

Antifouling paints however are generally known for their harmful effects to the living organism of marine water resulting in legislation that culminated in the global ban of tributyltin (TBT) (Figure 2). (L.D.Chambers et.al 2006)

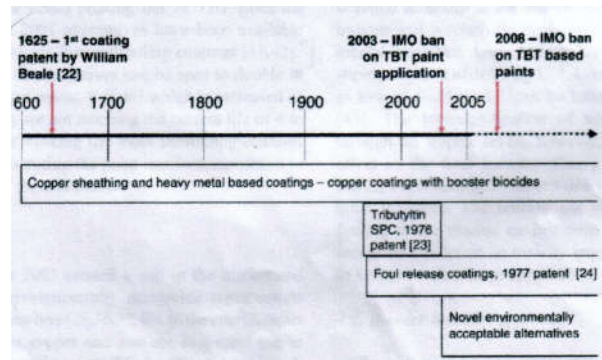


Fig. 2: Timeline for key Antifouling generations

The metallic pollutants present in such kind of paints however unsuitable to aquatic life. The suspended particles or the dissolved compounds of such metals taint the water resources more seriously. Marine coatings are meant to provide complete protection and performance against extremely odd conditions and should meet the challenges of today's physical environment i.e. they can give best performance without disturbing and affecting the environment. In yesteryears toxic ingredients were the main key to the antifouling paints but now these toxic substance have been fully replaced by non-toxic fouling release coatings.

Ships are under constant attack from marine environment and need to be protected from the influences of the key elements of the marine environment such as seawater, biological attack and temperature fluctuations. Methods of protecting marine structures i.e. ships must be capable of resisting such changes in marine environment. Protective organic coatings can offer these functions (C.G. Munger, 1984) and consequently are largely used in the shipping industry to increase the working life of systems and improve its reliability. Paint coatings provides resistance towards corrosion, helps in easing maintenance of ships, its appearance, prevents the accumulation of fouling on hull by unwanted marine organisms. Such accumulation of marine organisms on the substrate can cause large penalties to ships, biofouling can clog systems and on ship hulls it can increase the hydrodynamic drag, lower the manoeuvrability of the vessel and increase the fuel consumption. This leads to increased costs within the shipping industry through the increased use of manpower, fuel, material and dry docking time.

Marine-Fouling Organisms

Marine fouling organisms include members of both the plant and the animal kingdoms. Some 2000 species have been reported to cause fouling, many of which are unique to marine environment. Representative include algae, bacteria, fungi, protozoan, barnacles and other arthropods, mollusks, tunicates, hydroids and annelids. Antifouling systems are required wherever unwanted growth of biological organisms occur. Extensive damage, direct or indirect, to wood pilings, hulls, buoys, other immersed materials, devices and organic coatings are caused by fouling organisms. (Walter, H. 1971, Walters, H. and Elphick, J 1968, Bikales, N.M. and Segal, L. 1971, United States Naval Inst. Marine fouling and its Prevention 1952)

What is Marine Fouling

When a ship is immersed in marine water for a longer duration, the animal mass, algae or other vegetative growing's of sea stick to base, diverse species of hard and soft fouling form colonies on hulls because each requires a permanent anchorage in order to mature or reproduce. This process of attachment of the above objects to the base or "hull" of the ship is termed as fouling.

Occurance of Fouling

Marine water contains different types of vegetables and animal organisms, these organisms required certain substrates to grow on, it may be the bed of sea, the rock or only the saline water of sea. They can also grow on other substrates also like hulls or base of ships. When the ships are suspended in water for longer duration the organisms settles upon the submerged part of the ship and start growing on it. They go on multiplying on the hulls and settles permanently on it. Mainly two types of the following organisms are there (Gale, G.E 1953).

Animal Fouling

It includes the barnacle, selfish such as oysters, tubeworms, sea - anemones and hydroids. Mainly the larva of such animals sticks to the base of the ships and complete their life cycle there thus becoming a permanent inhabitant of it.

Vegetable Fouling

It mainly consists of seaweeds, these weeds sometimes grows very densely, and can attain good

height. This growth of weeds greatly hinders the speed of ship. Other vegetable fouling is algae, fungi, diatoms and various species of bacteria.

Fouling Effects

Fouling is said to be the greatest evil of ships. Biofouling of ships increases fuel consumption, increases drag resistance, decreases maximum attainable speed and promotes corrosion. Fouling of power plant intake bays necessitates frequent shut downs and measures such as chlorination. Fouling by calcareous organisms contributes the greatest penalty because of their profile, and their tenacious adhesion to surfaces. Each of calcareous organisms attaches in a slightly different way using different glues.

Following are some ill effects of fouling.

Reduces Speed

A layer of both the animal and vegetable organism greatly reduces the speed of ship. It restricts the further movement of ships there by results in slower speed.

Fuel Consumption

It has been estimated that fouling of hulls can create such turbulence as a ship moves through the water that fuel consumption is increased by as much as 30 percent (Perez, M. et al. 200, Brady, R.F 2000) Known antifouling coatings are based upon kinds of mechanical cleaning as well as the release of highly toxic biocides from matrix coatings or upon either combinations.

Corrosion

Corrosion is an electro-chemical process requiring moisture and oxygen having a difference in electrochemical potential. Heavy accumulation of fouling also promotes corrosion of underwater components of ships. (Brady, R.F., Griffith, J.R. et al. 1978)

Mechanical Damage

Fouling causes mechanical damage to coatings, moving parts of equipments goes inoperative.

Antifouling systems are required wherever unwanted growth of biological organisms occurs. This generally occurs in saline aqueous environment. Marine Engineered systems have been categorized

into seven key types of submerged structures of which ship hulls account for 24% of the total objects fouled (Raikin, A.I. 2004) Even though Steel and Aluminum are the materials for the construction of ship hulls they undergo fouling due to constant exposure to a diverse range of environments. Although coatings are used for hull protection, they fail due to the build up of inorganic salts (Clare A.S., Rittschof, D., Gerhart, J., Maki, J.S 1992) expolymeric secretions, and the calcium carbonate skeletal structures that from the fouling organisms. There are penalties associated with the unwanted colonization of a hull surface by marine organism (Townsin, R.L., 2003) they undergo hull roughness as well as wall shear stress. The effects of antifouling coatings, such as self-polishing copolymer and fouling release coating, on the hydrodynamic boundary layer have been shown little influence on either its thickness or shape factor, although friction velocity was increased (Candries M., Atlar, J. (2005). The negative effects of biofilm roughness on drag was studied by Shultz and Swain (Schultz M.P., Swain G.W., 2000)

Biological fouling exploits ship's hull by the settlement of microorganism, which in turn degrade the ship's performance.

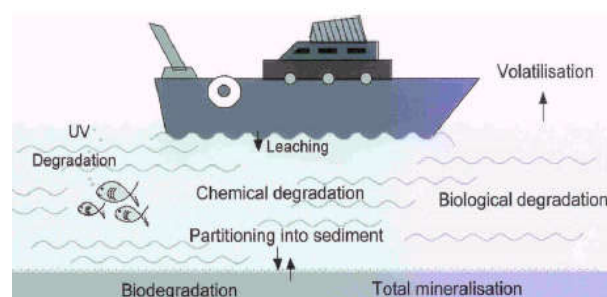


Fig. 3: Fate of active ingredients of antifouling paints in sea water

Historic Antifouling Methods

Ships were historically constructed by wood. The decay from bacteriological and animal attacks was in general mitigated by using hard tight wood, and by treating the wood with "poisoned" tar or oil paint. Later the ships was constructed from steel other forms of "decay" became dominating, and other solutions to prevent such decay (rust) was employed.



Fig. 4: Wooden Constructed Ships

Fouling was first reported on a papyrus dated around 412 BC in which is mentioned they used arsenic and sulfur mixed with Chian oil to help mitigate the problem. Christopher Columbus wrote "All ships were covered with a mixture of tallow and pitch in hope of discouraging barnacles and teredo, and every few months a vessel had to be hoed down and graven on some convenient beach."

In 1625, William Beale filed the first patent for an antifouling recipe that was based on iron powder, copper and cement. Fouling was reported to be up to ½ m long, and giving off odorous and aggressive gases, turning the white lead oxide pigmented paint on the topside darker on a sailing ship anchored in the Indian Ocean. Lord Nelson reportedly employed copper plates attached to the ship's hull to prevent fouling, greatly increasing his ships maneuverability in combat. Steel ships cannot use copperplates due to the galvanic corrosion induced by such bi-metallic couples.

The most common method of prevention of fouling on ship hulls and other underwater structures uses copper or organotin containing paints. Although organotin containing coatings are highly effective, they are also dangerous to the marine environment in which they are used because the tin leachates can poison non-target organisms such as fish, vegetation, and marine mammals.

The use of antifouling coatings for protection from the marine environment has long history. Earlier sailors have used toxic compounds to keep fouling creatures away from hulls. These were like Copper, Arsenic and Mercury. For example, Copper sheathing was earlier in use and was first used by British Naval Ships in 1779. (Callow, M., 1990, Pain, S, 1999)

Now a day organotin based antifouling paints is much in use around the world due to their effectiveness even at low concentration against most forms of fouling. However these too have some harmful effects over sea life and the use of toxic organotin derivatives in antifouling paints are fully prohibited.

Organotin compounds do not prevent the accumulation of algae on hull, so small amount of cuprous oxide is used in organotin coatings for control of algae and grasser. (Ghanem 1980)

The effectiveness of antifouling paints are generally based upon their toxicity i.e. how much amount of toxic ingredients do these paints possess in their formulations. e.g. Cuprous oxide, Triphenyl or Tributyl derivatives, as cuprous oxide prevents diatoms, algae, sponges and other hard fouling like

mollusca from sticking on the surface of hull, it is cheap and easily soluble in sea water. In early 80's antifouling paints have achieved their effectiveness by releasing biocides at their surface. Most of them have been metallic or organometallic substances because these compounds are effective against the broad range of organisms encountered in the marine environment (Phillip. AT 1973). It is clear that toxic compounds used previously and today in marine paints are responsible for some of the present marine pollution problems in coastal waters.

Antifouling paints are the source of most of the contamination of organotin compounds in harbor basins. Large amounts of copper and to some extent lead and mercury found in the sediments originate from these paints as well.

Need for Fouling Release Coatings

Antifouling coatings prevent the growth of marine organisms on hulls, for this growth decrease the speed, maneuverability and range of ships and raises propulsive fuel consumption by as much as 30%. Ultimately ships must be taken from the water and mechanically cleaned to remove fouling Earlier sailors have used poison to keep these creatures off their hulls. Such poisons are as arsenic, cadmium, lead and mercury have been long prohibited by most nations but copper and tin containing toxins continue to be used.

Modern Alternative to Antifouling Paints

Because of the increased evidence of ecosystem damage in areas close to concentrated use of tin-containing paints, application of these antifouling paints is being restricted and in some cases prohibited.

Fouling release-coating technologies are currently under development in response to the need for a nontoxic coating alternative to antifouling paints.

Thermoplastic, non-convertible surface organic coatings, which dry due to simple solvent evaporation, are today readily available although volatile organic compound (VOC) controls are limited in antifouling applications.

Many traditional antifouling systems are paints, which is a comprehensive term covering a variety of materials, enamels, Lacquers varnishes, undercoats, surfacers, primers, sealers, fillers, stoppers and many others (Turner, G.P.A.,1967.) Most antifouling coatings are organic and consists of a primer and a topcoat both of which can include anticorrosive

functions, however, the topcoat is often porous. Since the initial phasing out TBT from the antifouling industry in 2001 alternatives have been available (Omae, I 2003, Watermann, B 1999, Omae, I, 2003) including biocide-free antifouling coatings (Watermann, B et.al. 2005, Watermann, B, et.al. 2003) Fouling organisms may grow on the surfaces of these coatings but adhere poorly and can be removed by light brushing, water spray or by hydrodynamic self-cleaning. Silicone polymers have show better fouling release capability than fluoropolymers and other coatings.

This has been attributed to their being within an optimum range of critical surface tension, which is related (but not equal) to surface energy.

Other factors thought to contribute to silicones superior fouling release ability are their surface structure; extremely low glass transition temperature and low modulus. All of the current coating technology employs condensation cure chemistry.

The coatings are prepared by the reaction of a crosslinker with a silanol polymer in the presence of a condensation cure catalyst such as dibutyltin diacetate.

Types of Antifouling Coatings

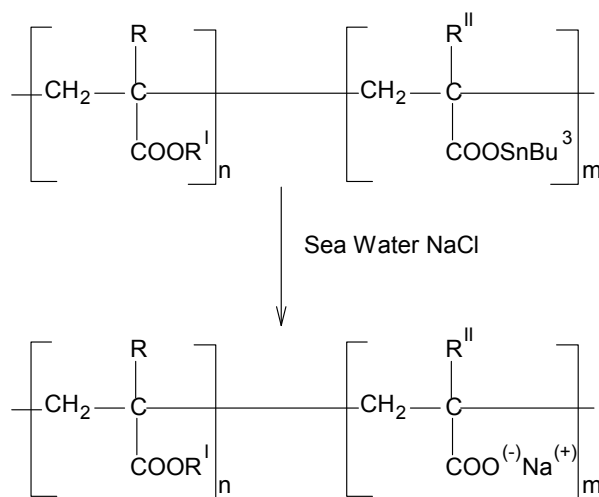
Self Polishing Type

These are Biocidal coatings. A revolutionary self polishing co-polymer technique employing a similar heavy metal toxic action to determine organisms was used with antifoulant Tributyltin (TBT) (Milne, A. Hails, G., 1976)

The self-polishing co-polymer technique uses both hydrolysis and erosion to control the antifouling activity. It is an organotin based compound reacted with acrylic polymers (Scheme-1).

The biocide is released following hydrolysis with water. The outer layer of such coating is water-soluble; once the biocide is released the polymer become water-soluble due to the formation of sodium and potassium salts and dissolves slowly, this results in smooth surface.

For example Tributyltin hydrolyzed off, it reacts with chloride ions from seawater to form tributyltin chloride. This type of coating is very effective and can be used for longer duration. (Takahashi, K. 1991, Takahashi, K and Ohyagi, Y 1990, Atherton, D., Verborgt, J and Winkeler 1979) They help save fuel.



Scheme 1: Chemical reaction of Organotin polymers in sea water

Thin linear release rate is responsible for the excellent antifouling performance observed with self-polishing paints. (Khanolka, R.R 2001, Kajer, E.B 1992).

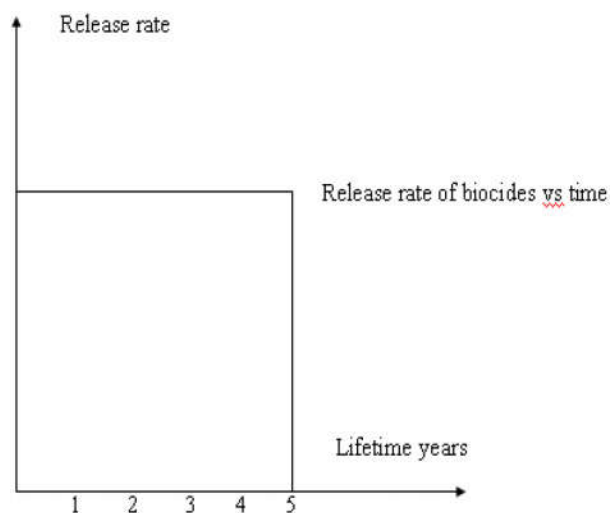


Fig. 5: Self polishing antifouling

Conventional, Soluble Matrix Type Antifouling

Based on cuprous oxide dispersed in gum rosin. Its mechanism based on the partial solubility of the binder, which provides adequate contact between seawater and cuprous oxide. Conventional antifouling work by the dissolution of the acidic rosin in seawater. In principal, the release of biocides remains constant until the paint has completely dissolved. These coatings are mostly used with most of the biocides being metallic or organometallic substances because the compounds are effective

against the broad range of organisms encountered in marine environment, (Philip, A.T. 1973)

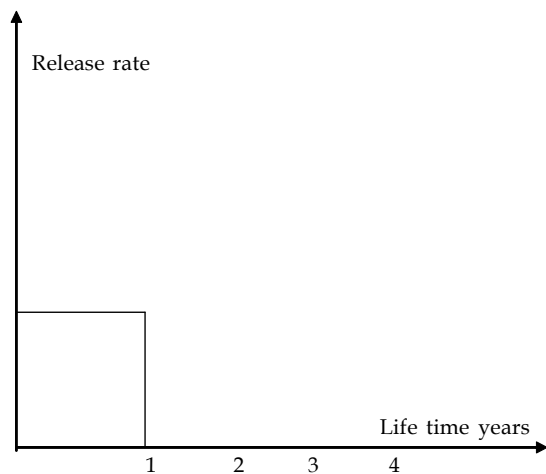


Fig. 6: Conventional antifouling

Advanced, Insoluble Matrix Antifouling

This coating release biocide and other water soluble ingredients, leaving an insoluble binder skeleton. As the thickness of the porous binder skeleton increases, the release of biocide decreases. Commonly used binders are vinyl resin and chlorinated rubber resin (Upadhya, Shivpujan C. 2002).

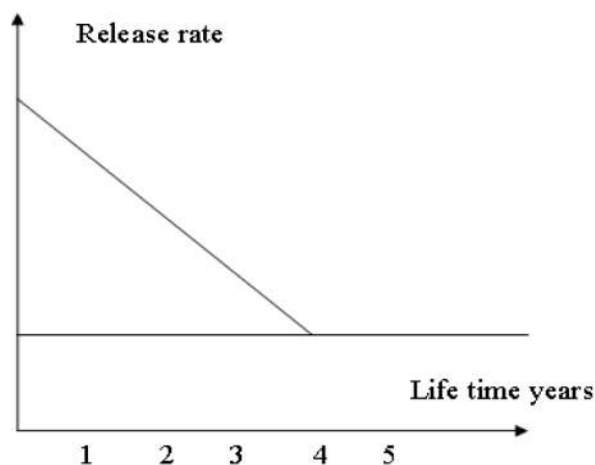
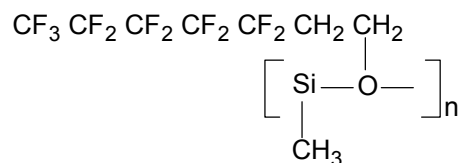


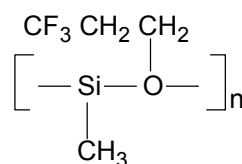
Fig. 7: Insoluble matrix antifouling

Flourinated Coatings

Polymers containing trifluoromethyl groups and fluorinated coatings were developed, as fluorochemicals (Upadhya Shivpujan C., 2002) wettability of the substrates, interatomic attractive forces and molecular interdiffusion and allows coating surface with low intrinsic adhesion.



PNFHMS



PTFPMS

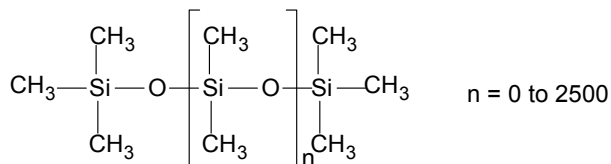
Scheme 2: Flourinated Silicones

Fluorinated coatings are yet to occupy market. These coatings have excellent resistance properties towards soiling and staining, they give fine color and gloss retention. These coatings are used for other marine uses.

Silicone Coatings

Silicone are fouling release coatings, were first reported in 1972, Polydimethylsiloxane (PDMS) was used as elastomers. Silicones are soft elastomeric materials, having surface energy of above 25mJ/m². Since silicone coatings are non-sticky hence did not give good adhesion property therefore it is necessary to develop a coating system that couples hard metal hull to the soft elastomeric silicone coating and ensure adhesion that can adjust marine environment for example: -

Polyurethane - silicone - hydrocarbon coatings,
Polybutadiene - silicone coatings,
Silicone urethane coatings etc.



Scheme-3 Structure of PDMS

Formulation Technique

Different types of Binders and Pigments are used

in antifouling coating (Borse, Hemant. R. 2003). Some are listed below:

1. Vinyl coating
2. Epoxy coating
3. Epoxy – polyamide coating
4. Epoxy – ester coating
5. Epoxy – coal – tar – coating
6. Chlorinated – rubber
7. Polyester – glass coatings
8. Urethane coatings

Vinyl Formulation (anticorrosive coat) by %

Read lead	25.18%
Polyvinyl chloride (Alcohol modified)	16.62%
Tricresyl phosphate	1.71%
Aluminum stearate	0.1%
Methyl isobutyl ketone	29.20%
Toluene	27.19%
	100%

Antifouling Coat

Cuprous oxide	80.83
Vinyl resin	8.08
Rosin	8.08
Tricresyl phosphate	3.01
	100 %

Fluorinated – Rubber Antifouling

Red iron oxide	15.2
Rosin	3.73
Talc	7.08
Mlk	20.31
Vinyl	11.16
Xylene	18.84
Bentone	270.51
Menthol	0.17
(Tributyl tin fluoride) TBT	11.86
	100 %

Due to strict environmental laws non – toxic fouling coatings have been prepared. Today's antifouling paints are effective because they contain heavy metals, which are toxic to fouling organisms. Compounds of arsenic, copper, lead, mercury and tin are now forbidden or almost restricted. Research

Table 1: Major Reviews on Antifouling Coatings

Authors	Theme	Year
Abarzua,S. and Jakubwski.S	Biogenic agents to prevent biofouling	1995
Montermosso,J.C. et. al	The polymers of trialkylin acrylates obtained by random or co (or ter) polymerization of tributyltin acrylate with methylmethacrylate	1958
Subramanium, R.V., et.al	Synthesis and properties of thermosett antifouling polymer systems containing tin by crosslinking cycloaliphatic epoxides with free carboxylic groups present on base polymer partially esterified with tributyltin oxide	1977
Pitman,C.U	Chemical anchoring of wild weeds to paints	1976
Videla,H.A	A general review of biofilm	1996
Ghanem,N.A.,et.al	New routes to attach covalently organotin moieties	1975
Van	Showed that the period of fouling protection by the antifouling paints can be substantially extended	1975
Londen,A.M.,et.al	Antifouling toxicants having high microbial activity against wide range of microorganisms based on isothiazolone derivatives.	1980
Miller,G.A and Lovegrove,T		
Herbert,P.A., et. Al	Described antifouling coatings based on chlorinated rubber	1975
Rascio,V.I.D and Carprar,J.J	Showed that some extenders can also be added to the paint compositions to obtain antifouling properties	1978
Giudice,C.A., et.al	Investigated the bioactivity levels of several antifouling coatings based on gum rosin	1983
Brady,R.F, et.al	Investigated antifouling coatings containing no toxicant but which derive their effectiveness from a surface that weakens or eliminates the adhesive bond between marine fouling and the surface of coating	1987
Cologer,C.P., et.al	Various underwater cleaning methods have been reviewed	1977
Morson,F.	Described a simplified quality control method applicable to Cu (I) oxide based antifouling paints	180
Konstantinou,J.K and Albanist,J.A	Reviewed the worldwide effects of the key booster biocides in antifouling	2004
Champ,M.A and Terlizzi	Reviewed the legislation that culminated in global ban of TBT	2000
Woods Hole	Catalogue of fouling organisms and historic antifouling technology	1952
Fischer et. Al	Technology for control marine biofouling	1984
Wahl.M	Discussed about some basic aspects of fouling andbiofouling	189
Clare,AS	Discussed the chemical structures, sources and mechanism of testing the efficiency of Antifouling paints	1996
Omae,I	Review of TBT ban and the alternatives focissing on the environmental issue of species	2003
Yebe et. Al	Antifouling technology was reviewed with particular emphasis on commercial products and the development of environmentally benign system	2004

Table 2: Shows the Types of Marine Paint, their Basic Properties and Common uses

Characteristics	Conventional coatings	Bituminous coatings	Vinyl coatings	Chlorinated rubber coatings	Zinc silicate coatings	Pure epoxy coatings	Coal tar epoxy coatings
Number of components	1	1	1	1	2	2	2
Mode of drying	Solvent evaporation and oxidation	Solvent evaporation	Solvent evaporation	Solvent evaporation	Solvent evaporation	Chemical curing	Chemical curing
Application (preferred methods)	Airless Spray, Brush, Roller	Airless Spray	Airless Spray, Conventional Spray	Airless Spray	Conventional Spray, Airless Spray	Airless Spray, Brush, Roller	Airless Spray, Brush, Roller
Qualities (anticorrosive)	***	****	****	****	*****	*****	*****
Antiabrasive	-	*	***	***	*****	*****	*****
Chemical Resistance	*	**	*** (Unmodified coatings)	***	**** (Limited by pH value)	*****	**
Solvent Resistance	*	*	**	**	***** A	***** B	**
Sea Water Resistance	**	**	**	***	** B	****	*****
Antifouling	**	-	***	***	-	-	-
Special qualities	Relatively inexpensive Wide range of colors Good gloss versatile coatings	Excellent water resistance	Good inter-coat adhesion Will dry at low temperature When modified with Coal Tar shows excellent anti corrosive properties	Excellent inter coat adhesion Will dry at low temperature	Excellent anti corrosive and abrasion resistant coatings	Hard, chemically resistant Particularly resistant to alkaline cargoes	Excellent sea water resistant
Additional data			Requires good surface preparation Sa2½ (Swedish standard SIS 05 5600-1967) thermoplastic (softens with heat)	Requires good surface preparation Sa2½ (Swedish standard SIS 05 5600-1967) Thermoplastic	Requires good surface preparation Sa2½ (Swedish standard SIS 05 5600-1967) Critical overcoating parameters and limited pot life	Requires good surface preparation Sa2½ (Swedish standard SIS 05 5600-1967) Critical overcoating parameters and limited pot life does not cure at low temp. (< 5°C)	Requires good surface preparation Sa2½ (Swedish standard SIS 05 5600-1967) Critical overcoating parameters and limited pot life does not cure at low temp. (< 5°C)
Common uses	Decks, accommodation, engine rooms, superstructures topsides	Internal under-water areas, Ballast Tanks, and void spaces	Bottom topsides, superstructures Coal Tar modified types are used on	All underwater areas, bootop, topsides, superstructures, decks	Decks cargo tanks shop primers	Internal tanks coatings cargo tanks superstructures	Internal tanks coatings underwater hulls, ballast

work is in progress for deriving alternatives to toxic coatings around the world (*Hittinger, K.J., Kluwer 1988*).

The last ten years has shown an increase in the focus on environmentally acceptable alternatives.

Non – toxic coating works by weakening or eliminating an adhesive bond between marine life and the coating. The fouling organisms dislodge by their own weight or by the motion of the ship through the water (*James D.Adkins, Ann.E.Mera Roe-short et al. 1996*).

Usually antifouling paint contains biocides or toxins held within its structure. The coating is designed to leach biocide slowly into the marine environment. Preventing any organism adhering to the point by poisoning the settling organism. The biocides generally have harmful effects both on fouling organisms for which it is designed to deter but also on marine life unconnected with fouling activity.

It is the potential impact of these points on marine life (www.marineare.org.uk/activities/recreation/r03-03.htm). Today's antifouling paints are based on metals, among the natural substances, metals are most ubiquitous of ultimate persistence. Amongst heavy metals lead, mercury, cadmium and arsenic are the ones, which severely effect the marine environment. Pices are being badly hitten by these heavy metals, studies on certain species of fishes reveled that these fishes exposed to such metals undergo severe damage of their body parts as well as cellular changes, results in their mortality (*Habib,F.Bajpai.M 2004*). The use of organotins was banned due to sever selfish deformities and the bioaccumulation of tin in some seals and fish (*Strand, J et al. 2005, Evans, S.M., et al. 1995*). Since the service life of antifouling coating is dependent on the dissolution rate and the concentration of the biocide in the coating film, the antifouling coatings based on organotins polymer systems are very efficient because the biocide is covalently bonded to the coating instead of being an external addition to such additives (*GiltizM.H, 1981*).

Qualities of Antifouling Paints

Antifouling paints should possess following qualities:

- Such coatings must be durable enough, so that it can withstand the harsh and unfavorable conditions of marine water.
- Should provide good adhesion i.e. It should properly adhere to base on which it is applied on even under most adverse conditions.

- It is essential for the paint to dry rapidly so the antifouling paint coating must give quick drying after the application on the ship.
- An antifouling coating should be designed in such a manner that it can be easily applied to the substrates, may be by means of spraying, brushing or rolling.
- The last and the most important quality of antifouling paint should by its price i.e. it should be economical. Expensive ingredients should be substituted too less expensive ingredients.

Advantages of Antifouling Paints

- These coatings are eco-friendly, as they do not posses any toxic material.
- Fouling can be easily cleaned as antifouling paint provides low surface energy
- Paint provide smooth surface to the hull thus saving fuel.
- Provide resistance to corrosion and chemical.
- Hinders the stocking of fouling due to non-stick characteristic.

Conclusion

With modern techniques of achieving good surface finish, the advent of high performance coatings, the system of applying coat on ship hull, the recent advances in the antifouling technology with introduction of self-polishing co-polymer compositions makes it possible for offering excellent protection to various segments of ships. The application of antifouling coatings however require careful inspection in order to gain good results in field performance of the products.

The new developments to antifouling coatings must be aimed at

- Excellent surface finish.
- Providing better application techniques so that the paint system can be applied on one or two coats.
- Coatings having excellent exterior durability.
- Superior antifouling, which can be straightaway applied on the anticorrosive paint.
- Antifouling paints should be non-toxic to avoid degrading marine environment.

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