifouling properties (Suzanne, 1993; Sawant et al., 1995). However, not much information is available on the compounds from terrestrial plants which could be used as antifouling agents. Plants are in fact miniature factories of nature for the production of food materials, essential oils, gums, resins, alkaloids, steroidal substances, glycosides and many other valuable compounds of daily use. The compounds synthesized by the plants are of such complexity and heterogeneity that human mind is left bewildered at the marvels and mysteries of plant processes. Due to this reason, the natural durability of plant species in marine environment is dependent on the nature and extent of these chemical constituents (Santhakumaran, 1994). A perusal of literature shows that certain quinones and sterens from some plants have been reported to prevent metamorphosis and growth of wood borer larvae (Bultman, 1976; Turner, 1976). Some of the plants are also being used since ages for intoxicating fish. Different parts of the plants, are crushed and the juice is allowed to mix with the water. The extract stupefies the fish and makes them float up, facilitating an easy
catch (Anon, 1961; Mitre, 1981). In view of this fact that extracts of some plants are being used locally for narcotizing and catching fishes, this work was taken up in order to find out whether the various local plants possess any antifouling compounds. The plants which have been investigated are *Catunaregam spinosa* (Rubeaceae), *Sapindus laurifolius* (Sapindaceae), *Gnidia glauca* (Thymelaceae), *Acacia pennata* (Leguminaceae) and *Barringtonia acutangula* (Lecythidaceae).

Different parts of these plants such as, fruits of *C. spinosa* and *S. laurifolius* and bark of *G. glauca*, *A. pennata* and *B. acutangula* have been used for isolating and identifying environmentally safe antifouling compounds.