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Alternatives to the use of TBT as an antifouling agent on the hull of ships with special reference to methods not involving leaching of toxic compounds to the water

Norwegian Institute for Water Research

REPORT

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Abstract

The International Maritime Organisation has agreed on a plan to ban the use of organotin for antifouling on large ships. Basic elements in the plan are: no new application of paint containing organotin after 1st January 2003. No use of organotin in antifouling systems for ships after 1st January 2008. This plan implies that alternatives to TBT must be available to the shipping industry within 2003. Various non-toxic antifouling strategies have been elucidated. At present there seems to be no good biocide free method ready to use for all types of vessels. Siliconbased non-toxic systems are available for ships with a speed of more than 15 knots. At present slower ships will have to be regularly cleaned or have to rely on biocidal systems. It is expected that biocides will be a part of antifouling systems on slow ships for many years. The use of copper-nickel hull and the electrolytic approach seems to have some potential. An obstacle for the use of these two approaches is that they are toxic in nature. Antifouling systems based on compounds found in marine organisms are promising on long term basis. The development of a complete antifouling system based on such naturally occurring compounds lies at least 5 years ahead. The use of information from research on natural products to design new antifouling paints, does *a priori*, not necessarily infer that the active ingredient is "environmentally sound". Such compounds therefore should be tested for possible environmental effects. A further development of such tests is a recommended area of future research.

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2. Antibegroing	2. Antifouling
3. Skip	3. Ships
4. Metoder	4. Methods

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Alternatives to the use of TBT as an antifouling agent on the hull of ships with special reference to methods not involving leaching of toxic compounds to the water

Preface

This report has been prepared on request from the Norwegian Maritime Directorate (NMD). The scope for the project is outlined in letter of 11.08.98 from Norwegian Institute for Water Research (NIVA) to NMD. The contract for the project was signed 01.09.98 (NMD) and 04.09.98 (NIVA). The project was financed through funding from The Norwegian Ministry of Environment (MD) to NMD.

The scope for the project was:

- Through relevant literature produce a "state of the art report" on alternative (non-toxic) methods to TBT for the prevention of fouling on ships.
- Arrange a workshop in order to facilitate the preparation of such a "state of the art report".
- Suggest promising areas for the future development of non-toxic antifouling method.

Karstein Thingvold was contact person at NMD during the course of the project.

John Arthur Berge was project leader at NIVA.

Oslo, 22/02 1999

John Arthur Berge

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Summary

Materials submerged in seawater experience a series of physical, chemical and biological events. These events result in the formation of a layer of attached organisms known as fouling.

The intensity of fouling varies strongly between regions and type of shipping and depends on where the vessels trade and operational profile. Generally the intensity of fouling is stronger in the tropics and in coastal areas than in more temperate areas and under oceanic conditions. Slow moving vessels generally are faced with larger fouling problems than fast vessels.

Tributyltin (TBT) is an effective biocide for the prevention of fouling, and is now the most commonly used antifouling agent used in paint for the underwater hull of large ships.
The basic environmental problem with the use of TBT as an antifouling agent is related to:

- Extremely low threshold for harmfull effects in certain molluscs.
- Effects non-target organisms in non-target habitats.
- Bioaccumulates in some marine organisms.
- Moderate to low degradability in sediments.
- Contamination levels can reach high values in harbours and semi-enclosed areas.

This has led to restrictions on its use on small boats in a number of countries.

At the International Maritime Organisation (IMO) MEPC meeting in November 1998 a plan for implementing a ban on the use of organotin for antifouling on large ships was agreed. The basic elements in the plan were:

- No new application of paint containing organotin after 1st January, 2003.
- No use of organotin in antifouling systems for ships after 1st January 2008.
- Establishment of a system to evaluate alternatives to the use of organotin as an antifouling agent on ships.

This plan implies that alternatives to TBT must be available to the shipping industry within a few years.

Most antifouling methods used at present prevent marine growth by release of biocides. The main method used for control of the biocide release is the self-polishing systems (SPC). SPC rely on a chemically controlled process to release the biocide from the paint. The main biocides used for this system has been TBT, copper and organic boosting biocides. Today, more than 80% of the world's fleet use SPC. Several biocides other than TBT are available. Most important are copper, Irgarol, Diuron, Sea-Nine 2, Zinkphyrithione.

In this report we give an account of possible, mainly non-toxic methods for antifouling.

Copper-nickel hull
Alloys of copper-nickel have good resistance to biofouling. Literature gives little information on new developments in the use of copper-nickel as an antifouling agent on large ships. The method is probably at least as environmentally safe as the use of traditional copper-based coatings (without boosting biocides). The mechanism behind the antifouling properties of the system is not fully known. Too little independent information is available to foresee the long-term potential of the system. As the system probably will be impossible to use on existing large ships, the system is not a likely alternative

to the use of TBT within the time frame in question (2003, 2008). In any case considerable development is needed on the shipbuilders side.

Electrolytic system
An antifouling system based the formation of ClO^- through electrolysis of seawater has been developed. The system is, stricly speeking, not "non-toxic". The system requires that the hull of the ship is covered with a three-layered coating. The middle layer is a conductor. The conductor on each side of the ship is isolated from each other and functions as cathode and anode respectively. By applying a direct current between the to electrodes, ClO^-develops and prevents fouling. It is expected that ClO- which escape from the coating do not represent a threat to marine life in the open sea, but could be more of a problem in harbours. The success of the system from an environmental point of view lies in its possible acceptance as a "non-toxic"method. The system is probably most effective on slow going ships and ships in harbours.

The use of copper-nickel hull and the electrolytic approach seems to have a potential. The main obstacle for the use of antifouling methods based on these two approaches, are partly that they are toxic in nature.

Physical methods for antifouling
Ultra smooth surfaces are sought in order to weaken or eliminate the adhesive bond between fouling organism and the coating. The organisms may be dislodged by their own weight or by the motion of the ship through the water. Silicone elastomers and to a lesser degree fluoropolymers have received most attention regarding their potential use as non-stick coatings. The development of a non-stick material is however not only a matter of the surface properties but also of the adherend used by the potential foulers. The non-stick approach is in its nature non-toxic. In essence it is the speed needed to remove these organisms that limits the use of the non-stick method. For the most recent products on the marked this recommended minimal speed is approximately 15 knots. This means that for a relative large proportion of the Norwegian fleet "non-stick" coatings will at present not alone be a good alternative to the use of TBT. One of the challenges in the future will be to reduce the minimum speed needed for the non-stick coatings to be effective.

Little information are available on the possible use of physical methods like surface texture (protruding physical structures), UV-light, sound and electric stunning on large ships. It is concluded that these methods are either unpractical or too dubious in nature to be recommended for further development for large ships.

Regular cleaning (Mechanical, high pressured water)

The most obvious non-toxic option for slow moving ships is to be regularly cleaned. Slower ships with coatings without a biocide effect probably need to be cleaned 4 to 6 times pr year and under certain conditions even more often. The system requires an international network of cleaning stations at strategic locations world-wide. It is believed that periodical cleaning alone is not likely to be a satisfactory (for the ship owners) antifouling system for large ships, partly due to the need for frequent treatment, but could be a good approach in combination with non-stick systems. Future research and development should focus on optimising a "low-stick/periodical cleaning system" in a direction to service ships with a speed below 15 knots.

Grazing/predation
An important factor controlling the distribution of rocky-shore organisms is grazing and predation. The use of grazing or predating organisms to reduce the number of foulers on stationary structures could have some potential, but is not likely to be a method with sufficient efficacy on large moving ships.

The use of natural occurring compounds

Many marine organisms have the ability to produce substances with antifungal, antibacterial, antialgal, antiprotozoan or antimacrofouler properties. Such biogenic substances may be used for the prevention of fouling.

The natural compounds identified are diverse in structure and often complex. Some of the identified compounds have common structural features, which could lead to identification of the functional group responsible for the antifouling effect. The identification of such key groups could facilitate synthesis of compounds that are structurally simpler than those identified in marine organisms and thus probably more easy to produce on an industrial scale sufficient to supply the marine paint industry.

The use of information from research on natural products to design new antifouling paints, does a priori, not necessarily infer that the active ingredient is "environmentally sound". Such compounds therefore should be tested for possible environmental effects. The development of more comprehensive tests is a recommended area of future research.

Antifouling systems based on compounds found in marine organisms are promising on long term basis. The development of a complete antifouling system based on such naturally occurring compounds lies at least 5 years ahead.

Various non-toxic antifouling strategies have been elucidated. At present there seems to be no good fully tested biocide free method ready to use for all types of vessels. Non-toxic systems are, however, available (or will in the near future) for ships with a speed of more than 15 knots. At present slower ships will have to be regularly cleaned or have to rely on biocidal systems. It is expected that biocides will be a part of antifouling systems on slow ships for many years.

1. Introduction

Materials submerged in seawater experience a series of physical, chemical and bological events. These events result in the formation of a layer of attached organisms known as fouling. In the marine environment any solid surface will become fouled. The establishment of a fouling community is an extremely complex process, which generally follows a basic sequence. In the course of this sequence the prevailing process change from a purely physical to a predominately biological (Wahl, 1989). Schematically this sequence is composed of 4 phases (Wahl, 1989) as follows:

- Biochemical conditioning/formation of primary film
  Organic film develops from substances in the water. The process starts spontaneously after submersion of a substrate (minutes).

- Primary colonization by bacteria.
  First reversible colonization of bacteria within a few hours, followed by non reversible colonization of bacteria where extracellular bridging polymers are made.

- Secondary colonization by unicellular eukaryonts (yeasts, protozoa and diatoms) starts a few days after submersion. Diatoms are usually dominating and attach by mucus secretion

- Tertiary colonization by multicellular eukaryonts (macroalgae, barnacles, mussels, tunicates, coelenterates, bryozoans, polychaetes etc.). This phase start after 1 to several weeks. This phase results in a highly differentiated 3-dimensional structure.

Biofouling is a dynamic process and the different stages may overlap or occur in parallel. Biofouling promotes corrosion, creates roughness (mainly tertiary colonisers) and thus reduce speed per unit of fuel, increase overall fuel costs and the emissions from the engine to the air, and reduce the time a vessel can be at sea. Biofouling is thus an important problem in marine technology.

The intensity of fouling varies strongly between regions and type of shipping. The challenge depends mainly on where the vessels trade and operational profile (speed of the vessel and the length of time in harbours). Generally the intensity of fouling is stronger in the tropics and in coastal areas than in more temperate areas and under oceanic conditions. Slow moving vessels generally are faced with larger fouling problems than fast vessels. These are all factors to be considered in order to give a ship sufficient protection against fouling.

Tributyltin (TBT) has been used as an effective biocide in antifouling paints since the seventies and is now the most commonly used antifouling agent used in paint for the underwater hull of large ships.

TBT is one of the most toxic substances known and unintended environmental effects from TBT were found in the Arcachon Bay in France in the late 1970s on the Pacific oyster (*Crassostrea gigas*) (Alzieu *et al.*, 1986 with references, Alzieu 1998, Ruiz et al. 1996).

Effects of organotin compounds have since the 1970s been reported for a variety of marine species (fish, gastropods, crustaceans, echinoderms, microalgae) at concentrations that may be found in anthropogenically influenced areas (Beaumont & Newman, 1986 a and b; Walsh *et al.*, 1986; Hall, 1988; Bryan *et al.*, 1986, 1989; Johansen & Møhlenberg, 1987; Bushong et al., 1990; Fent & Meier, 1994).

In the last decade much attention has been paid to induction of male sex characters in female snails, known as "imposex" or "intersex"(Bryan *et al.*, 1986; Gibbs & Bryan, 1986; Gibbs *et al.*, 1987; Horiguchi *et al.*, 1994, Minchin et al. 1996, Poloczanska and Ansell, 1999). Most investigations points to TBT as the agent responsible for "imposex" and "intersex" (Matthiessen; and Gibbs 1998).

Both individual states and international bodies (EU) have been concerned with the environmental effect of TBT. In 1990 the International Maritime Organisation (IMO) agreed on a resolution banning sales of TBT-based antifouling paints for boats under 25 m of length and prohibited the use of all antifouling paints with a mean leaching rate exceeding 4 $\mu g/cm^2$ per day.

Unintended effects of TBT in the marine environment have led to restrictions on its use as antifouling agent on small boats in a number of countries. Monitoring in areas where such restrictions have been enforced, indicates a reduction in environmental concentrations (IMO, 1994; Shiraishi & Soma, 1992; Evans *et al.,* 1995) and some recovery in populations suffering from imposex (Evans *et al.,* 1991; Bryan *et al.,* 1993; Evans *et al.,* 1995). This indicates that environmental problems caused by organotin have been reduced in some areas previously heavily affected by small boats. Gastropods heavily effected by TBT may however still be found in harbours for small boats 10 years after the introduction of the ban for the use of TBT on small (<25m) boats.

Similar recoveries have not been found in Norway in areas with high intensity of traffic with larger ships. Data from the southern Norwegian coast (Færder) in relatively open areas, with a regular traffic of large ships, still (1997) shows biological effects of TBT on *Nucella* (Green et al. 1999). These findings are interpreted as a clear consequence of the use of TBT on large ships since the small boats visiting the area, according to regulations, should not be using TBT. This means that significant decreases in TBT levels in the marine environment can only be achieved by banning the use of TBT also on large (>25m) ships (Berge et al. 1997).

IMO has compiled information about harmful effects of TBT, and at the IMO MEPC meeting in November 1998, a plan for implementing a ban on the use of organotin for antifouling on large ships was agreed (unanimous assembly resolution). The basic elements in the plan were:

- No new application of paints containing organotin after 1st January 2003.
- No use of organotin in antifouling systems for ships after 1st January 2008.
- Establishment of a system to evaluate alternatives to the use of organotin as an antifouling agent on ships.

The IMO plan for a total ban on the use of organotin as an antifouling agent on ships means that alternatives to organotin must be available to the shipping industry within a few years.

In the present report we give an account of possible methods available today, as well as point to promising ways for the developing of future products not involving leaching of toxic compounds to the water.

A workshop with the title *Alternatives to the use of TBT as an antifouling agent on the hull of ships* was arranged during the course of the project. Proceedings from this workshop are found in Appendix A (page 35).

2. Chemical methods for antifouling -use of biocides

2.1 Basic approaches for the use of biocides in antifouling coatings

Most antifoulings prevent marine growth by release of biocides. Three main approaches are used for control of the biocide release (Anderson, 1998)

Soluble matrix technology .
This system rely on a physical/mechanical controlled process to release the biocide from the paint rather than on a chemical controlled process as in the self polishing system (see below). Over time a leached layer with a reduced biocide concentration develops on the surface. This occurs because it has been difficult to find a matrix that erodes at a rate comparable to the biocide. As a result the length of time that the system can work is at best 3 years. The main biocides used for this system are copper usually together with a boosting co-biocide.

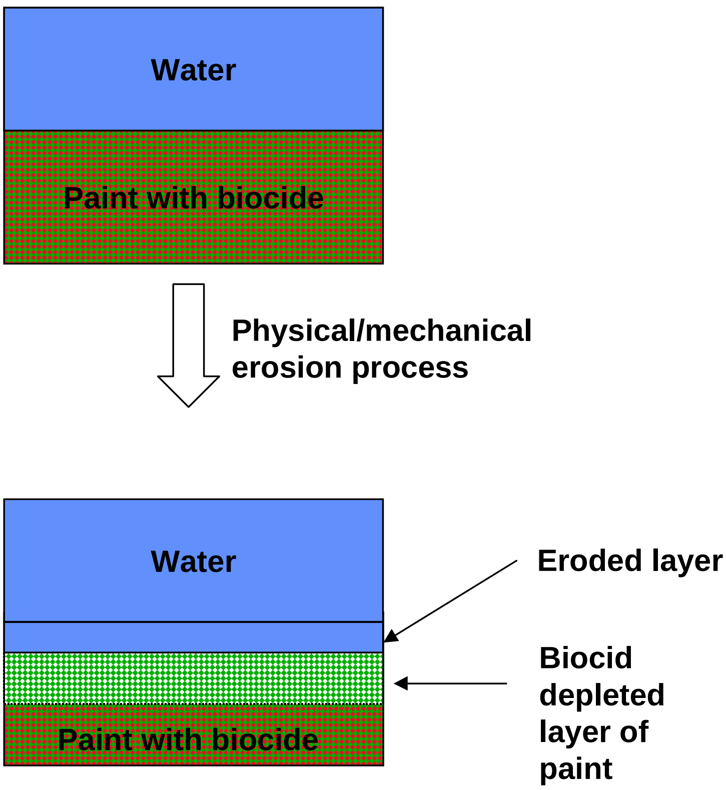

Figure 1. Principles for the mechanism in Soluble Matrix technology.

Contact leaching
These products are hard, mechanically tough antifoulings that do not erode. They are highly loaded with biocides that leach through the surface of the hard matrix over time. These systems are efficient for antifouling for a maximum of 2 years since after this time the surface layer are depleted and too little biocide reach the surface to be effective.

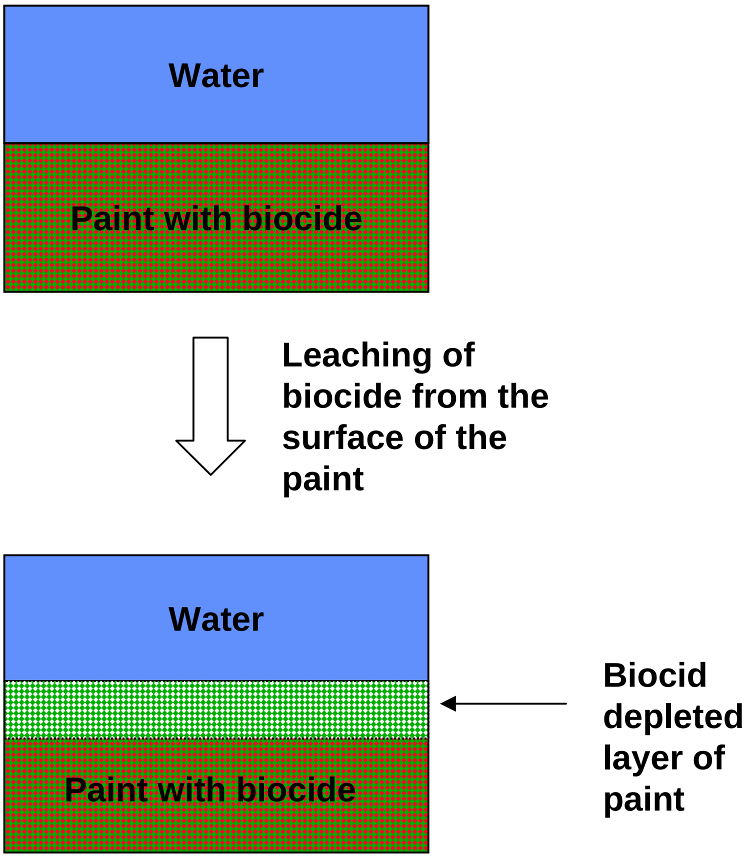

Figure 2. Principles for the mechanism in Contact Leaching technology.

Self-polishing systems (SPC).

This approach rely on a chemically controlled process to release the biocide from the paint. The biocide is chemically bonded to the polymer (ester linkage) and the rate of the release of the biocide follow the rate of the hydrolysis (polishing rate) of the polymer. This polishing rate is proportional to the speed of the ship. Over time no thick layer will develop on the surface and the antifouling effect stops first when the coating disappears. As a result, the length of time that the system can work is up to 5 years. The main biocides used for this system has been TBT, copper and organic boosting biocides.

Self-polishing (SPC) systems were first introduced in the 1970's. Today, more than 80% of the world's Deep Sea fleet use SPC.

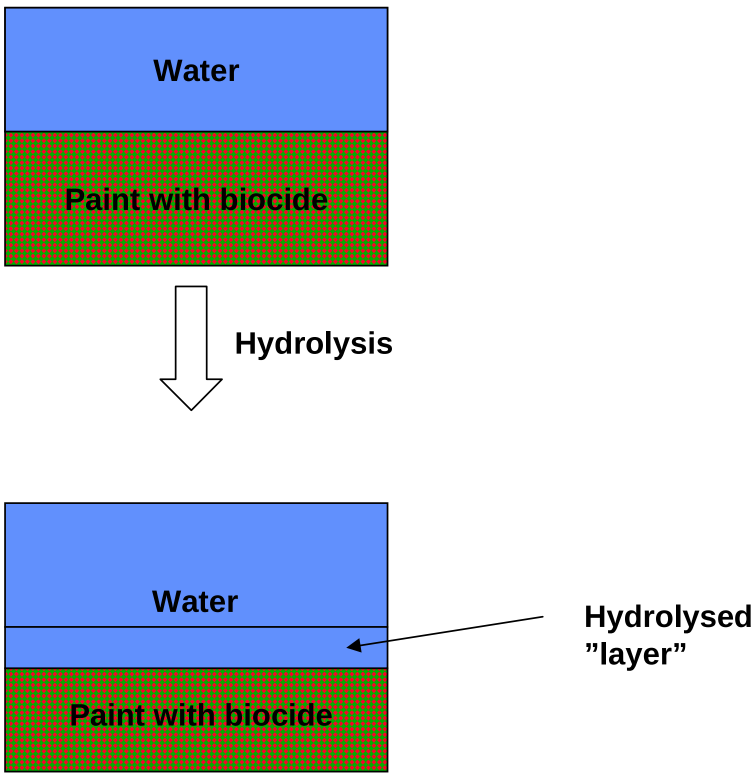

Figure 3. Principles for the mechanism in the Self-polishing systems (SPC).

2.1.1 Toxicity of TBT

TBT is toxic to a broad range of organisms (table 1). This is also the basis for its success as an antifouling agent. The antifouling activity of all types of TBT coatings is based on the leaching of TBT to the water and a toxic/repulsive effect on foulers. Leaching rate is estimated to be 1-10 µg TBT/cm^2 per day to ensure antifouling protection (Alzieu, 1998).

Table 1. Toxicity of TBT to different taxonomic groups (data recalculated from Madsen et al. 1998).

Taxonomic group	Effect recorded	Exposure time	Concentration (ng TBT/l)
Algae	EC_{50}	3-5 d	300-1000
Algae	LOEC	18 d	100
Crustaceans	LC_{50}	48h-6d	400-100000
Crustaceans	LOEC	6d-56d	10-300
Fish	LC_{50}	48h-21d	900-27000
Fish	LOEC	28-225d	100-500
Molluscs (juveniles)	LC_{50}	48h	1000-3600
Molluscs,	EC_{50}, growth	48h-20d	50-240
Molluscs,	EC_{50}, calcification		<10
Molluscs	LOEC, imposex		<1

LOEC=Lowest observed effect concentration

The basic environmental problem with the use of TBT as an antifouling agent is related to:

- Extremely low threshold for harmful effects (hormone disrupter) in certain molluscs (table 1).
- Effects in non-target organisms in non-target habitats world-wide.
- Bioaccumulates in marine organisms (invertebrates, and marine mammals).
- Moderate to low degradability in sediments.
- Contamination levels can reach high values in harbours and semi-enclosed areas.

2.1.2 Biocides other than TBT for antifouling

A ban on TBT-based paints is justified due to their harmful impact on marine ecosystems, but substitutes based on the release of other biocides also give rise to major concerns (ASMO, 1998). Several alternative biocides to TBT have been suggested or are available: tin-free coatings based on copper(I)oxid (or other copper compounds like coppercyanat), tin-free coatings based on organic biocides (**Table 2**).

To several of the copper based coatings is also added an organic boosting biocide. Even antibiotics like tetracycline has illegally been used in antifouling paint (Peterson et al. 1993).

Table 2. Some none TBT based organic biocides used in antifouling paints

Compound
Irgarol (2-metyltio-4-tert-butylamino-6-cyclo-propylamino-s-triazin)
Diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea)
Sea-Nine 21 (4,5-diklor-2-n-oktyl-4-isotiazolin-3-on)
Kathon LX (5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-on)
Zinkphyrithione (bis(1-hydroxy-2[1H]pyridinethionato-O-S)-(T4)zink)

Some brief informations on individual antifouling biocides are given below. For more details see Madsen et al. (1998).

Copper (Cu, CuSCN, Cu_2O)

Copper-based coatings leach copper into the water. In the aquatic environment it is the Cu^{2+} ion which is regarded to give the main antifouling effect. Copper is a naturally occurring metal in water and sediment in the marine environment and is non-degradable.

Copper can be bound in a copper acrylate copolymer. On contact with water the surface layer reacts (hydrolysis) with sodium ions in the seawater, releases copper and produces a soluble layer on the surface of the coating. This layer dissolve at a pre-determined rate (self-polishing), and thus maintain a constant release of copper. Copper is often used in combination with a organic degradable biocide (zinkphyrithione) or Irgarol.

Irgarol

The triazine herbicide Irgarol1051 (2-metylthio-4-tert-butyla-mino-6-cyclopropylamino-s-triazine) manufactured by the Swiss company Ciba-Geigy has been introduced in some comparatively new antifouling paints (Tolosa et al. 1996) in combination with copper (Dahl and Blanck, 1996) or TBT. Irgarol inhibits primary colonisation and the growth of algae through its effect on photosynthesis.

Substantial levels of Irgarol have been found in coastal waters (Tolosa et al. 1996, Dahl and Blanck, 1996) and microalgal communities in contaminated coastal waters are likely to be damaged (Dahl and Blanck, 1996).

Biologists are warning that little is known about the toxicity of Irgarol 1051 to other marine organisms, or its behaviour in the environment (Pearce, 1995). The limited information that is available gives cause for concern (Pearce, 1995).

Diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea)

Diuron has effects on planst by interfering with the photosynthesis. Used in combination with copper as an alternative to Irgarol.

Sea-Nine 21 (4,5-diklor-2-n-oktyl-4-isotiazolin-3-on)
Sea-Nine is based on a compound from the 3-isothiazolone class.
According to the producer (Rohm and Haas Co. in Philadelphia, USA), Sea-Nine is not a reproductive toxin and does not bioaccumulate in marine organisms. Madsen et al. 1998 however states that there is

too little information on the bioaccumulations properties of the compound and suggests that Sea-Nine degrades slowly in sediments.

The minimum release rate required for inhibition of many species is approximately 5 $\mu gcm^{-2} d^{-1}$, wheras barnacles and diatomes require >20$\mu gcm^{-2} d^{-1}$ (Vasishtha et al. 1995).

A biocide related to Sea-Nine are Kathon LX, a 3 to 1 mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-on .

Zinkphyrithione (bis(1-hydroxy-2[1H]pyridinethionato-O-S)-(T4)zink)

Apart from preventing fouling this biocide also affect fungi, bacteria and yeast. Zinkphyrithion is used in shampoos for hair treatment. The substance is highly degradable in seawater by hydrolysis and photolysis. Degradation products are stable. Zinc Pyrithione has received U.S. EPA Registration for Use in Marine Antifouling Paints. Zinkphyrithione has had a widespread use since 1991 in Japan, where it has been an important biocide for paint formulations on thousands of ships, including many large ocean-going vessels. In Europe, this biocide has chiefly been used in antifouling paints for yachts.

2.2 Copper-nickel hull to prevent fouling

Fouling organisms attach themselves to some metals and alloys more readily than they do to others. Steels, titanium and aluminium will foul readily, whereas lead plating was used against fouling on ships as long as 2000 years ago (Clare, 1996). The British Admiralty used sheets of copper nailed to wooden ships as far back as in 1761.

Copper-based alloys, including copper-nickel, have good resistance to biofouling, and boats with a hull of copper-nickel are found to bee free of fouling (and corrosion) for several years (Plesman, 1997). The copper-nickel alloys chosen for application in sea generally contain 10-30 percent nickel. Copper-nickel as a hull material was first used in 1941 in the construction of a yacht with a 2mm thick hull.

Generally there are little information in the scientific literature on the antifouling effect of copper-nickel. Most of the information presented here has been obtained from internet (http://marine.copper.org/1-toc.html) if not stated otherwise.

The mechanism of the antifouling effect is unclear. The effect seems to be strongly linked to the nature of the film formation on the alloys' surfaces. It has been claimed that the initial cuprous oxide film that forms on the surface is fouling-resistant, but when it oxidises after extended exposure to form a green cupric hydroxychloride, fouling seems to increase. Because the cupric hydroxychloride film is unstable, it can be easily removed, preventing permanent attachment of marine organisms. Once the cupric hydroxychloride is sloughed off, the exposed surface regains its resistant to fouling.

Tests indicate that resistance to biofouling relies on the copper-nickel being in the freely corroding state (no cathodic protection). With cathodic protection, some biofouling will occur. The need for copper and copper-nickel to be freely corroding to exhibit biofouling resistance has led some researchers to believe that it is the copper ion entering the sea water that is toxic to marine organisms. The mechanism behind the antifouling effect is however not fully known.

A number of copper-nickel hull ships less than 25 m in length were constructed before 1991(http://marine.copper.org/5-table1.html). For larger ships, solid copper-nickel hulls are impractical, and no such ships have been built.

Larger ship can instead be covered with thin sheets of copper-nickel on top of the steel hull. Economic analysis indicates that copper-nickel sheathing of large ships can compete economically with other more conventional antifouling systems (http://marine.copper.org/5-methods.html). Copper-nickel hulls require special attention to prevent contact corrosion.

Other alloys have also been suggested (Mukherjee, 1997)

The literature gives little information on new developments in the use of copper-nickel as an antifouling agent on large ships. Most of the information presented here are from before 1991 and stems from the Copper Development Association, a non-trading organisation sponsored by the copper producers and fabricators to encourage the use of copper and copper alloys.

In an article from 1991 on Copper-Nickel Alloy Sheathing of Ship Hulls and Offshore Structures (http://marine.copper.org/5-sheathing.html) Dale T. Peters from Copper Development Association concludes:
"Copper-nickel as a ship hull material, as verified in the experiences of the many smaller craft built to date, does, as has been claimed, provide corrosion protection and eliminate fouling of the hull, both of which contribute to reduced requirements. But these concepts have not yet been combined on a large ocean-going vessel to effect the advantages observed when the concept is applied to smaller craft. This may be because a variety of technical and economic issues remain unresolved in the minds of members of the ship building community"

Problems related to TBT have increased our awareness on toxic compounds from antifoulants. Even copper-based coatings are restricted in use in certain areas. It is unclear to what degree the use of copper-nickel is a non-toxic method for antifouling. This probably means that leaching of copper (and nickel) from possible future ships plated with copper-nickel sheets has to be considerably less than from conventional copper based coatings in order to be an environmentally acceptable method. In addition the concept has not yet been fully tested technically on large ships.

In our opinion the application of copper-nickel on large ships to avoid fouling is an interesting concept, at least for new ships. The lack of more recent information (after 1991) from several independent sources makes it, however, difficult to judge the strength of the concept as an antifouling system on future large ships. More development and testing are probably a prerequisite for its potential future success.

2.3 Electrolytic system, formation of ClO^-

The Japanese Ship and Ocean Foundation (SOF) and Mitsubishi Heavy Industries (MHI) have developed an antifouling system based the formation of ClO^-through electrolysis of seawater (Bretram, 1996).

The system requires that the hull of the ship is covered with an insulating layer (Epoxy resin). This layer is then covered with a conductor made of karbon-acryl resin (the conductor on the two sides of the boat are isolated from each other and functions as cathode and anode respectively). The conductor is protected with a third layer (carbon-acryl resin). By applying a direct current between the two electrodes the biocide ClO^-develops at the anode and prevents fouling. The direction of the current has to be changed regularly in order to protect both sides of the ship. The use of ClO^- for antifouling is a concept that has been used in cooling water systems for many years.

The system has been tested both on panels in the harbour of Nagasaki and on a few ships and is reported to be promising and will be tested further (Bretram, 1996).

The method rely on the biocidal properties of ClO-, the system is therefore, strictly speaking, not "non-toxic". It is expected that ClO- which escape from the hull will react with other compounds in the water and probably do not represent a threat to marine life in the open sea but could be a problem in harbours.

The success of the system lies in its possible acceptance as a "non-toxic" system and the costs of applying the relatively complicated coating. In our opinion the system is probably most effective on slow going ships and for ships in harbours.

3. Physical methods for antifouling

3.1.1 Ultra smooth/non-stick surfaces

Ultra smooth surfaces are sought in order to weaken or eliminate the adhesive bond between fouling organisms and the coating. The organisms may be dislodged by their own weight or by the motion of the ship through the water. Ultra smooth surfaces prevent the fouling organisms to settle permanently.

For most organisms, minimal adhesion is associated with low surface energy. The free energy of the surface is believed to be the dominant factor in adhesion. Surface free energy is the excess energy of the groups, atoms or molecules on the surface compared with their counterparts in the thermodynamically homogeneous interior (Brady, 1997). The size of the free energy represents the capability of the surface to interact spontaneously with other materials. Silicone elastomers and to a lesser degree fluoropolymers (teflon=polytetrafluoroethylene), have received most attention regarding their potential use as non-stick coatings (Callow and Fletcher, 1994). The development of a non-stick material is however not only a matter of the surface properties but also of the adherend used by the potential foulers (Brady, 1997).

Silicone elastomeres are based on a backbone of (-Si-O-) units with the non-backbone valencies of the silicone attached to other types of organic radicals (Clarkson, 1998 referred in Callow and Callow, 1998a). Silicone elastomeres are one of the most flexible chain molecules known. The basic molecular structure of a silicone elastomere with pendant methyl groups, is shown in figure 4.

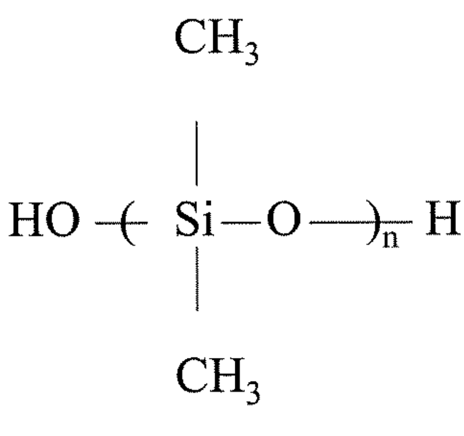

Figure 4. Siliconebased polymere (hydroxyterminated polydimetylsiloxane)

Non-stick coatings are supposed to provide smooth, low friction, hydrophobic surface. Investigations indicate that minimal long-term adhesion is associated with surfaces having initial surface tensions between 20 and 30 dynes/cm (mN/m), i.e. low energy surfaces (Callow and Fletcher, 1994). In order to be defined as a non-stick coating, it has been suggested that it must be possible to detach all fouling deposits with a mechanical (brush) or hydrodynamic (water lance or flow) force of less than 20 pounds per square inch (psi) (Baier 1998). The mechanical strength of non-stick coatings is generally limited compared to other coatings.

Several siliconebased formulations have been tested. A poly dimethyldiphenylsiloxane has been found to have a hydrophobic surface and also showed good resistance to fouling (Edwards et al. 1994).

Filler-free polymeric dimethylated vinylsiloxanes is claimed to be the best of such coatings (Baier, 1998).

The "ultra smooth" coatings developed so far are mostly based on silicone compounds. About 40 patents based on "ultra-smooth" (non-stick) technology have been registered but only few products are commercially available (Watermann et al. 1997).

Some producers of such silicone based coatings claim it will be effective for up to 60 months on fast ships. Slow ships require more frequent cleaning. On slow ships the coating does not completely prevent fouling but make the surface easier to clean.

There have also been some efforts to improve the properties of non-stick coatings by chemically linking a biocide to the siliconbased elastomere (Dixon et al. 1994, Clarkson and Evans, 1995). This combines the non-stick and biocide strategy (Dixon et al. 1994). The tests performed have shown that the initial biocidal effect in these "hybrid" coatings is caused by a surplus of unreacted biocide, which initially leach from the polymer (Clarkson and Evans, 1995). The biocide in the polymere can thus not be classed to be non-leaching in its nature (Clarkson and Evans, 1995).

Siliconbased coatings may also unintentionally contain other potentially toxic compounds. Example of this is organotins used as catalyst during polymerization of the silicone elastomere (Waterman et al. 1997). Since an applied catalyst like diorganotin can be contaminated with triorganotin, coatings may also contain small amounts of toxic compound. Experiments by Watermann et al 1997, however, indicate that leaching of organotin from siliconbased coatings are orders of magnitude lower than recommended for organotin based coatings. The presence of other catalyst related compounds like fatty acids (from dibutyltin dilaurate) may even enhance adhesion and chemoattraction of fouling alga (Callow and Callow, 1998a). Such examples show that coatings based on the "non-toxic" concept should also be tested/evaluated for possible environmental effects.

Some commercially available silicone based coatings are Bioclean DX (Cugoku), Biox (Kensai Paint Company Ltd) and Intersleek (International, Courtaulds Coatings) and Everclean (NOF) which in experimental field trials all are shown to be effective in the prevention of macrofouling (Watermann et al. 1997). Laboratory assays with cyprids (*Balanus amphitrite*) indicate that some silicone-based products do not reduce initial settling. The adhesion forces of settled adult barnacles to silicone based coatings are however generally reduced by a factor of 20 compared to other conventional coatings (Watermann et al. 1997).

At presence the non-stick concept based on silicone containing coatings seems to be a realistic non-toxic alternative to the use of TBT for antifouling on fast ships. Furthermore, several coatings based onon the non-stick concept are commercially available.

One of the producers (International, Courtaulds Coatings) will shortly have two versions of their silicone based product available, one for Fast Craft, and one for Scheduled Ships (Containers, Reefers, Cruise Liners, Car Carriers, Large Ro-Ro's etc.). At present they only sell the Fast Craft version. The Fast Craft version is for vessels going at > 30 knots, whereas the Scheduled Ships version is for vessels trading at > 15 knots (Pers.com. Colin Anderson)

International do not have any geographical restrictions on these products and they are claimed to work well in both the high fouling areas such as the Caribbean as well as in the low fouling areas such as the Baltic.

3.1.2 Surface texture

Suggested systems based on special surface texture is inspired by the idea that physical structures on the surface will prevent settlement of larvae and spores. The basic idea is in many respects opposite to the none-stick concept (see 3.1.1.)

One suggested system is based on having a multiplicity of ribbons made of thin plastic film planted on a surface. The idea is that the ribbons fixed to the surface will flutter in the seawater and prevent marine growth on the surface (Taniguchi et al. 1990). There is no information available on results from practical tests of the system.
The system may perhaps reduce/delay fouling somewhat but in our view the concept is not likely to be sufficiently effective for antifouling on large ships. If such a system would be effective for antifouling, the large hull roughness would probably increase fuel consumption to a degree that is not compatible with the requirements of the shipping industry. A similar conclusion is reached based on a Swedish test with a fibre containing paint (Madsen et al.1998).

3.1.3 UV-light

Experiments have demonstrated the sensitivity of mussel larva to ultraviolet radiation (Chalker-Scott et al. 1994). Their study used a xenon arc lamp (400 watt). Various life stages of *Dreissenia polymorpha* (veligers, -post-veligers, young adults, and adults) were exposed to one of four ranges of radiation: 1) visible light (radiation >400 nm); 2) visible light + UV-A (320-400 nm); 3) visible light + UV-A + UV-B (280-320 nm); and 4) visible light + UV-A + UV-B + UV-C (radiation < 280 nm).

The study showed that veliger and post-veliger larvae were extremely sensitive to even short exposures of UV-C and UV-B. UV-C and UV-B were both effective in inducing 100% mortality. In contrast, neither visible light nor UV-A induced behavioural changes. Young adult and adult mussels are more resistant to UV-C and UVB as their shells are opaque, yet they can also be killed if exposure periods are long enough. No information is available on the practical application of UV-light as a method for preventing fouling on ships.

3.1.4 Sound (ultrasound, low frequent sound)

To assess the potential for non-toxic fouling control using 28 Hz vibration, experiments have been conducted in laboratory studies using settlement stage barnacles and bryozoans (Rittschof and Costlow, 1987). The vibrations were not alone sufficient to prevent fouling. Also Branscomb and Rittschof, (1984) reports that low frequency sound waves (30Hz) is a means of inhibiting barnacle settlement, although percent settlement tends to increase with age of the larvae. The metamorphosis of cyprids are affected up to the 13 day stage (Branscomb and Rittschof, 1984).

Several commercial sound-based systems for small boats have been on the marked. Barnaclean™ Hullsonic™ and Soniclean are three such anti-fouling systems. Product information from the producer claims that Barnaclean™ is the original sonic antifouling system. This system use a pulsed low-frequency sonic signal that prevents hull fouling from barnacles, zebra mussels, oysters clams and tubeworms.

The Hullsonic™ system is claimed to prevent attachment by barnacles, mussels and similar marine animals on vessels up to 120' in length.

The Soniclean system comprises a number of sonic resonators. The number of resonators are dependant on the size of the hull or structure, typically ten feet apart. In operation, the resonators emit a complex and unique mixture of oscillating tones through the hull, which are barely audible to the human ear. The effect of this is to deter crustaceans from attaching themselves to the structure or hull. The available information indicates that the system may reduce fouling by early settlement of crustaceans. There is, however, little information on possible effects on other potential fouling organisms.

There are indications that the vibrations may do some harm to glass-fibre hulls of small boats. It is also possible that the vibration may be a nuisance to the crew on board the ship.
Generally there are a limited information on the performance of the system.

3.1.5 Electric stunning

Pulsed electric fields can affect the settling of zebra mussels. Experiments suggest that pulsed (100 Hz) electric fields (20 V/cm) can stun mussel larvae and affect settlement of the zebra mussels (Schoenbach et al. 1997). It was concluded that complete prevention of settlement is likely to be achieved by increasing the electric field at reduced pulse duration. No information is available on the application of electrostunning as a method for preventing fouling on ships.

4. Mechanical methods for antifouling

4.1 Mechanical and high pressure cleaning

A clean underwater hull can be maintained by regular mechanical cleaning. Today the development of mechanical cleaning technology has just started and the practical implementation of such methods is limited. Mechanical cleaning systems are suggested for pleasure crafts in Denmark (Madsen et al. 1998). Mechanical cleaning systems require frequent treatment when used on traditional paints without some sort of biocide effect. Small boats in coastal areas in temperate regions probably have to be mechanically cleaned 4-6 times pr. year (Madsen et al. 1998). The cleaning frequency necessary for larger ships will vary considerably. Generally the frequency will be higher in tropic regions than in temperate regions. The frequency will also be lower for ships predominantly sailing in oceanic areas compared to in coastal areas.

A relatively hard smooth coating is needed to prevent damage by the cleaning system. The non-stick coatings are due to their relative soft nature probably not particularly well suited for mechanical cleaning.

For large ships the system requiresan international network of cleaning stations at strategic locations world-wide.

Periodical mechanical cleaning alone is not likely to be a satisfactory antifouling system for large ships, due to the need for frequent treatment.

In combination with other systems (super smooth surface) high pressure cleaning is a realistic alternative to the use of TBT. The cleaning frequency will probably increase considerably on ships with a speed slower than 15 knots. The algal (predominantly diatoms) slime reported to develop after some time on "non-stick" coatings can be removed by high pressure cleaning with water. After such treatment the coating will be effective against antifouling again.

5. Biological methods

5.1 Grazing organisms

An important factor controlling the distribution of rocky-shore organisms is interaction between the organisms, including grazing and predation as important regulating factors. The most familiar example is probably starfish-predation on populations of mussels. Marine biofouling communities do not usually include limpets, but these are common on most rocky shores and have a major effect on the structure of the intertidal benthic communities. Limpets are generalist herbivores, but nevertheless known for their ability to keep underwater surfaces free from barnacles (Menge 1976; Denley & Underwood 1979) and other organisms such as serpulid polychaetes, bryozoans and seaweed, as shown by Safriel *et al.* (1993) in their experiments. Transplantation of adult limpets onto newly submerged objects may effectively prevent the development of biofouling by the means of the limpets feeding on newly attached algae and by dislodging newly attached animals. However, barnacles attaining a certain size-range (species dependent) normally become immune to limpet-induced mortality and this leads to reduced effect of the limpets. Safriel *et al.*(1993) ran their experiment for 215 days and maximal effect of limpets was attained after 65-90 days (depending on depth). However, throughout the whole period biofouling mass was significant reduced by the transplanted limpets.

Biological cleaning of submerged artificial surfaces has so far been tried experimentally. However, the results gained by Safriel and Erez (1994)and Safriel et al (1993, 1994) indicates the potential of limpets as agents for long-term biological control of biofouling on stationary objects, and that the topic needs further studies.

The use of grazing or predating organisms to reduce the number foulers on stationary structures could have some potential, but is not likely to be a method with sufficient efficacy on large moving ships.

5.2 Natural physical and chemical defence against fouling

Aquatic organisms run the risk of being overgrown by other organisms, and have therefore evolved strategies to avoid this. Physical, chemical and behavioural defence are the main strategies evolved (Becker and Wahl, 1996).

Two of the reasons for looking towards naturally occurring strategies in order to find new methods or compounds for the prevention of fouling are:

- Given the huge number of species in the marine environment, the probability of finding suitable methods/compounds are large.

- A belief that such methods will be more environmentally safe than our current method. We do however know that some of the most toxic compounds known are of biogenic origin.

5.2.1 Physical defence-sloughing of surface tissue

Exudation of mucus and shedding of surface tissue (epithelial cells) can influence biofouling and reduce overgrowth (Keats et al. 1997). Fish are, apart from some specialised parasites, free from fouling organisms, probably partly due to exudation of mucus. Similar systems have not been developed for ships, although, the self-polishing systems partly rely on the gradual disappearance of the top layer of coating.

5.2.2 Chemical defence

Many marine organisms have the ability to produce substances with antifungal, antibacterial, antialgal, antiprotozoan or antimacrofouler properties (Wahl et al. 1994, Olguin-Uribe et al. 1997, Tsukamoto et al. 1997, Hattori et al. 1997, Konig and Wright, 1997, Jensen et al. 1998, Callow and Callow, 1998b). Isolated natural antifoulants belong to many different groups of organic substances (see review by Clare 1996) some of which are fatty acids, terpens, terpenoids, lipoproteins, glycolipids, phenols, lactons, alkaloids and peptids.

Substances with antifouling properties have been extracted from bacteria (Kon-ya et al 1994b), algae (De-Nys et al. 1995, Todd et al. 1993, Callow and Callow, 1998b), corals (Gerhart et al.1988, Mizobuchi et al. 1996), sponges (Willemsen, 1994; Fusetani, et al. 1996), bryozoans (Kon-Ya et al. 1994a) and ascidians (Teo and Ryland, 1995, Wahl et al. 1994).

Such biogenic substances may in the future be used for the prevention of fouling (Abarzua and Jakubowski, 1995). It has been reported that the antifouling activities of some of these compounds match TBT (Kon-Ya et al. 1994).

Antifouling systems based on compounds found in marine organisms are promising (Fusetani, et al. 1996, De-Nys et al. 1995, Clare, 1995), but not without problems (Clare, 1996).

- We do not yet fully know how such defences systems work and evidence for an ecological role is still poor
- The compounds may be highly species specific and effect only a small fraction of potential fouling organisms.
- The compound in question has to be shown to be effective for a wide range of fouling organisms both in tropic and temperate regions.
- The active, often complex, compounds involved may be difficult and expensive to synthesise.
- Production of natural biocides must be based on industrial/biotechnological production rather than harvesting. A large scale harvesting of naturally occurring populations in order to extract active compounds may lead to environmental consequences.
- The toxic properties of the compound have to be tested, and the environmental consequences of large-scale use must be evaluated and approved as for other new biocides.

The structural properties of naturally occurring antifouling compounds may give clues to what type of function groups on the molecule which are responsible for the observed effect, and be a key to finding out how these compounds can repel fouling organisms. Some similarity in functional groups has been noted for some of the biologically active natural compounds. The presence of furan or lactone rings is one common feature for some of the compounds (Clare, 1996).
The identification of such key groups could facilitate the finding of compounds that are structurally simpler than those identified in marine organisms and thus probably more easy to produce on an industrial scale.

When a suitable naturally occurring antifouling compound has been identified and proved environmentally safe, the challenge is to incorporate the compound in a coating that can prevent fouling for 3-4 years.

Patents involving the use of naturally occurring compounds have been awarded.

The development of a complete antifouling system based on such naturally occurring compounds lies probably at least 5 years ahead.

5.2.3 Bacteria/ Enzymes

The presence of bacterial polymers on a submerged substratum stimulates settlement, attachment and metamorphosis of fouling larvae. The proteins (lecitins) produced by some larvae, bind specifically to extracellular bacterial polysaccharides. The use of enzymes or bactericides to break the sticking of the bacteria (Plesman, 1997) first to colonise a submerged surface may thus be a future method for the prevention of fouling.

The bacteria may through secretion of exopolymers affect settling by modifying surface energy and texture. The effect on the settling organism may however vary depending on the conditions under which the bacterial film develops and the species of the bacteria within the film.

There are also evidence that metabolites from some ascidians influence bacterial settlement (Wahl et al. 1994)

An antifouling method based on bacteria or enzymes is in an early stage of development and studies on the influence of bacterial exopolymers on the attachment of a diatom show that there is a complex relationship between surfaces and attaching organisms (Gawne et al. 1998).

Tetracycline is a man made bactericide used in human and veterinary medicine and affects a broad spectrum of bacteria. Illegal use of antibiotics in antifouling paint has been reported (Peterson et al. 1993). Tetracycline in antifouling paint is unlikely to be an effective antifoulant (Peterson et al. 1993).

From an environmental point of view the introduction of large amounts of antibiotics to the marine environment is unacceptable and may also in the long run not be effective due to development of resistant bacteria. Experiments have shown that such resistance may develop if antibiotics are introduced to marine sediments (Nygaard et al. 1992).

6. Environmental safe antifouling systems - recommended areas of research and development

The environmental problems posed by TBT and other biocides in antifouling coatings have led to efforts to develop non-toxic alternatives. Two main avenues are being pursued (c.f. Clare, 1998)

- The development of non-stick coatings that interfere with the normal adhesion of marine organisms.
- The isolation of natural marine products that inhibit settlement of potential epibionts on the host organism and accordingly could be incorporated into coatings to inhibit fouling on man made structures.

The non-stick approach is in its nature a non-toxic method, where it is the physical properties of the surface of the coating and hydrodynamic energy which in combination prevent the permanent attachment of fouling organisms. The system requires that the structure to be protected from fouling has to be moved regularly relative to the water in its surroundings in order to provide sufficient energy to remove settled organisms. In essence it is the speed needed to remove these organisms that limits the use of the non-stick method. For the most recent products on the marked this minimal recommended speed is approximately 15 knots. This means that for a relative large proportion of the Norwegian fleet, non-stick coatings will not alone be a good alternative to the use of TBT. One of the challenges in the future will be to reduce the minimum speed needed for the non-stick coatings to be effective.

The effort to combine the non-stick and biocide strategy (Dixon et al. 1994) by incorporating a biocide in the silicone polymer by chemical linkage (Dixon et al. 1994, Clarkson and Evans, 1995) is interesting if this could result in improved antifouling properties without leaching of the biocide. So far this seems not to have resulted in major improvements. In general, a chemical has to be soluble in the tissue of an organism in order to have a toxic effect. From a theoretical point of view it seems that to combine the non-stick and biocide strategy with the object to produce an improved coating caused by a non-leaching biocide, is a contradiction.

An alternative strategy would be to include a "deactivated biocide" in the polymer in a manner which triggers activation and leaching only on contact with important fouling organisms or important parts/chemicals of their adhesive system (Barnacles: cyprid cement). Such a system is at present hypothetical. The development of more comprehensive non-stick systems requires both more fundamental knowledge about the physiological mechanisms of larval attachment and will be a challenge for the organic polymer chemists (Brady 1997). It thus seems that an universal non stick coating for ships of all speeds remains well in the future.

The "natural product approach" is based on a belief that such natural products do not cause environmental disturbances. This is generally true based on the amounts produced under normal conditions in the field. The situation may however be considerable different if they are produced on an industrial scale for the use on large ships around the world.

The literature on natural antifoulants is wide and scattered and the list of compounds with some sort of antifouling activity is long and the potential for discovering additional natural antifoulants is great (se review by Clare, 1996). Many of the natural products identified are not commercially exploitable from natural populations without resulting in serious environmental consequences.

Generally, the natural compounds identified are diverse in structure and often complex. Some of the identified compounds have, however, common structural features, which could lead to identification of the functional group responsible for the antifouling effect. The identification of such key groups could facilitate synthesis of compounds that are structurally simpler than those identified in marine organisms and thus probably more easy to produce on an industrial scale sufficient to supply the marine paint industry.

The use of information from research on natural products to design new antifouling paints, does *a priori*, not necessarily infer that the active ingredient is "environmentally sound". Such compounds therefore should be tested for possible environmental effects on the same terms as recommended for traditional "man-made" biocides.

Given the huge number of species in the marine environment, the probability of environmental effects in non-target habitats and organisms is considerable. The effects caused by the use of TBT clearly shows the difficulty in designing tests that cover most relevant ecological units in the marine environment. The development of more comprehensive tests is therefore a recommended area of future research. In any case such tests will hardly be able to exclude the risk that serious environmental effects may be found at a later stage. This advocates that fate and degradation properties of suggested natural or semi-natural compounds will be of utmost importance.

Antifouling systems based on compounds found in marine organisms are promising on long term basis. The development of a complete antifouling system based on such naturally occurring compounds lies at least 5 years ahead.

There are generally little information on the possible use of physical methods like surface texture (3.1.2), UV-light (3.1.3), sound (3.1.4) and electric stunning (3.1.5) on large ships. With the reservations inherent in the limited information available, we conclude that these methods are either unpractical or too dubious in nature to be recommended for further development for large ships.

The use of copper-nickel hull (2.2) and the electrolytic approach (2.3) seems to have a potential. The main obstacle for the use of antifouling methods based on these two approaches, are partly that they are toxic in nature. The electrolyte approach may be an alternative to slowly moving ships or ships that lay in harbours for long periods.

The use of copper-nickel in preventing antifouling is an old but still interesting concept. The method is probably at least as environmental safe as the use of traditional copperbased coatings (without boosting biocides). We do, however, not fully know the mechanism behind the antifouling properties of the system. The amount of leaching of copper should be compared with traditional copper-based coatings. In our opinion too little independent information is available to foresee the long-term potential of the system. As the system probably will be impossible to use on existing large ships, the system is not a likely alternative to the use of TBT within the time frame in question (2003, 2008). In any case considerable development is needed on the shipbuilders side.

In essence it is only the non-stick approach for antifouling, which are both realistic for use on fast (<15 knots) ships and at the same time non-toxic in nature.

The most obvious non-toxic option for slow moving ships is to be cleaned regularly. Slower ships with coatings without a biocide effect probably need to be cleaned up 4 to 6 times pr year and under certain conditions even more often. The system requires an international network of cleaning stations at strategic locations world-wide. We believe that periodical cleaning alone is not likely to be a satisfactory (for the ship owners) antifouling system for large ships, partly due to the need for frequent treatment, but could be a good approach in combination with non-stick systems. Future research and development should focus on optimising a "low-stick/periodical cleaning system" in a direction to service ships with a speed below 15 knots.

Several research programs related to the development of new environmental sound methods for antifouling have been launched (Examples: MASTEC in Sweden, NERC Special topic (MBTP) in England, several projects in Germany (http://members.aol.com/limnomar/pro-foul.htm), ANTIFOUL in the EU program BRITE/EURAM). New developments are expected from such programs and from ongoing research performed by the producers of marine paints during the next years.

Various non-toxic antifouling strategies have been elucidated. At present there seems to be no good fully tested biocide free method ready to use for all types of vessels. It is expected that biocides will be a part of antifouling systems on slow ships for many years. It is therefore important that the fate and possible effects of all types of compounds (also natural based) on none-target organisms in none-target habitats are known and found acceptable. In essence we are striving to find methods that prevent settlement on the hull of ships but cannot accept harmful effects on non-target species in non-target habitats. In order to accomplish this it is essential to elaborate existing test systems.

7. References

Alzieu, C., J. Sanjuan, J.P. Deltriel and M. Borel, 1986. Tin Contamintion in Arcachon Bay: Effects on Oyster Shell Anomalies. Mar. Pollut. Bull. 17 (11):494-498.

Alzieu, C., 1998. Tributyltin: case study of a chronic contamination in the coastal environment. Ocan & Coastal Management, 40, 23-36.

Abarzua, S. and Jakubowski, S., 1995. Biotechnological investigation for the prevention of biofouling. I. Biological and biochemical principles for the prevention of biofouling. Mar. Ecol. Prog. Ser. 123, 301-312.

Anderson C.D., 1998. TBT and TBT-free antifouling paints- efficiency and track record.

ASMO, 1998. Cause for concern about inputs in the marine environment of new antifouling agents as alternatives to TBT. Oslo and Paris conventions for the prevention of marine pollution environmental assessment and monitoring committee (ASMO), 98/5/5-E.

Baier, R., 1998. Polymeric surfaces designed to optimize both fouling-release and drag reduction properties. Abstract from MASTEC-Non-toxic control of marine biofouling symposium in Sweden, 1998.

Becker, K. and Wahl, M., 1996. Behaviour patterns as natural antifouling mechanisms of tropical marine crabs. J.Exp.Mar.Biol.Ecol.,1996, 203, 245-258.

Berge, J.A., Berglind, L. Brevik, E.M., Følsvik, N., Green, N., Knutzen, J., Konieczny, R., Walday, M. 1997. Levels and environmental effects of TBT in marine organisms and sediments from the Norwegian coast. A summary report. NIVA report no. 3656-97, 36p.

Beaumont, A.R. and P.B. Newman, 1986a. Low level of tributyl tin reduce growth of marine micro-algae. Mar. Pollut. Bull. 17:457-461.

Bretram, V. 1996. Innovatives Antifouling-System. Hansa., Hamburg, 133 (2), 43-44.

Brady, R. F., 1997. In Search of Non-stick Coatings, Chemistry & Industry, 17, 219-222,

Branscomb, E.S.; Rittschof, D., 1984. An investigation of low frequency sound waves as a means of inhibiting barnacle settlement. J. Exp.Mar.Biol.Ecol. 79, 149-154.

Bryan, G.W., G.R. Burt, P.E. Gibbs and P.L. Pascoe, 1993. *Nassarius reticulatus (Nassariidae: Gastropoda)* as an indicator of tributyltin pollution before and after TBT restrictions, J. mar. biol. Ass. U.K., 73:913-929.

Bryan, G.W., Gibbs, P.E., L.G. Hummerstone and G.R. Burt, 1986. The decline of the Gastropod *Nucella lapillus* around south-west England: Evidence for the effect of tributyltin from antifouling paints. J. mar. biol. Ass. U.K., 66:611-640.

Bryan, G.W., P.E. Gibbs, R.J. Huggett, L.A. Curtis, D.S. Bailey and D.M. Dauer, 1989. Effects of Tributyltin Pollution on the Mud Snail, *Ilyanasa obsoleta*, from the York River and Sarah Creek, Chesapeake Bay. Mar. Pollut. Bull., 20:458-462.

Bushong, S.J., Ziegenfuss, M.C. and Unger, M.A., 1990. Chronic tributyltin toxicity experiments with the Chesapeake Bay copepod, Acartia tonsa. Environmental Toxicology and Chemistry, 9: 359-366.

Callow, M.E.; Fletcher, R.L., 1994. The influence of low surface energy materials on bioadhesion - a review. Marine Biofouling and- Corrosion. 34, 333-348.

Callow, M.E. and Callow, J.A., 1998a. Enhanced adhesion and chemoattraction of zoospores of the fouling alga *Entromorpha* to some foul-release silicone elastomers. Biofouling, 13, 157-172.

Callow, M.E. and Callow, J.A., 1998b. Attachment of zoospores of the fouling alga entromorph in the presence of zosteric acid. Biofouling, 13, 87-95.

Chalker-Scott,-L.; Scott,-J.; Titus,-J., 1994. Brief exposure to ultraviolet radiation inhibits locomotion of veligers and juvenile *D. polymrpha*, 37. Conference of the International Association of Great Lakes Research and Estuarine Research Federation, Windsor, On (Canada), 5-9 Jun 1994, IAGLR, 166, 41.

Clare, A. S. 1995. Natural ways to banish barnacles. New Scientist, Feb 1995, 38-41.

Clare, A. S. 1996. Marine natural product antifoulants: Status and potential. Biofouling, 9, 211-229

Clare, A.S., 1998. Towards nontoxic antifouling. J. Mar. Biotechnol.1998, 6(1), 3-6.

Clarkson, N. and Evans, L.V., 1995. Further studies investigating a potential non-leaching biocide using marine fouling diatom *Amphora coffeaeformis.* Biofouling, 9, 17-30.

Clarkson, N., 1998. The antifouling potential of silicone elastomer polymers. In: Fingerman, H., Nagabhushanam, R and Thompson, M.F. (eds), Recent Advances in Marine Biotechnology, Vol. III (In press).

Dahl, B., and Blanck, H., 1996. Toxic effects of the antifouling agent Irgarol 1051 on periphyton communities in coastal water microcosms. Mar. Pollut. Bull. 32, 342-350.

De-Nys, R.; Steinberg, P.D.; Willemsen, P.; Dworjanyn, S.A.; Gabelish, C.L.; King, R.J., 1995. Broad spectrum effects of secondary metabolites from the red alga *Delisea pulchra* in antifouling assays. Biofouling 8, 259-271.

Denley E.J. & A.J. Underwood. 1979. Experiments on factors influencing settlement, survivorship and growth in two species of barnacles in NSW. J. exp. Mar. Biol. Ecol. 36: 269-293.

Dixon,B.G., Morris, R.S. and Walsh, M.A., 1994. A waterborne and non-stick antifouling paint. Journal of Waterborn Coatings, 15, 4-9.

Edwards, D.P.; Nevell, T.G.; Plunkett, B.A.; Ochiltree, B.C., 1994. Resistance to marine fouling of elastomeric coatings of some poly(dimethylsiloxanes) and poly(dimethyldiphenylsiloxanes). Marine Biofouling and Corrosion, 34, 349-359.

Evans, S.M., A. Hutton, Kendall, M.A. and A.M. Samosir, 1991. Recovery in Populations of Dogwhelks *Nucella lapillus* (L.) Suffering from Imposex. Mar. Pollut. Bull., 22:331-333.

Evans , S.M., T. Leksono and P.D. McKinnell, 1995. Tributyltin Pollution: A Diminishing Problem Following Legislation Limiting the Use of TBT-Based Anti-fouling Paints, 1995. Mar. Pollut. Bull. 30, 14-21.

Fent, K. and W. Meier, 1994. Effects of Triphenyltin on Fish Early Life Stages. Arch. Environ. Contam. Toxicol. 27:224-231.

Fusetani, N.; Hiroto, H.; Okino, T.; Tomono, Y.; Yoshimura, E., 1996. Antifouling activity of isocyanoterpenoids and related compounds isolated from a marine sponge and nudibranchs, J. Nat.-Toxins, 5, 249-259.

Gawne, B., Wang, Y., Hoagland, K.D. and Gretz, M.R., 1998. Role of bacteria and bacterial exopolymer in the attachment of *Achnanthes longipes (Bacillariopyceae)*. Bifouling, 13. 137-156.

Gerhart,-D.J.; Rittschof,-D.; Mayo,-S.W., 1988. Chemical ecology and the search for marine antifoulants. Studies of a predator-prey symbiosis. J. Chem. Ecol. 14, 1905-1918.

Gibbs, P.E. and G.W. Bryan, 1986. Reproductive failure in populations of the dog-whelk, *Nucella lapillus*, caused by imposex induced by tributyltin from antifouling paints. J.mar. biol. Ass. U.K., 66:767-777.

Gibbs, P.E, G.W. Bryan, P.L. Pascoe and G.R. Burt, 1987. The use of the dog-whelk, *Nucella lapillus*, as an indicator of tributyltin /TBT) contamination. J. mar. biol. Ass. U.K., 67:507-523.

Green, N., Berge, J.A., Helland, A., Hylland, K., Knutzen, J. and Walday, M., 1999. Joint Assessment and Monitoring Progam (JAMP). National Comments regarding the Norwegian Data for 1997. NIVA-report no. 3980, 144pp.

Hall, L.W. Jr., 1988. Tributyltin environmental studies in ChesapeakeBay, Mar. Pollut. Bull. 19, 431-438.

Hattori,-T.; Adachi,-K.; Shizuri,-Y., 1997. New agelasine compound from the marine sponge *Agelas mauritiana* as an antifouling substance against macroalgae, J. Nat. Prod., 60, 411-413.

Horiguchi, T., H. Shiraishi, M. Shimizu and M. Morita, 1994. Imposex and organotin compounds in *Thais clavigera* and *T. bronni* in Japan. J. mar. biol. Ass. U.K., 74:651-669.

IMO (International Maritime Organization) 1994. Use of triorganotin compounds in anti-fouling paints. Results of TBT monitoring studies. Marine Environment Protection Committee - 35 session Agenda item 17, 7p.

Jensen,-P.R.; Jenkins,-K.M.; Porter,-D.; Fenical,-W, 1998. Evidence that a new antibiotic flavone glycoside chemically defends the sea grass *Thalassia testudinum* against zoosporic fungi Appl. Environ. Microbiol., 64, 1490-1496.

Johansen, K. and F. Møhlenberg, 1987. Impairment of egg production in *Acartia tonsa* exposed to tributyltin oxide. Ophelia, 27:137-141.

Keats-D.W.; Knight-M.A.; Pueschel-C.M., 1997. Antifouling effects of epithallial shedding in three crustose coralline algae (*Rhodophyta, Coralinales*) on a coral reef . J. Exp. Mar. Biol. Ecol., 213, 281-293.

Kon-Ya,-K.; Shimidzu,-N.; Adachi,-K.; Miki,-W., 1994a. 2,5,6-Tribromo-1-methylgramine, an antifouling substance from the marine bryozoan Zoobotryon pellucidum. Fish. Sci. 60, 773-775.

Kon-ya, K., Shimidzu, N., Miki, W and Endo, M., 1994b. Indole derivates as potent inhibitors of larval settlement by the barnacle, *Balanus amphitrite*. Biosci. Biotech. Biochem., 58, 2178-2181.

Konig, G.M.; Wright, A.D. 1997. *Laurencia rigida*: chemical investigations of its antifouling dichloromethane extract. J. Nat. Prod; 60, 967-970.

Madsen, T., Gustavson, K., Samsøe-Petersen, L., Simonsen, F. 1998. Kortlægning og vurdering af antibegroningsmidler til lystbåde i Danmark. Rapport nr. 384 fra Miljø-og Energiministeriet Miljøstyrelsen. 108s.

Matthiessen, P.; Gibbs, P.E., 1998. Critical appraisal of the evidence for tributyltin-mediated endocrine disruption in mollusks. Environ. Toxicol. Chem., 17, 37-43.

Menge B.A. 1976. Organization of New England rocky intertidal community: Role of predation, competition and environmental heterogenity. *Ecol. Monogr.* 46: 355-393.

Minchin, D.; Stroben, E.; Oehlmann, J.; Bauer, B.; Duggan,, C.B.; Keatinge, M. , 1996.Biological indicators used to map organotin contamination in Cork Harbour, Ireland, Mar. Pollut. Bull. 32, 188-195.

Mizobuchi, S; Adachi, K; Miki, W. 1996. Antifouling polyhydroxysterols isolated from a Palauan octocoral of *Sinularia sp.*, Fish. Sci. 62, 98-100.

Mukherjee,-D., 1997. Fighting the marine corrosion - a two-pronged strategy, Invention-Intel., 32 (12), 485-493.

Nygaard, K., Lunestad, B.T., Hektoen, H., Berge, J.A. and Hormazabal, V. 1992. Resistance to oxytertacycline, oxolinic acid and furazolidone in bacteria from marine sediments. Aquaclture, 104:31-36.

Olguin-Uribe,-G.; Abou-Mansour,-E.; Boulander,-A.; Debard,-H.; Francisco,-C.; Combaut,-G., 1997. 6-Bromoindole-3-carbaldehyde, from an *Acinetobacter sp.* bacterium associated with the ascidian *Stomozoa murrayi*, J. Chem. Ecol., 23, 2507-2522.

Pearce, F., 1995. Alternative antifouling widespread in Europe.New-Sci. 145(1960), 7.

Peterson, S.M., Batley, G.E. and Scammell, M.S., 1993. Tetracycline in antifouling paints. Mar. Pollut. Bull., 26, 96-199.

Plesman, M., 1998. Revent progress in antifouling, International Maritime Organization, Marime Environment Protection Committee (MEPC), MEPC 42/INF.7

Poloczanska, E.S. and Ansell, A.D., 1999. Imposex in the whelks *Buccinum undatum* and *Neptunea antiqua* from the west coast of Scotland, Mar. Environ. Res., 47, 203-212.

Ruiz, J.M. , Bachelet, G., Caumette, P. and Donard, O.F.X., 1996. Three decades of tributyltin in the coastal environment with emphasis on the Arcachon bay, France. Environ. Pollut. 93, 195-203.

Rittschof,-D.; Costlow,-J.D.,1987. Macrofouling and its management by nontoxic means.

Advances in Aquatic Biology and Fisheries, Natarajan, P.;Suryanarayanan, H.;Azis, P.K.A. (eds.), pp. 1-11.

Safriel U.N. & N. Erez. 1994. Effect of limpets on the fouling of ships in the Mediterranean. *Mar. Biol.* 95: 531-537.

Safriel U.N., Erez N. & T. Keasar. 1993. Long term effects of transplanted limpets on an experimental marine biofouling community. *Biofouling*. 6: 261-278.

Safriel U.N., Erez N. & T. Keasar. 1994. How do limpets maintain barnacle-free submerged artificial surfaces? *Bull. Mar. Sci.* 54(1): 17-23.

Schoenbach,-K.H.; Abou-Ghazala,-A.; Alden,-R.W.; Turner,-R.; Fox,-T.J., 1997. Biofouling prevention with pulsed electric fields. Conference proceedings: seventh international zebra mussel and aquatic nuisance species conference. 242 pp.

Shiraishi, H. and M. Soma, 1992. Triphenyltin compounds in mussels in Tokyo Bay after restriction of use in Japan. Chemosphere, 24:1103-1109.

Taniguchi, Y., Ohwada, Y. and Araki, M.,1990. Anti-fouling surface structure, anti-fouling covering material and method of planting ribbons for producing anti-fouling surface structure and covering material, US Patent no 4923730.

Teo,-S.L.-M.; Ryland,-J.S., 1995. Potential antifouling mechanisms using toxic chemicals in some British ascidians, J. Exp. Mar. Biol. Ecol., 188,49-52.

Todd, J.S., Zimeran, R.C., Crews, P. and Alberte, R.S., 1993. The antifouling activity of natural and synthetic phenolic acid sulphate esters. Phytochemistry, 34, 401-404.

Tolosa, I., Readman, J.W., Blaevoet, A., Hhilini, S., Bartocci, J. and Horvat, M. 1996. Contamination of mediterranean (Côte d´Azur) Coastal Waters by organotins and Irgarol 1051 used in antifouling paints. Mar. Pollut. Bull. 32, 335-341.

Tsukamoto,-S.; Kato,-H.; Hirota,-H.; Fusetani,-N. 1997. Seven new polyacetylene derivatives, showing both potent metamorphosis-inducing activity in ascidian larvae and antifouling activity against barnacle larvae, from the marine sponge *Callyspongia truncata*. J. Nat. Prod. 60, 126-130.

Vasishtha, N., Sundberg, D. and Rittschof, D., 1995. Evaluation of release rates and control of biofouling using monolithic coatings containing an isothiazolone. Biofouling,9, 1-16.

Wahl, M., Jensen, P.R. and Fenical, W., 1994. Chemical control of bacterial epibiosis on ascidians. Mar. Ecol. Prog. Ser., 110, 45-57.

Wahl, M., 1989. Marine epibiosis. I. Fouling and antifouling: some basic aspects. Mar. Ecol. Prog. Ser., 58, 175-189.

Walsh, G.E., L. L. McLaughlin, M.K. Louise, C. H. Deans and E.M. Lores, 1986. Inhibition of Arm Regeneration by *Ophioderma brevispina* (*Echinodermata, Ophiuroidea*) by Tributyltin Oxide and Triphenyltin Oxide. Ecotoxicology and Environmental Safety 12:95-199.

Watermann, B., Berger, H-D., Sönnichsen, H., and Willemsen, P., 1997. Performance and effectiveness of non-stick coatings in seawater. Biofouling, 11, 101-118.

Willemsen,-P.R., 1994. The screening of sponge extracts for antifouling activity using a bioassay with laboratory-reared cyprid larvae of the barnacle *Balanus amphitrite*. Marine Biofouling and Corrosion, 34, 361-373.

APPENDIX A

PROCCEDINGS

FROM

WORKSHOP
26 NOVEMBER 1998 9A.M. T0 3 P.M

ALTERNATIVES TO THE USE OF TBT AS AN ANTIFOULING AGENT ON THE HULL OF SHIPS

NORWEGIAN MARITIME DIRECTORATE
OSLO

IN CORPORATION WITH

NORWEGIAN INSTITUTE
FOR WATER RESEARCH
(NIVA)

WORKSHOP - 26 NOVEMBER 1998
NORWEGIAN MARITIME DIRECTORATE, OSLO

ALTERNATIVES TO THE USE OF TBT AS AN ANTIFOULING AGENT ON THE HULL OF SHIPS

AGENDA

1. Opening
   Ivar A. Manum , The Norwegian Maritime Directorate

2. The environmental problem with TBT
   John Arthur Berge, The Norwegian Institute for Water Research

3. The TBT problem seen from the Environmental Authorities' point of view.
   Sveinung Oftedal, The Norwegian Ministry of the Environment

4. The latest development following the meeting at IMO MEPC 2nd to 6th of November.
   Jens Henning Koefoed, The Norwegian Maritime Directorate

5. The problem as seen from the shipping industry
   Arne Peder Blix, The Norwegian Shipowners' Association

6. A brief overview of methods for antifouling
   John Arthur Berge, The Norwegian Institute for Water Research

7. Presentation of available products
   A:Ragnar Jahr, Jotun,
   B:Colin D. Anderson, International,
   C:Stefan Andreasson, Hempell [1)]

8. Any other matter

[1)]Presentation not given due to acute illness

WORKSHOP - 26 NOVEMBER 1998
NORWEGIAN MARITIME DIRECTORATE, OSLO

ALTERNATIVES TO THE USE OF TBT AS AN ANTIFOULING AGENT ON THE HULL OF SHIPS

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Presentations at the workshop

Presentation 1

Opening of the of the workshop (in Norwegian with an English summary), Ivar A. Manum , The Norwegian Maritime Directorate

Sjøfartsdirektoratet

SJØFARTSDIREKTØREN's INNLEDNING PÅ TBT-SEMINARET I SJØFARTSDIREKTORATET TORSDAG 26.11-1998

Når Sjøfartsdirektoratet fikk informasjon om at hunn-snegler langs norskekysten utviklet penis på grunn av miljøgiften Tributyltin som kom fra bunnstoff på skip, ble vi igjen minnet om at all utvikling har en pris, og at i dette tilfelle er prisen for høy. For skipsfarten var utviklingen av de TBT-holdige bunnstoffene et betydelig og nærmest historisk skritt forover. Disse stoffene gjorde skipsfarten mer lønnsom, gjorde det mulig å dokksette skip med lengre intervaller og var muligens med å legge grunnen for å kunne bygge de helt store tankskipene. De gjorde også at skipsfarten kunne redusere bruken av de tidligere bly- og kobberbaserte mønjene med alle deres arbeidsmiljø- og miljøproblemer. Når vi nå i ettertid får klargjort at TBT finnes igjen i organisme langs hele kysten, og at det er svært sannsynlig at vi får TBT i oss når vi spiser sjømat må det reageres raskt! Nasjonalt og internasjonalt har det vært intens debatt om hvor fort disse stoffene kan forbys benyttet i bunnstoff for skip. Gjennom arbeidet i IMO og det nasjonale samarbeidet med Statens forurensningstilsyn står Sjøfartsdirektoratet sentralt i kampen for å få forbudt TBT som aktivt stoff i bunnstoff for skip så snart som mulig.

Nå har vi lagt bak oss MEPC 42 i London, som i et enstemmig utkast til assembly-resolusjon angir fart og retning mot et globalt forbud mot maling med TBT-holdig bunnstoff i 2003 og et forbud mot tilstedeværelse av TBT i bunnstoffer i 2008. Dette er gode nyheter sett fra vår side. Det er likevel uhyre viktig å peke på at mye, viktig, arbeid gjenstår. Det skal utarbeides tekst i en ny avtale om bunnstoffer, samt om hvordan alternative systemer skal vurderes for fremtiden. Norge kan med andre ord ikke slå seg til ro med dette i og for seg gode resultatet, uten at vi ser etter brukbare alternativer, både for miljøet i sin helhet og for skipsfarten. Dagens tema er å beskrive alternativer til TBT-holdig bunnstoff. Jeg ønsker dere lykke til, og gleder meg til å se resultatet...

WORKSHOP - 26 NOVEMBER 1998
NORWEGIAN MARITIME DIRECTORATE, OSLO

ALTERNATIVES TO THE USE OF TBT AS AN ANTIFOULING AGENT ON THE HULL OF SHIPS

English summary of opening address:

When the Norwegian Maritime Directorate realised that bottom paint containing Tributyl tin affected snails along our coastline, and that we risk contamination of seafood by TBT etc, with possible consequences on consumers, we found that time had come for a change... The price we pay for TBT is far to high in environmental costs.

Through the national co-operation with the State Pollution Control Authority, the Ministry for the Environment and through IMO, NMD has been in the forefront in the reduction of use of TBT in international shipping. The recent IMO development, including the development of an agreed draft assembly resolution, banning application of TBT from 2003 and presence of TBT from 2008 is a success so far. Much work remains, to develop legal text, and to develop procedures to identify /and accept) alternative anti-fouling systems.

I wish this seminar success, and look forward to hear the results of this one-day event...

Overheads used during presentation 2.

The environmental problem with TBT

John Arthur Berge

The Norwegian Institute for Water Research

The environmental problem with TBT

John Arthur Berge

Norwegian Institute for Water Research
(NIVA)

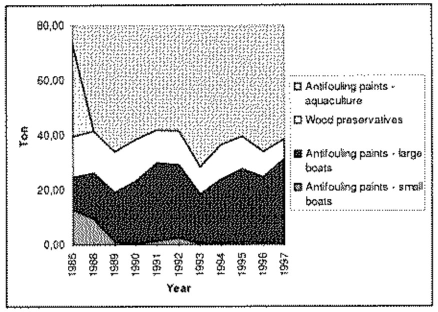
NIVA

The environmental problem with TBT?

- Extremely toxic to certain molluscs (hormone disrupter).
- Effects in non-target organisms worldvide.
- Bioaccumulates in marine organisms (invertebrates, and marine mammals).
- Degradability: moderate (low in sediments).

NIVA

TBT in Norway



NIVA

Half-life for TBT

- Sea-water:
  Days-months.
- Biota:
  Weeks-months.
- Sediment:
  Months-years (>10) .

NIVA

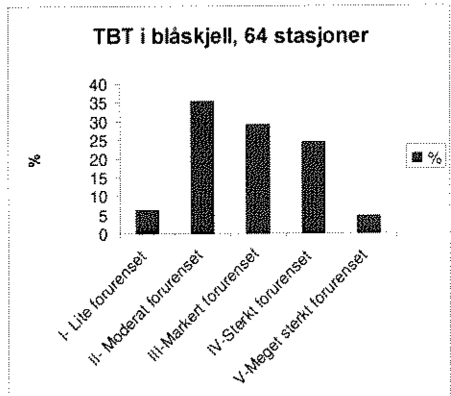
Toxicity of TBT to marine organisms

Taxonomic group	Effect recorded	Exposure time	Concentration (ng TBT/l)
Algae	EC_{50}	3-5 d	300-1000
Algae	LOEC	18 d	100
Crustaceans	LC_{50}	48h-6d	400-100000
Crustaceans	LOEC	6d-56d	10-300
Fish	LC_{50}	48h-21d	900-27000
Fish	LOEC	28-225d	100-500
Molluscs (juveniles)	LC_{50}	48h	1000-3600
Molluscs,	EC_{50}, growth	48h-20d	50-240
Molluscs,	EC_{50}, calcification		<10
Molluscs	LOEC, imposex		<1

LOEC=Lowest observed effect concentration
Data recalculated fromMadsen et al. 1998

NIVA

Classification Concentrations of TBT in blue mussels from Norwegian harbours



Classification (mg/kg d.w.)
I < 0.1
I I = 0.1-0.5
III = 0.5-2
IV = 2-5
V = >5

NIVA

Effects of TBT on blue mussels (Mytilus edulis)

- Blue mussels are not especialy sensitive to TBT.
- Threshold for effects on energy budget: 2 mg TBT/kg d.w.
- Threshold for effects on feeding activity:3-4 mg/kg d.w.

NIVA

Concentrations of TBT in the water from Norwegian harbours?

- Bioconcentrationfactor (BCF) for TBT i blue mussels: 10000
- The concentrations of TBT found in mussels results in calculated concentrations in the water in the range 1-300 ng TBT/l, mostly 5-50 ng/l.
- Threshold for effects on sensitive marine organisms: ~1-2 ng TBT/l.

NIVA

How much TBT is needed to induce effects in sensitive organisms in the top 10 m of a coastal area?

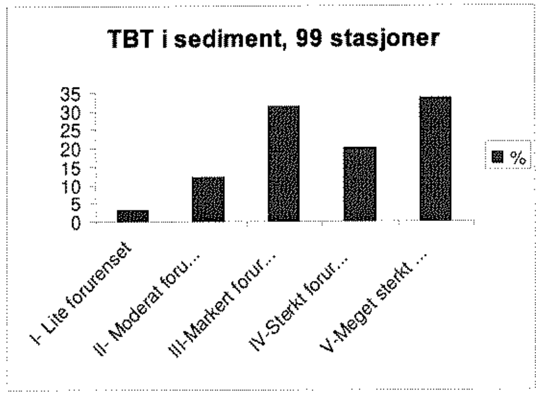
Threshold for effects on sensitive marine organisms:1 ng TBT/l.

- Inner Oslofjord (192km^2): 1.9kg.
- Baltic Sea (366000 km^2): 3.7t
- North Sea (575000km^2): 5.9t

Sales volume of TBT in Norway in 1997 for antifouling purposes:31.5t

NIVA

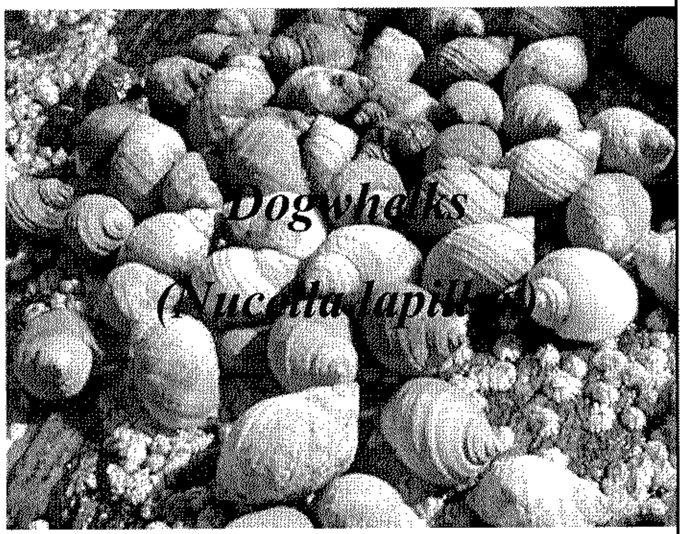
<u>Classification</u> Concentrations of TBT in sediments from Norwegian harbours



<u>Classification(µg/kg t.v.)</u>
I < 1
II = 0.1-5
III = 5-20
IV = 20-100
V = >100

NIVA

Sensitive species to TBT



NIVA

What is imposex ?

- Induction of male sex characters in female snails, known as "imposex", observed mainly in neogastropods.
- Development of penis and vas deferens (sperm duct) in females
- Imposex is an effect of TBT.

NIVA

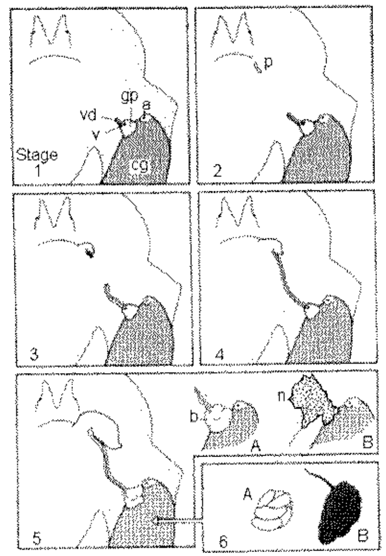
How do we characterise imposex?

- By identifying the development of male sex characters in female snails in 7 stages.
- Vas Deferens Sequence (VDS)
  Stage 0= Normal female,

  Stage 6= Penis developed, complete sperm duct, genital papilla overgrown, aborted egg capsules can be seen.
- VDSI represents the mean VDS for all the analysed females from a station.
- Dogwhelks with a VDS of 5 or 6 are sterile.

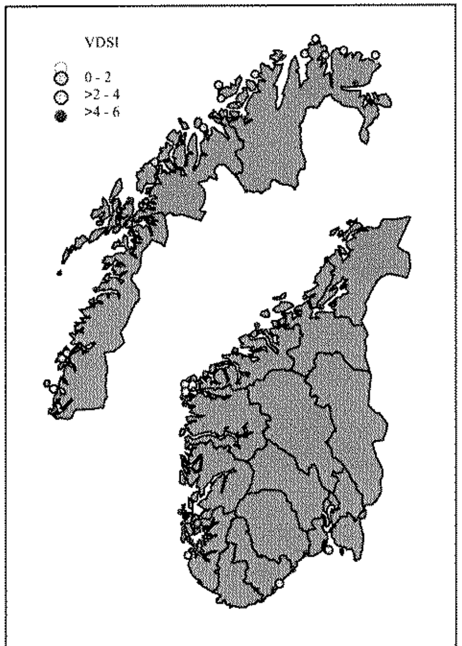
NIVA

Imposex stages



NIVA

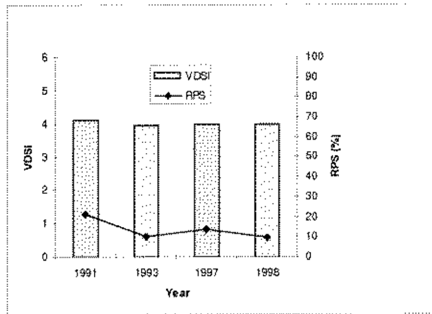
The occurrence of imposex along the Norwegian coast



Vas deferens sequence index (VDSI) in dogwhelks (*Nucella lapillus*) along the Norwegian coast, 1993-1995.

NIVA

Imposex in dogwhelks from the outer part of the Oslofjord



NIVA

Suggested mechanism for TBT-induced imposex in snails

- TBT causes an inhibition of the metabolic system which transforms male sex hormones to female sex hormones.
- The shift in favour of the male sex hormone content induces imposex.

NIVA

TBT in marine mammals

- Results from analysis of organotins in marine mammals was first available in 1994 (Iwata et al. 1994).
- Rrecent studies indicate that marine mammals are exposed to TBT.

NIVA

Butyltin in marine mammals

Species (Norwegian)	Species (English and scientific)	Area	Concentration MBT+DBT+TBT (ng/g w.w.)
Nise	**Harbour porpoise (*Phocoena phocoena*)**	**"Havøysund", Norway**	**849**
	Harbour porpoise (*Phocoena phocoena*)	Black Sea	**156**
	Harbour porpoise. (*Phocoena phocoena*) (neonatal)	Polish part of Baltic	**18, 27**
	Finless porpoises (*Neophocaena phocaenoides*)	Seto-inland Sea, Japan	**10200**
	Finless porpoises (*N. phocaenoides*)	Pacific coast of Chiba, Japan	**1120**
	Finless porpoises (*N. phocaenoides*)	Ise Bay, Japan	**3290**
Sperm	Spermwhale (*Physeter macrocephalus*)	Netherlands	**42**
	Spermwhale	Denmark	**76**
Hvithval	*Beluga (Delphinapterus leucas)*	St. Lawrence River	**294**
	Atlantic Spotted Dolphin (*Stenella coeruleoalba*)	USA Atlantic and Gulf Coast	**360**
	Stellers sea lion (*Eumetopias jubatus*)	Western Hokkaido, Japan	**150**
Stellers sjøløve	Stellers sea lion (*Eumetopias jubatus*)	Eastern Hokkaido, Japan	**220**
	Stellers sea lion (*Eumetopias jubatus*)	Alaska	**17**
	Pygmy Sperm Whale (*Kogia breviceps*)	USA Atlantic and Gulf Coast	**390**
Sjøoter	Southern Sea Otter (*Enhydra lutris nereis*)	California	**1320**
	Risso's dolphin (*Grampus griseus*)	Pacific Coast of Japan	**3600**
	Bottlenose dolphine (*Tursiops truncatus*)	USA Atlantic and Gulf Coast	**1400**
	Bottlenose dolphin (*Tursiops truncatus*)	Italy	**1200-2200**

NIVA

Effects of TBT on marine mammals?

- Butyltins can exert a whole range of toxic effects (destruction of plasma membranes, lymphocyte depletion, decreased phagocytic activcity)
- TBT and dibutyltin (DBT) are also documented immunosupressing agents in mammals and fish.
- Harmful effects of TBT in marine mammals are probable but still not fully substantiated.

NIVA

Conclusions

- Unexpected low threshold for toxic effects of TBT on certain molluscs.
- TBT from antifouling paint has resulted in negative effects on non-target organisms in natural habitates in coastal areas worldvide.
- TBT from antifouling paint bioaccumulates in marine mammals, negative effects are suspected but yet not fully documented.

NIVA

Overheads used during presentation 3.

The TBT problem seen from the Environmental Authorities` point of view.

Sveinung Oftedal

The Norwegian Ministry of the Environment

Helse- og miljøfarlige kjemikalier

Strategisk mål:

"Utslipp og bruk av helse- og miljøfarlige kjemikalier skal ikke medføre helseskader eller skader på naturen evne til produksjon og selvfornying. Konsentrasjonene av de de farligste kjemikaliene skal bringes ned mot bakgrunnsnivået for naturlig forekommende stoff, og til så godt som null for menneskeskapte sammensetninger"

St prp nr 1 (1998-1999)

Tabell 3.5.1 Liste over prioriterte kjemikalier som omfattes av resultatmål A (Prioritetslisten)

A: Utslippene skal reduseres vesentlig innen 2000 og søkes stanset innen 2005:	**B: Utslippene skal reduseres vesentlig senest innen 2010:**
Ozonnedbrytende stoffer Halon Klorfluorkarboner (KFK) Metylbromid Tetraklormetan 1,1,1 Trikloretan	*Tungmetaller* Bly Kadmium Kobber Kvikksølv Krom
Organohalogene miljøgifter Høyklorerte, kortkjedede parafiner PCB Pentaklorfenol	Brommerte flammehemmere 1,2 Dikloretan (EDC) Dioksiner og furaner Heksaklorbenzen Klorerte alkyl benzener (KAB) Muskxylener Tetrakloreten (PER) Triklorbenzen Trikloreten (TRI)
Øvrige organiske miljøgifter Nonylfenol og nonylfenoletoksilater* Oktylfenol og oktylfenoletoksilater * Enkelte tensider	PAH Tributyltinnforbindelser Trifenyltinnforbindelser

* stanses innen år 2000

Norsk TBT politikk

- Nordsjødeklarasjonen 1987
- Nasjonale tiltak (TBT-forskriften 1993)
    - forbud på skip mindre enn 25 m
    - kvoter (max 30 tonn pr år)
- Utfasingslinje i IMO
- Nordsjødeklarasjonen 1995 - vurdere regionale tiltak
- MEPC 40 - utfasing innen fem år (2003)
- MEPC 42
- Nordsjølandenes draft resolution
  "urges governments....2001-2006"
- Aproved resolution
  "MEPC - legally-binding global instrument - 2003-2008"

Vurdering av resultatet

- I tråd med nasjonale mål
- I tråd med norsk posisjon
- Statsråden fornøyd
- Kan bety mye for arbeidet i IMO
- Videre nasjonale tiltak må vurderes løpende

- Jobben gjenstår!

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NORWEGIAN MARITIME DIRECTORATE, OSLO

ALTERNATIVES TO THE USE OF TBT AS AN ANTIFOULING AGENT ON THE HULL OF SHIPS

Overheads used during presentation 4

The latest development following the meeting at IMO MEPC 2nd to 6th of November

Jens Henning Koefoed

The Norwegian Maritime Directorate

MEPC 42 RESULTATER- TRIBUTYL TIN

- Enstemmig utkast til assemblyresolusjon
- Enighet om tidsplan (2003, påføring, 2008 bruk)
- **Enighet om at det skal utvikles et regelverk som skal tre i kraft før 2003**
- Enighet om at regelverket skal dekke forbud og miljømessig vurdering av alternativene

Arbeidet fremover:

- Avtale trått i kraft innen 2003
  - Tekst klar i år 2000: →2 års forhandlingstid
  - Konferanse i 2001
  - Ratifikasjon i 2002

Prosessen:

1. Utarbeidelse av grunntekst (innhold i fremtidig lovgivning)
2. Diskusjon av prosedyrer for vurdering av alternativer

➢ Alternative ingredienser i bunnstoff

➢ Alternative systemer

Nasjonale aktører

Myndigheter:

Regjeringen (Miljverndepartementet, Nærings- og Handelsdepartementet, mv)

Sjøfartsdirektoratet, SFT

Privat sektor

Rederiorganisasjonene
Leverandørene
De grønne organsiasjonene

Extract from MEPC 42 report:

The committee agreed to .....

Encourage delegations to submit papers on basic structure (of legal instrument) and on methodology for considering alternative systems to MEPC 43

Overheads used during presentation 5.

The problem as seen from the shipping industry

Arne Peder Blix

The Norwegian Shipowners` Association

HOW THE SHIPPING INDUSTRY MEETS ENVIRONMENTAL CHALLENGES RELATED TO TBT

Arne Peder Blix
Norwegian Shipowners' Association

POLICY OF NSA (1)

1. NSA has the environmental aspects of the shipping and the offshore industry as a priority area.
2. NSA shall contribute to increased research and development to promote improved and more efficient methods and equipment to reduce harmful effects on the environment.

POLICY OF NSA (2)

3. NSA shall work actively to establish binding international regulations to limit the pollution from shipping as well as to establish effective enforcement and control to ensure compliance.
4. NSA shall co-operate with authorities, classification societies , research institutions and environmental organisations to achieve specific goals.

POLICY OF NSA (3)

5. NSA shall promote the environmental awareness in the shipping industry, charterers and other actors involved.
6. NSA shall promote environmental friendly transportation by stimulating to increased use of sea transportation and intermodal concepts.

POLICY OF NSA (4)

7. NSA shall encourage Norwegian and foreign authorities and the market to stimulate design and operation of environmental friendly ships and mobile offshore platforms through incentives and differentiation of premiums, fees and dues.
8. NSA shall systematically inform Norwegian politicians, media and the public to ensure their awareness of the efforts the industry is doing to improve and the result that are achieved, and to demonstrate that sea transportation is the most environmental friendly alternative for a wide range of transportation tasks.

The Problem as seen from the shipping industry

- MEPC 42:
  - Agreed ban of Application 2003
  - Ban of use 2008
- Imperative for the shipping industry to strive for International regulation - not national or regional
- Initially MARPOL was aimed at prevention of pollution to the sea --> TBT, Ballast water and possibly future others are more of an "Environmental Protection" character
- New legal instrument for Environmental Protection including TBT, Ballast water, CO_2 ?

The Problem as seen from the shipping industry

- Alternatives to TBT must be carefully chosen in order to avoid unknown side-effects
- Performance standard for anti-fouling products?

Concerns:

- Necessary to have anti-fouling product with performance of 50-60 months
- Dry-docking of a VLCC ⟹ 2 mill USD...
- Yard capacity vs. increased off-hire,
- Application precautions - personnell protection, mix with earlier paint, cracking, timeconsumption in yard.

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Overheads used during presentation 6.

A brief overview of methods for antifouling

John Arthur Berge

The Norwegian Institute for Water Research

A brief overview of methods for antifouling

John Arthur Berge

Norwegian Institute for Water Research
(NIVA)

NIVA

Biofauling

- In the marine environment any solid surface will become fouled

- **Primary film**
- Stage 1. Conditioning:Organic film develops from substnces in the water (minutes).
- Stage 2a. Reversible colonization of bacteria (houers).
- Stage 2b. Non reversible colonization of bacteria - extracellular bridging polymer are made.

NIVA

Biofouling

- **Primary colonizers**: Diatoms, bacteria
- **Secondary colonizers:**spores of macroalgae, and protozoans.
- **Tertiary colonizers:** Macroalgae, barnacles, mussels, tunicates, coelenterates, bryozoans, polychaetes etc

NIVA

Methods for antifouling

- Chemical methods-use of biocids
- Mechanical methods - Hydrojetting, brushing
- Physical methods-ultra smooth surfaces, surface renewal, sloughing.
- Biological methods- use of grazers

NIVA

Principles for the appliction of biocids in antifouling paint

Three basic methods

- Soluble Matrix technology
- Contact Leaching
- Self-polishing systems (SPC).

NIVA

Soluble Matrix technology

- Rely on physical/mechanical controlled process to release the biocid
- The matrix erodes at a rate different to the biocid.
- Over time a leached layer with a reduced biocid concentration develops on the surface.
- As a result the length of time that the system can work is at best 3 years.
- The main biocides used for this system is copper usually together with an boosting co-biocid.

NIVA

Contact leaching

- These products are hard, mechanically tough antifoulings that do not erode.
- They are highly loaded with biocides which leach through the surface of the hard matrix over time.
- These systems are efficient for for a maximum of 2 years since
- After this time the surface layer are depleted and too little biocide reach the surface to be effective.

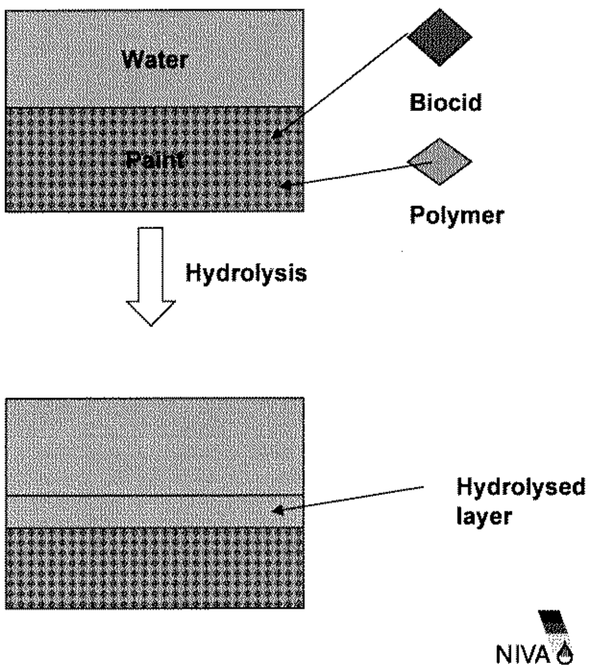
NIVA

Self-polishing systems (SPC).

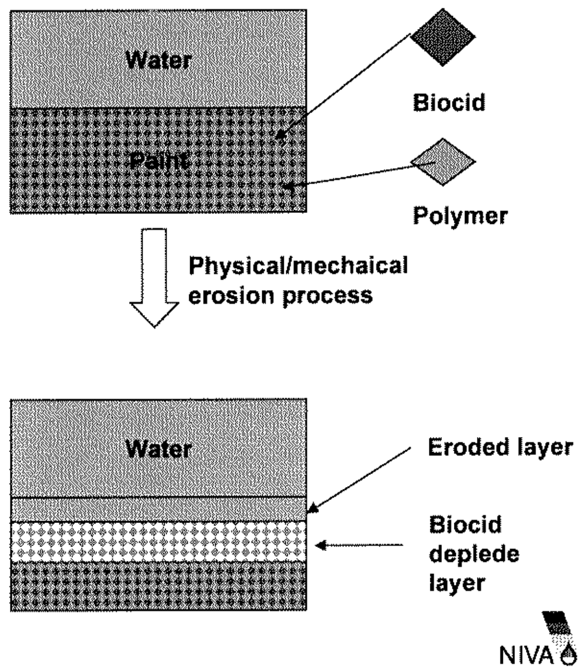
- Rely on a chemically controlled process to release the biocid from the paint.
- The release of the biocid follow the rate of the hydrolysis (polishing rate) of the polymer.
- This polishing rate is proportional to the speed of the ship.
- No thick depleted layer will develop on the surface
- The length of time that the system can work is up to 5 years.
- Main biocides used for this system has been TBT, copper and organic boosting biocids.

NIVA

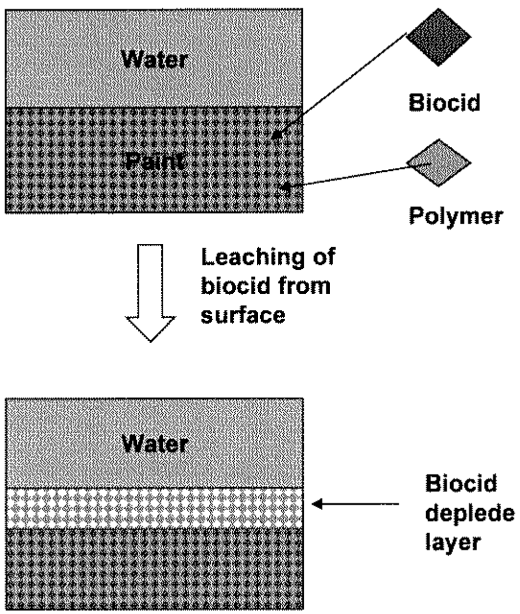
Self-polishing systems (SPC).



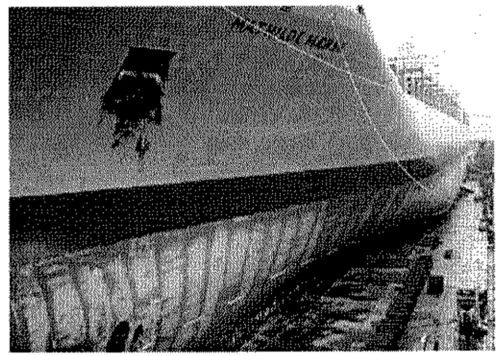
Soluble Matrix technology



Contact leaching



Ship treated with a Self-Polishing system



From Dr. Colin D. Anderson

Ultra smooth surfaces

- Ultra smooth surfaces are used in order to weaken or eliminate the adhesive bond between fouling organism and the coating.
- The organisms may be dislodged by their own weight or by the motion of the ship through the water.
- Utrasmooth surfaces prevents the fouling organsms to settle permanatly.

NIVA

Ultra smooth surfaces

- Silicone based
- Teflon based

- Such ultra smooth surfaces can also be used in combination with a biocid.

NIVA

Periodical mechanical cleaning

- Today the development of mechanical cleaning technology has just started and the practical implementation of such methods is limited.
- Mechanical cleaning is a system suggested for pleasure crafts in Denmark.
- For large ships the system require cleaning stations at strategic locations worldvide - international network
- Require frequent treatment when used on traditional paints.

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Periodical mechanical cleaning

- Periodical mechanical cleaning alone is not likely to be a satisfactory antifouling system for ships.
- In combination with other systems (super smooth surface) mechanical cleaning could be an realistic alternative to the use of TBT.

NIVA

Electrolytic system

- The Japanese Ship and Ocean Foundation (SOF) and Mitsubishi Heavy Industries (MHI).
- Antifouling system based the formation of hypochlorite (ClO^-) through electrolysis of seawater.

NIVA

Requirements for electrolytic system

Three layers on the hull

- 1. An insulating layer (Epoxy resin).
- 2. Conductor made of carbon-acryl resin. The conductor on the two sides of the boat are isolated from each other and functions as cathode an anode respectively.
- 3. The conductor is protected with a third layer (carbon-acryl resin).

NIVA

Application of electrolytic system

- By applying a direct current between the to electrodes the biocid hypochlorite (ClO^-) develops at the anode and prevents fouling.
- The direction of the current has to be changed regularly in order to protect both sides of the ship. years.
- The system has been tested both on panels in the harbour of Nagasaki and on a few ships and is reported to be promising.
- Requires further testing.

NIVA

Mechanism - electrolytic system

- The method relys on the biocidal properties of hypochlorite (ClO^-)
- The system is therefore, stricly speeking, not “nontoxic”.
- It expected that ClO- which escape from the hull will react relatively quickly with other compunds i the sea water.
- The success of the system lies in its possible acceptance as a “non-toxic” system and the costs for applying the relatively complicated coating.

NIVA

Electric stunning

- Pulsed electric currents can effect the settling of larva.
- Experiments suggest that pulsed (100 hz) electric fields (20 V/cm) can stun mussel larva and effect settlement of the zebra mussels.
- No information is available on the application of electrostunning as a method for preventing fouling on ships.
- Hull configuration, danger to humans and the voltage required do not facilitate electric stunning as a future method for antifouling.

NIVA

Copper-nickel in hull material

- Boats with a hull of copper-nickel are found to bee free of fouling (and corrosion) for several years
- The mechanism of this effect is not well known.
- The material has been used on pilot boats in Sweeden and on ferries in New Zealand.
- Copper-nickel hulls require special attention to prevent contact corrosion.

NIVA

UV-light

- Experiments have demonstrated the sensitivity of larva to ultraviolet radiation
- Study has howed some larvae to be extremely sensitive to even short exposures of UV-C and UV-B (inducing 100% mortality).
- In contrast, neither visible light nor UV-A induced behavioral changes.
- Young adult and adult mussels are more resistant to UV-C and UV-B as their shells are opaque, yet they also can be killed if exposure periods are long enough.

NIVA

UV-light

- No information is available on the practical application of UV-light as a method for preventing fouling on ships.
- Conclusion:Unrealistic as a future method for antifouling (hull configuration, docking interval)

NIVA

Ribbons or spiny/hairy surfaces

- Inspired by the idea that physical structures on the surface will prevent settlement of larvae and spores.

- US Patent using plastic ribbons

NIVA

Ribbons or spiny/hairy surfaces

- No information on results from practical tests.

- Concept not likely to be successful (hull roughness high, will not prevent settling effectively

NIVA

Naturally occurring antifouling systems in organisms

- Some marine organisms produce substances with antibacterial, antialgal, antiprotozoan and antimacrofouler properties.
- Isolated substances belong generally to the fatty acids, terpens, terpenoids, lipcproteins, glycolipids, phenols, lactons, alkaloids and peptids.
- Some of these biogenic substances may be used for the prevention of fouling.
- It has been reported that the antifouling activity of some of these compounds match TBT.

NIVA

-

The use of naturally occurring compounds for antifouling

- Antifouling systems based on such compounds are promising.
- The environmental consequences of large scale use of natural biocids must be investigated.
- The production of natural biocids must be based on industrial/biotechnological production and not on harvesting - environmental consequences?
- The development of a complete antifouling system based on such naturally occurring compounds lies probably at least 5 years ahead.

NIVA

The use of grazing organisms for antifouling

- Distribution of rocky-shore organisms is influenced by grazing/predation.
- The most familiar example is probably starfish-predation on populations of mussels.
- Transplantation of adult limpets onto newly submerged objects may effectively prevent biofouling by means of the limpets feeding on newly attached algae and by dislodging newly attached animals.

NIVA

Conclusion - Grazing organisms

- Results indicates some potential for the use of grazing organisms to control biofouling on stationary objects.
- The use of grazing organisms are not an realistic method for the prevention of biofouling on moving ships.

NIVA

CONLUSIONS

- Many options are being considered by various parties.
- At present there seems to be no biocid free method ready to use for all types of vessels.
- New low toxicity methods will reflect what kind of biocid which willl be accepted as environmental safe in the future.
- Extensive environental testing are needed.

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Preferred options for future development of "non-toxic" methods

- Super smooth surfaces, possibly in combination with a biocide without non target effects.
- Self-polishing systems with biocids without non target effects
- Biocids based on naturaly occuring compounds
- Electrolytic system
- Copper-nickel in hull material

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Overheads used during presentation 7A.

Presentation of available products

Ragnar Jahr

Jotun

Jotun represented by:

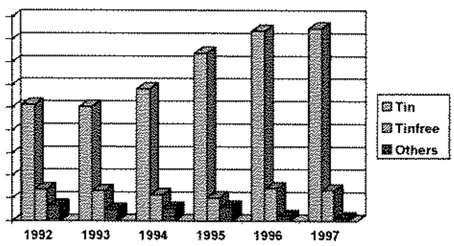
- Mrs. Kjersti Gjerdevik
  Micro Biologist
  Environmental Affairs
  Jotun Marine Coatings
- Mr. Ragnar Jahr
  Chemical Engineer
  Sales Director
  Jotun Marine Coatings

Setting the Scene

What is happening in the market today?

- Antifouling prices under severe pressure
- Price per litre the main selection criteria
- Antifouling - a commodity product?
- For certain operators, the importance of the Antifoulings vary with the price of the bunker oil.
- The Norwegian shipping community needs guidance with regards to what to choose.

Volume Development - Antifouling



Performance of Tin Free A/F

Statistics from CDO for drydockings '91-97
Vessels in acceptable condition

- Antifouling Seavictor 50 76%
- Antifouling Seavictor 40 73%
- Antifouling Seaguardian 87%
- Antifouling Sargasso 74%

Development of Antifoulings

Influencing factors the past thirty years:

Demands from shipowners for better performance with economy
Increased emphasis on surface roughness and hull performance
Big variations in fuel oil prices over the period
The trend to extend periods between drydockings
The increasing awareness of environmental issues

Paint Regulations

In the 1980's

- A number of countries restricted the use of TBT on small vessels (less than 25 m in length)

Paint Regulations

In the 1990's

- Application of TBT antifoulings was banned in Japanese and New Zealand shipyards
- TBT release rate restrictions in force in Norway, Sweden, the US, Canada, Netherlands and Australia.
- VOC regulations in the US and UK

Paint Regulations

Future

- IMO/MEPC 42 meeting in 1998 gave the guidelines for the future
  - A world wide ban on application of TBT containing antifouling from 2003.
  - A world wide ban on TBT containing antifouling exposed to the sea from 2008.

Tin Free Antifoulings

Why do owners/managers use tin free?

- Some because they have to
- Some because they have a green policy
- Some because they foresee what is coming

➡ ***Very few because of the confidence they have in the tin containing ones.***

What to use

- Ocean going vessels
  - Seaguardian
  - Seavictor 40
  - Seavictor 50
- Coastal vessels
  - Sargasso

Status on Tin Free Antifouling

Tin free technology is here to stay

- Introduced in the early 90's as an equivalent to selfpolishing tin copolymer antifoulings
- Not yet equal in performance to tin, but the quality is improving
- When used for 60 months protection, an under-water cleaning might be needed at the end of the period.
- When tin free antifouling is required, the products are available.

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Overheads used during presentation 7B

Presentation of available products

Colin D. Anderson

International

ALTERNATIVES TO TBT ANTIFOULINGS

- Tin-Free Soluble Matrix
  - CDP ("Controlled Depletion Polymer")
- Tin-Free Self-Polishing Copolymer (SPC)
  - Intersmooth Ecoloflex
- Biocide-Free
  - Intersleek

International

CDP Antifoulings

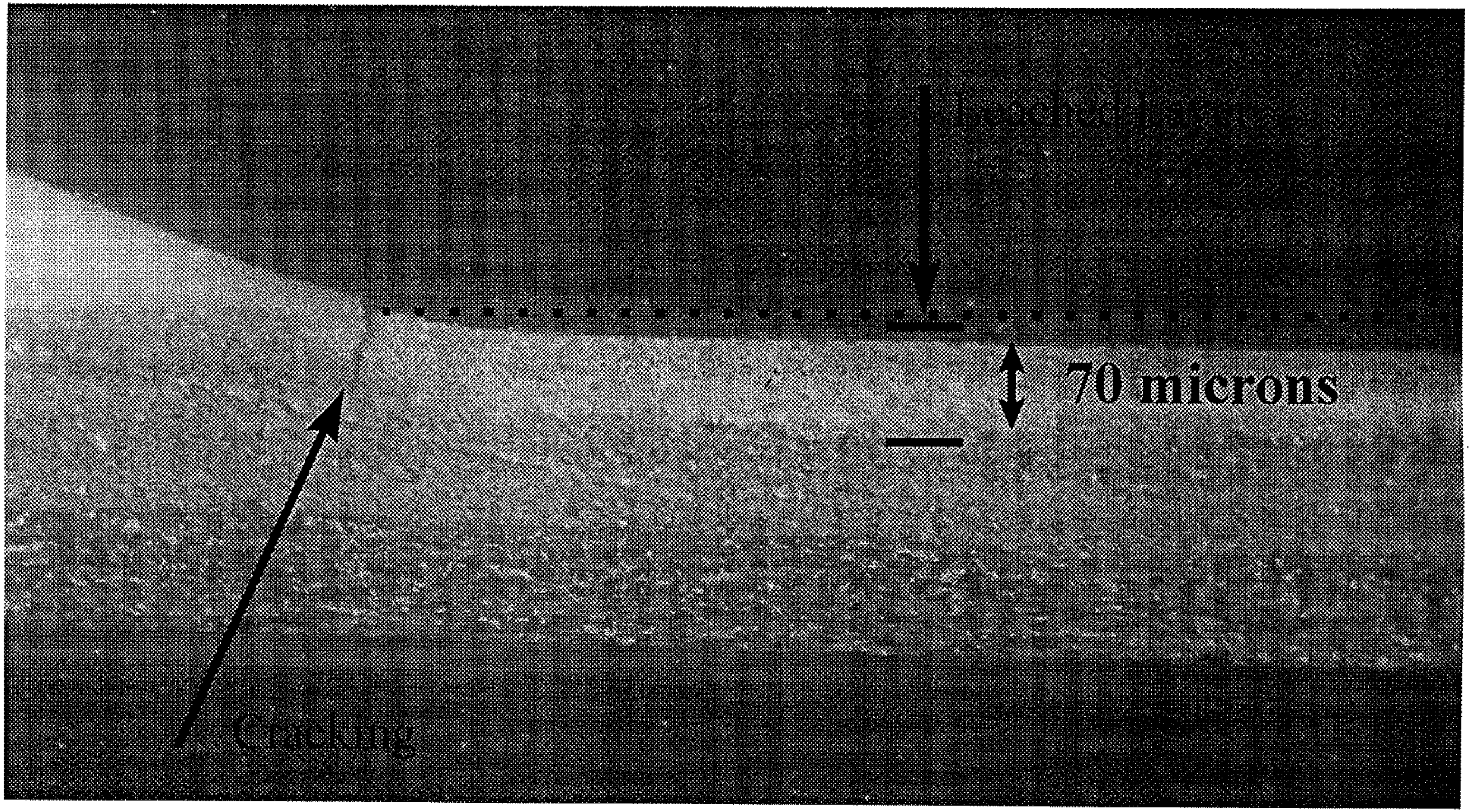
- A physical, not chemical, dissolution of the paint film, which gradually slows down over time so maximum effective life = 30~36 mo.

- Unpredictable polishing rates so performance less predictable.

- Thick Leached Layers so extra care/cost is needed at M&R.

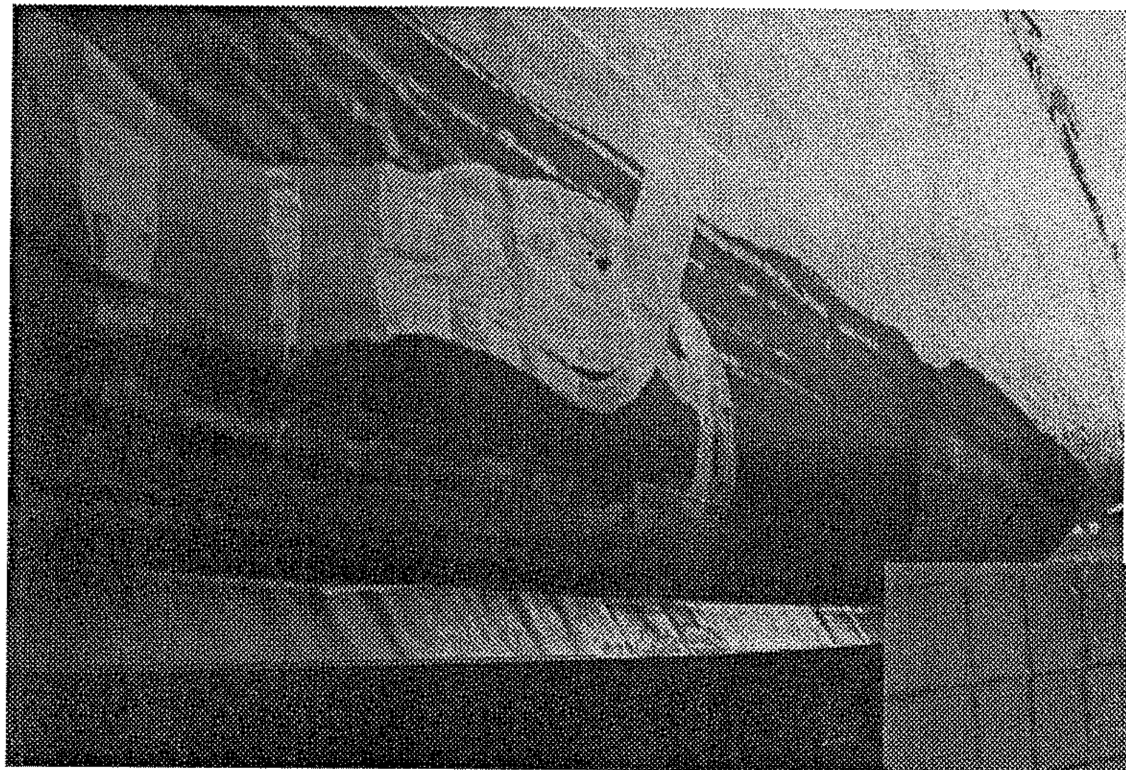
International

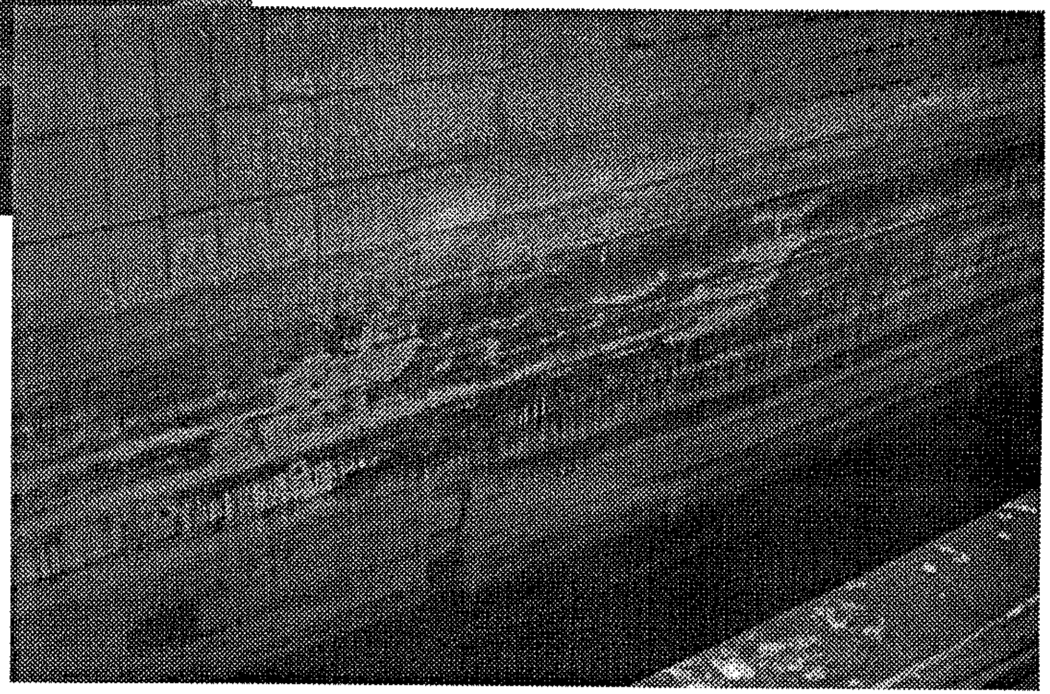
CDP Cross Section



International

Typical CDP Outurns (25 months)





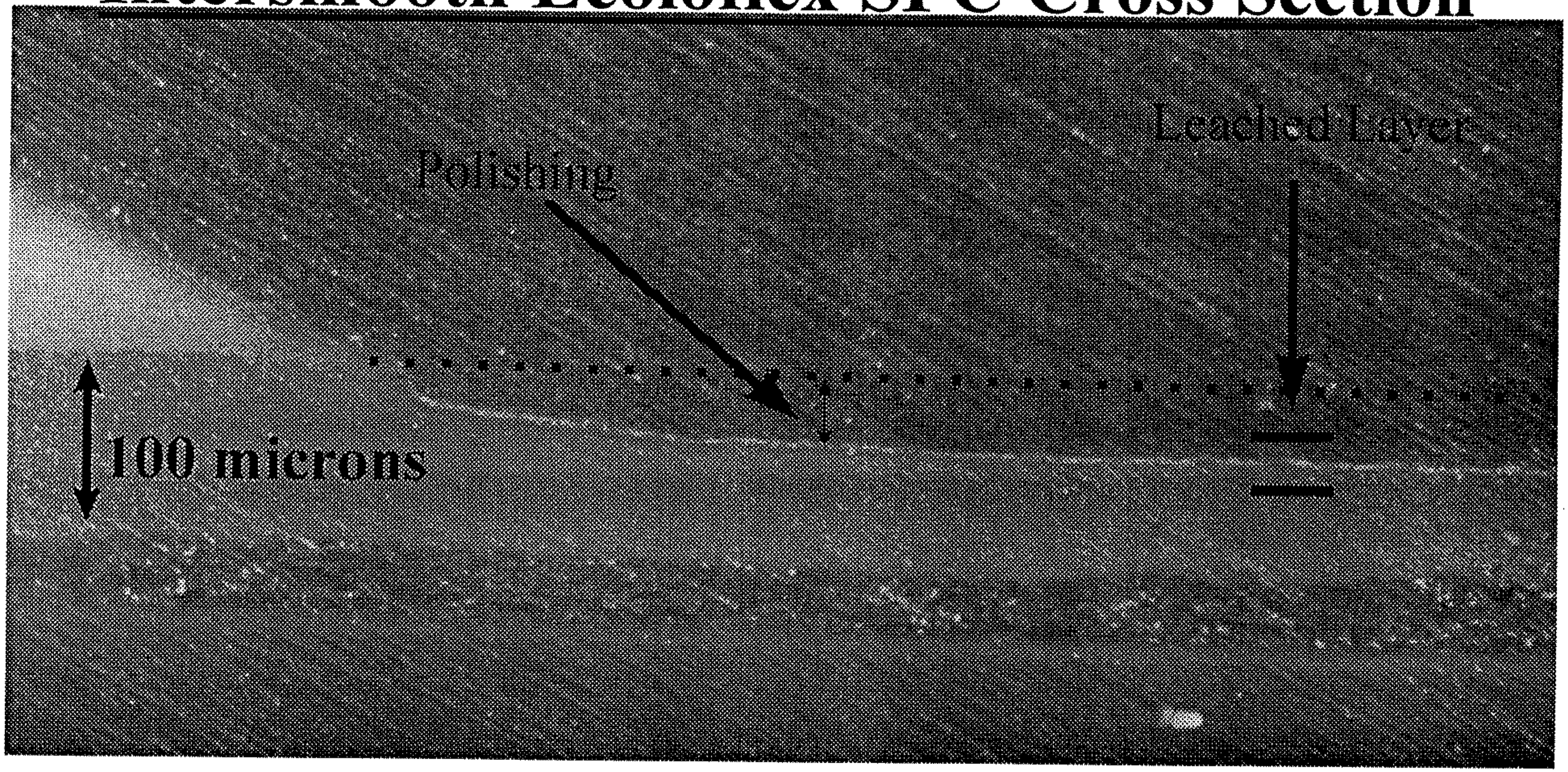
International

Intersmooth Ecoloflex SPC Technology

- Intersmooth Ecoloflex SPC technology was developed by IP and Nippon Paint Marine Coatings.
- The “1st Generation” products were introduced in Japan in 1990,when TBT was banned there. The “2nd Generation” in 1994.
- A new Boosting Biocide (that degrades rapidly) is used, with a novel Copper Acrylate polymer.

International

Intersmooth Ecoloflex SPC Cross Section



International

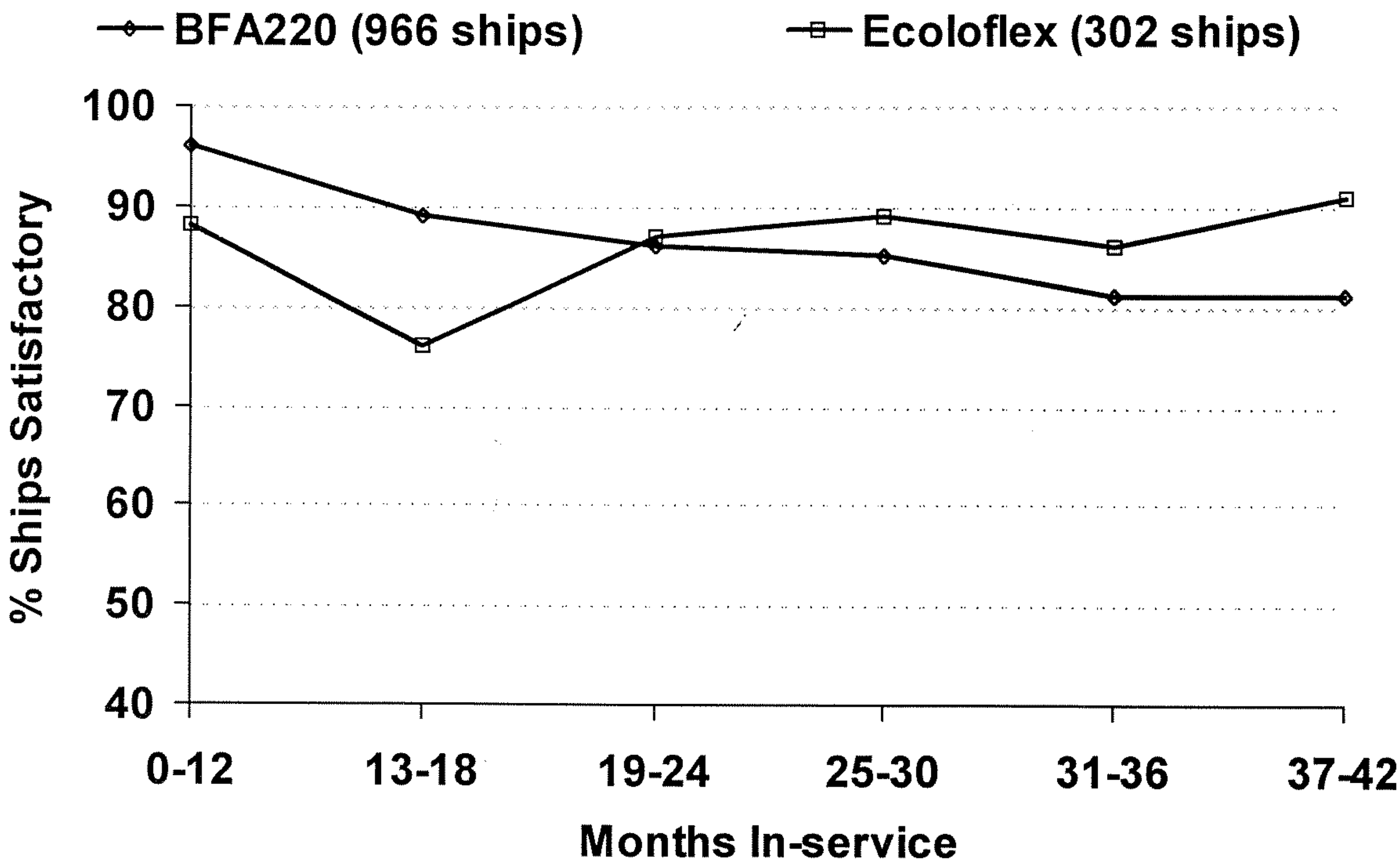
Dataplan Ecoloflex Tr. Rcd (No. of ships)

	← 2nd Generation			→	← 1st Gen.		→	
	'98*	'97	'96	'95	'94	'93	Pre 93	Total
Bulkers	40	78	58	57	48	38	50	**369**
Chem Carriers	1	2	4	4	2	5	2	**20**
Containers	28	28	21	11	15	7	14	**124**
General Cargo	12	5	3	8	6	2	14	**50**
LPG	8	6	12	8	8	6	11	**59**
Ferry/RoRo	6	6	7	16	18	21	50	**124**
Product Carrier	3	4	9	5	4	3	17	**45**
Tanker	5	6	9	7	10	21	36	**94**
Other	30	32	33	32	34	32	78	**271**
TOTAL	**133***	**167**	**156**	**148**	**145**	**135**	**272**	**1156**

*** = Part year figures only**

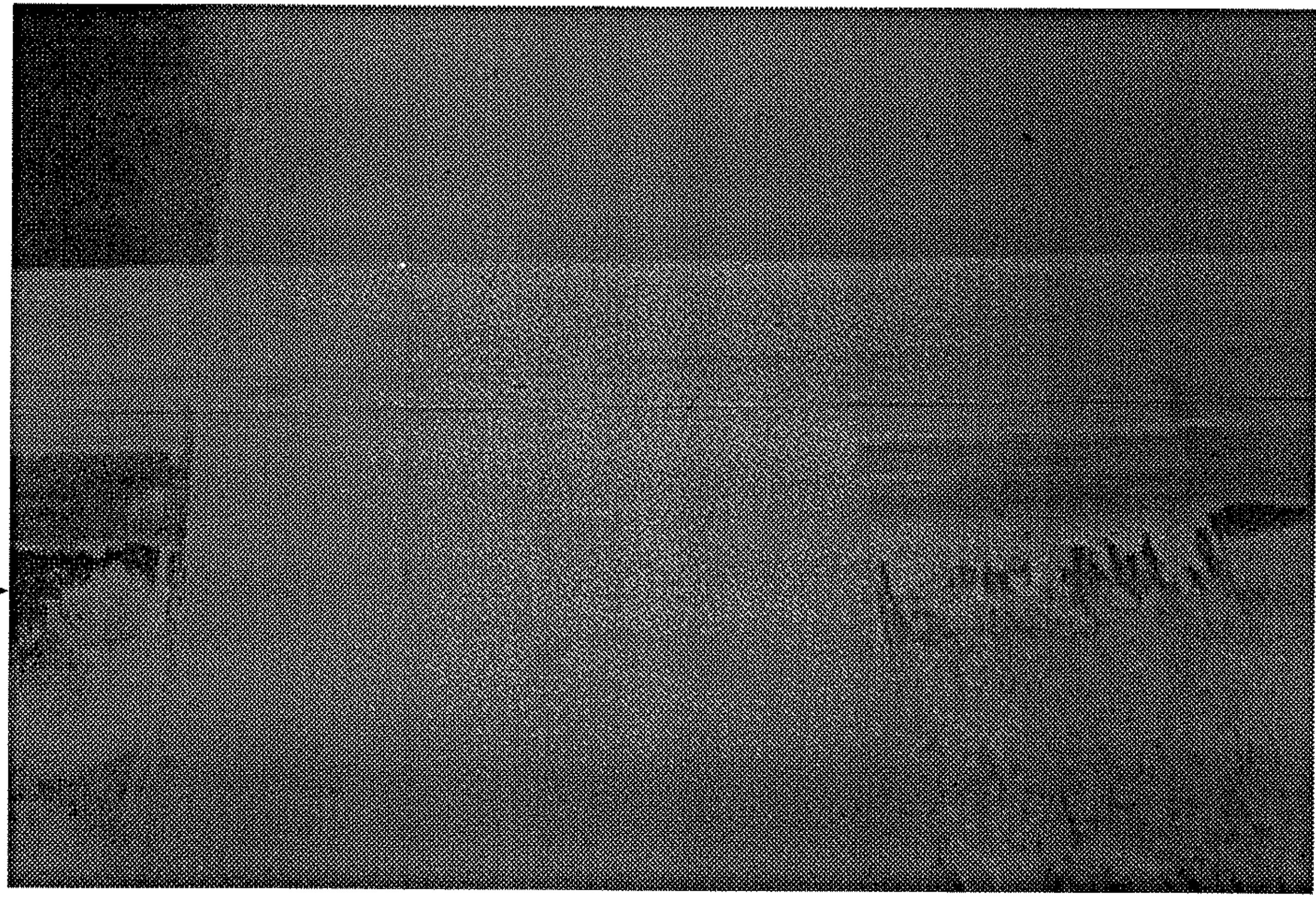
TOTAL dwt = 53.6 million

D'plan Performance - Ecoloflex vs. BFA220



International

Intersmooth Ecoloflex vs. CDP

CDP →  ← CDP

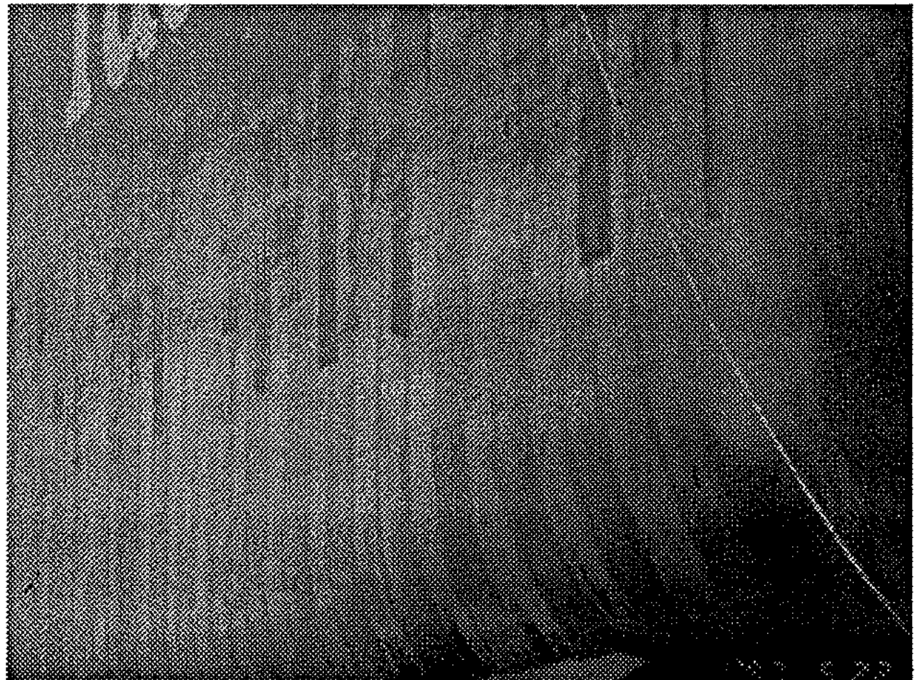
360 Ecoloflex   460 Ecoloflex

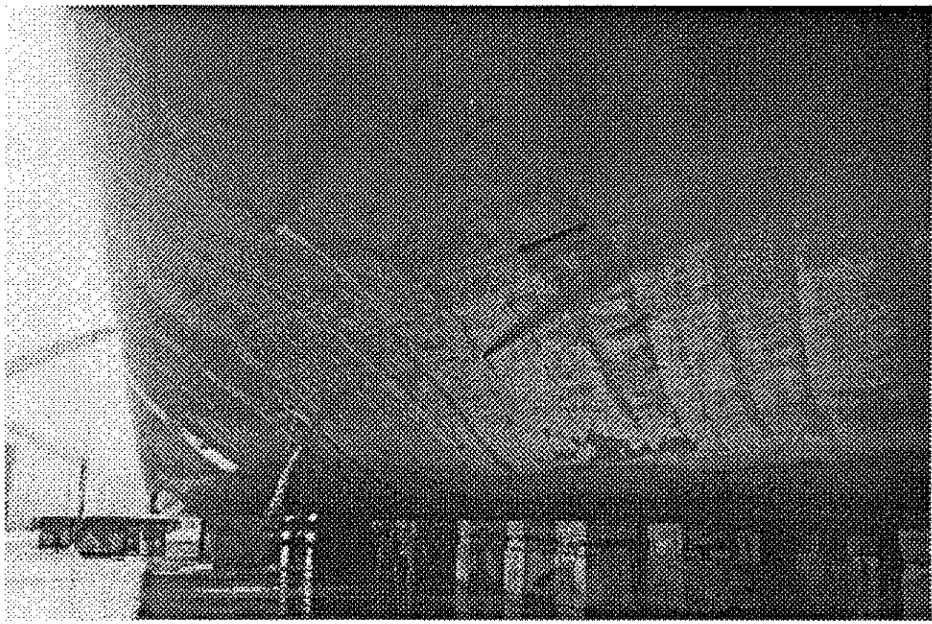
International

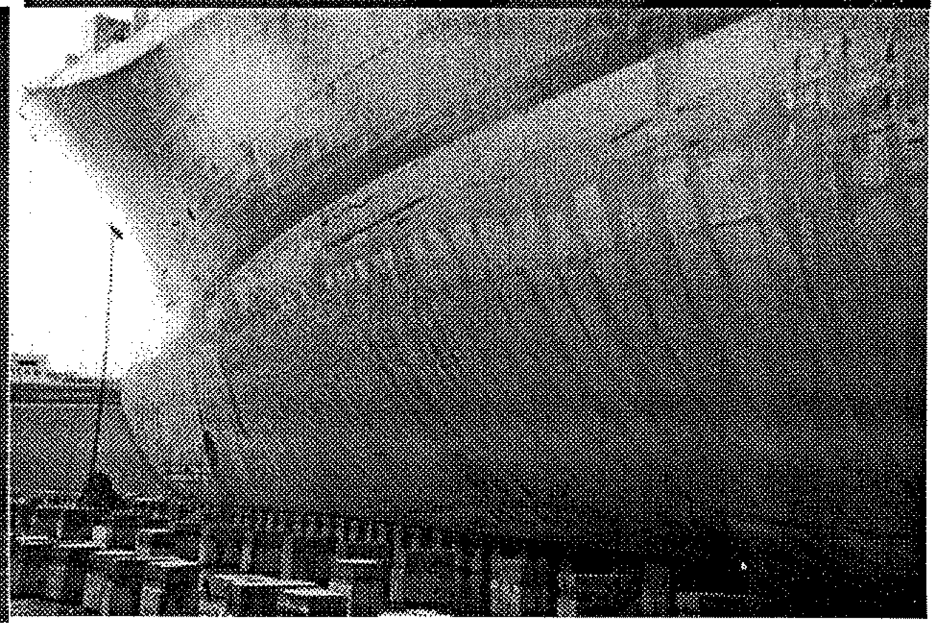
<u>"Jervis Bay"</u>

(Container)

25 months







International

"Cygnus"

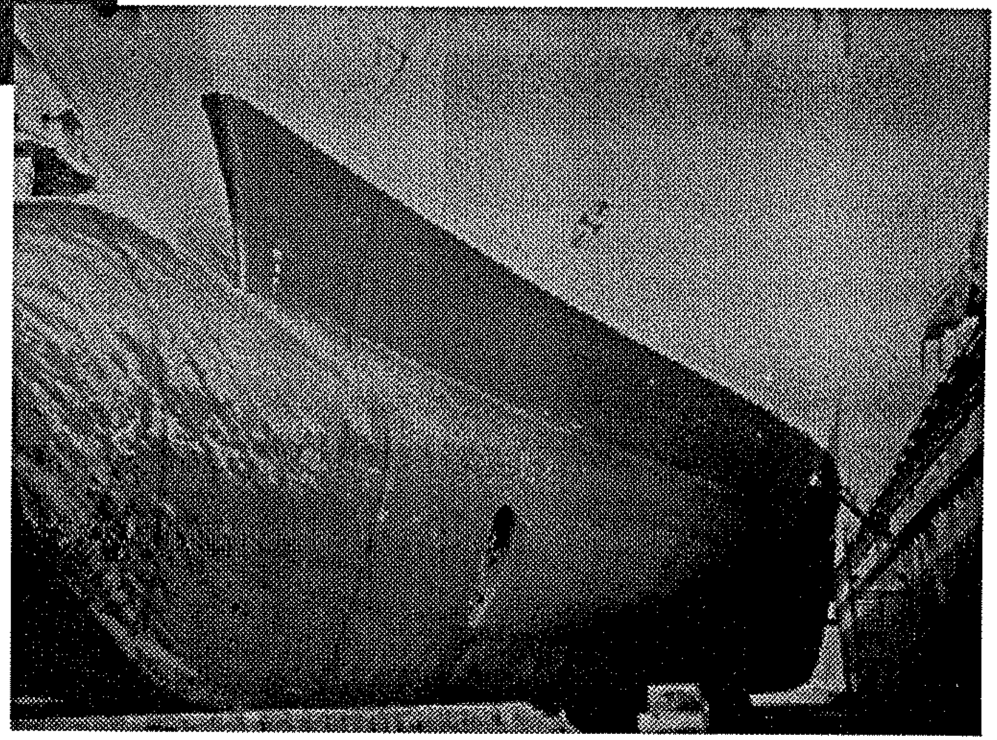
(Car Carrrier)

24 months

"Fuji Maru"

(Cruise Ferry)

12 months



Non-Toxic Fouling Control

- Fouling settlement can be prevented by making the surface too "slippery" for fouling organisms to stick to.

- International has developed a system to do this for Scheduled Ships called "Intersleek 700".

Intersleek Features

- Ultra-smooth
- Low friction in water.
- Can "self-clean" at high speeds.
- Chemically durable, retaining its initial smooth glossy surface.

International

Intersleek - Environmental Benefits

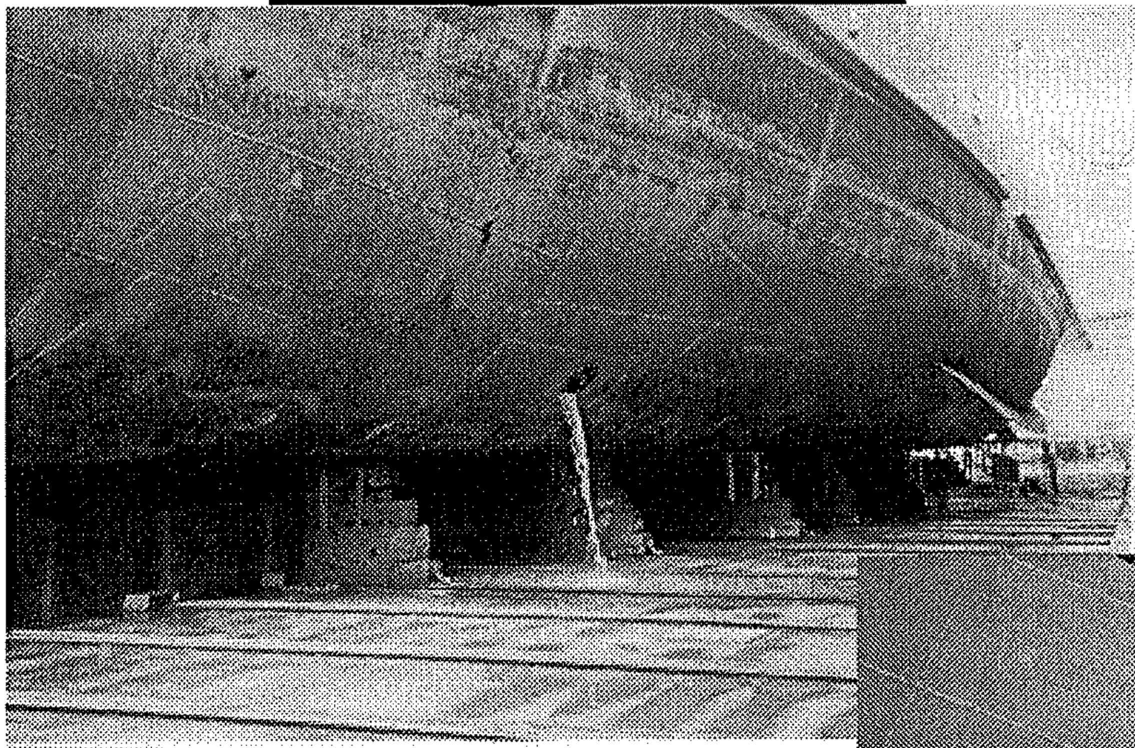
- No leaching of biocides into the sea.
- No costly wash-water treatment needed.
- No restrictions on worldwide use.
- VOC < 400 gm/litre.

Intersleek - Operational Benefits

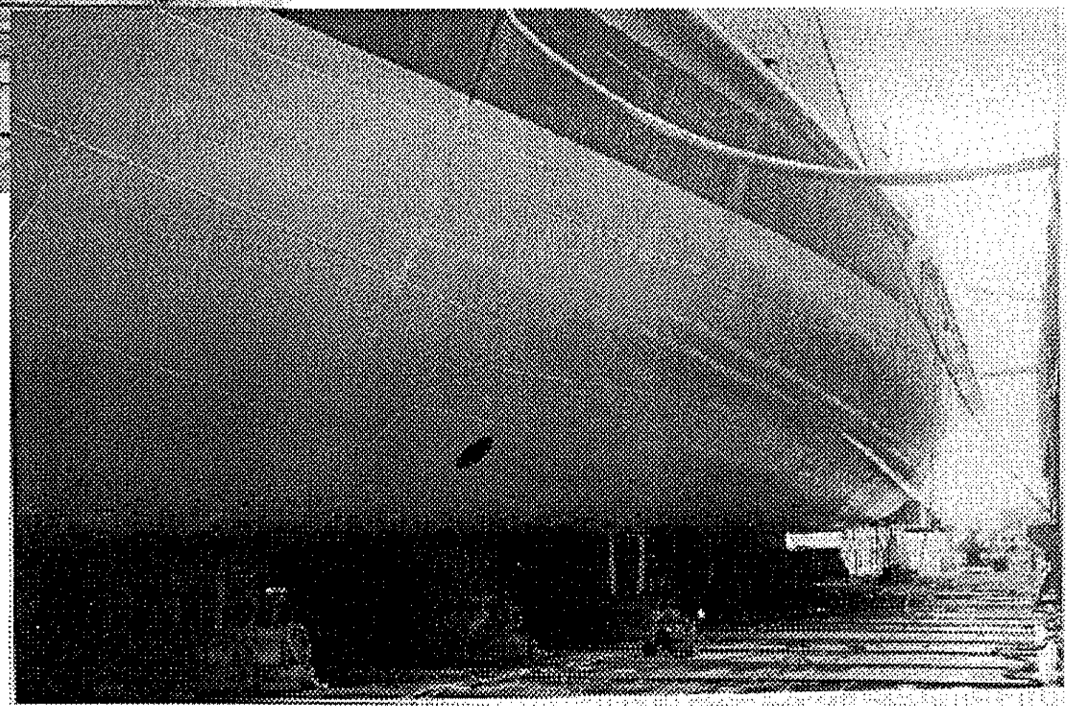
- Equivalent speed/fuel performance to TBT SPC
- Total drydock interval flexibility (0-60 mo.)
- Reduced M&R costs (wash/touch-up only)
- Direct conversion from TBT SPC is possible (outside North America)

International

"Tropic Lure" *(June '98, 61 mo.)*



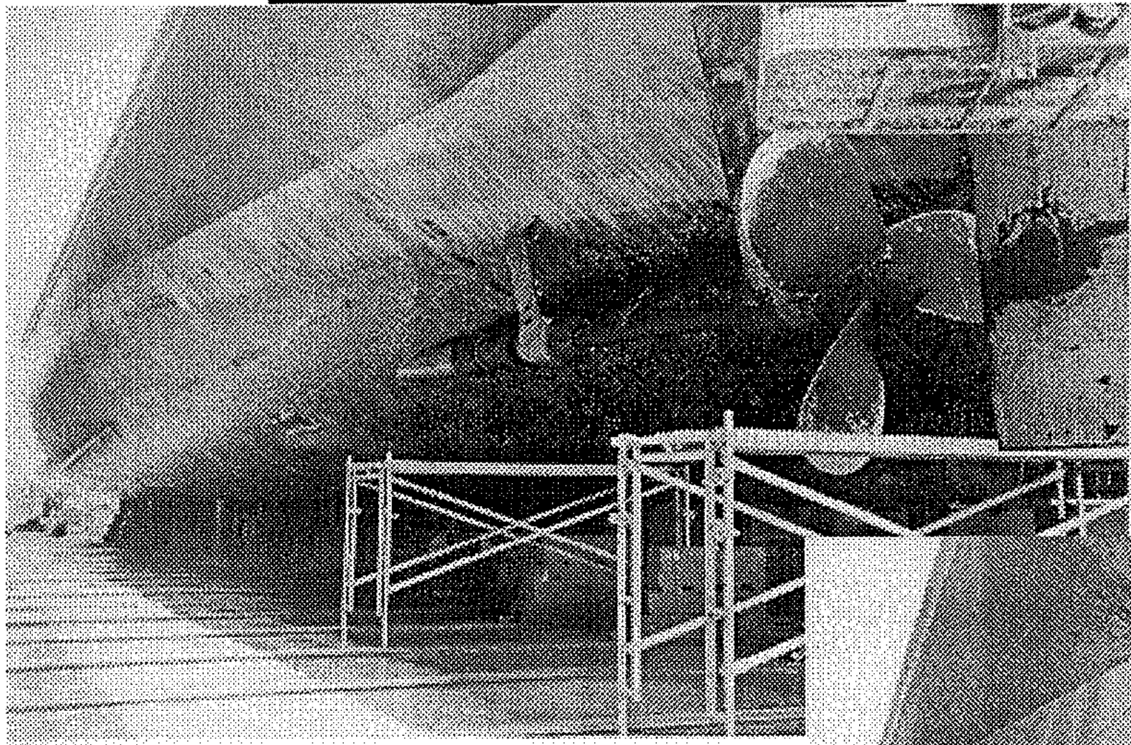
Before Cleaning



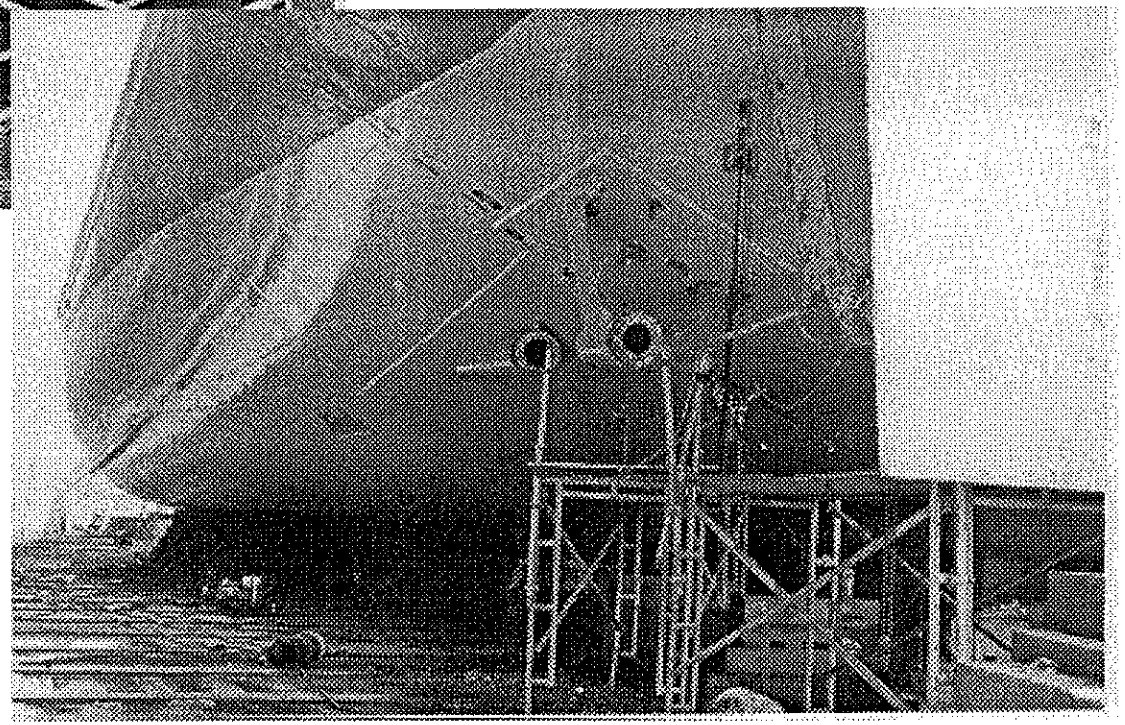
After Cleaning

International

"Tropic Lure" (June '98, 61 mo.)

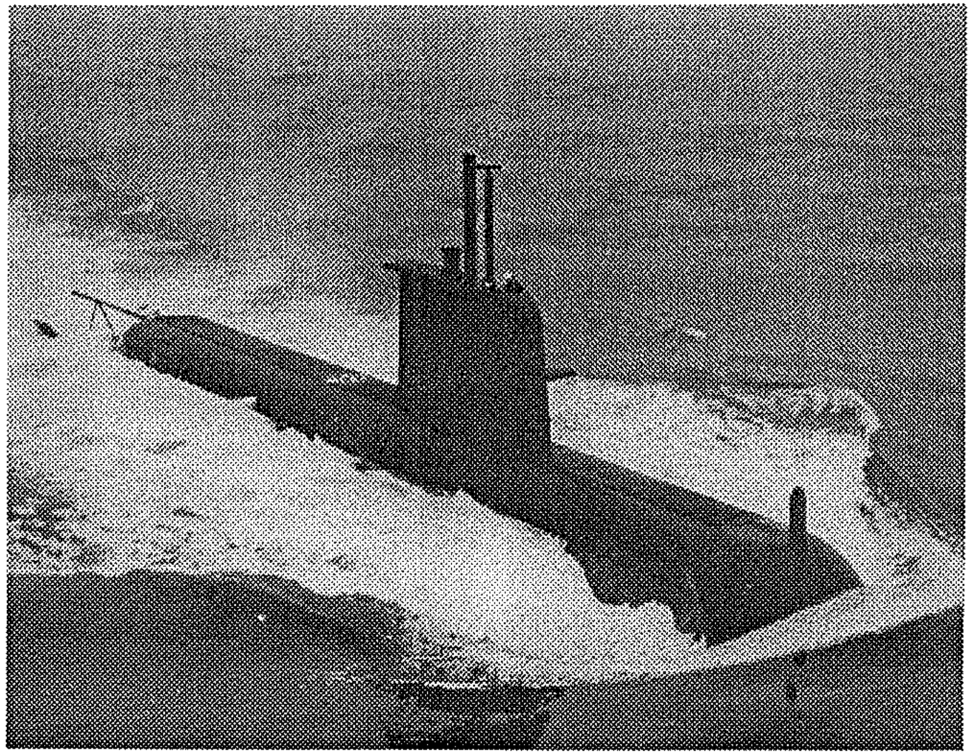


Before Cleaning

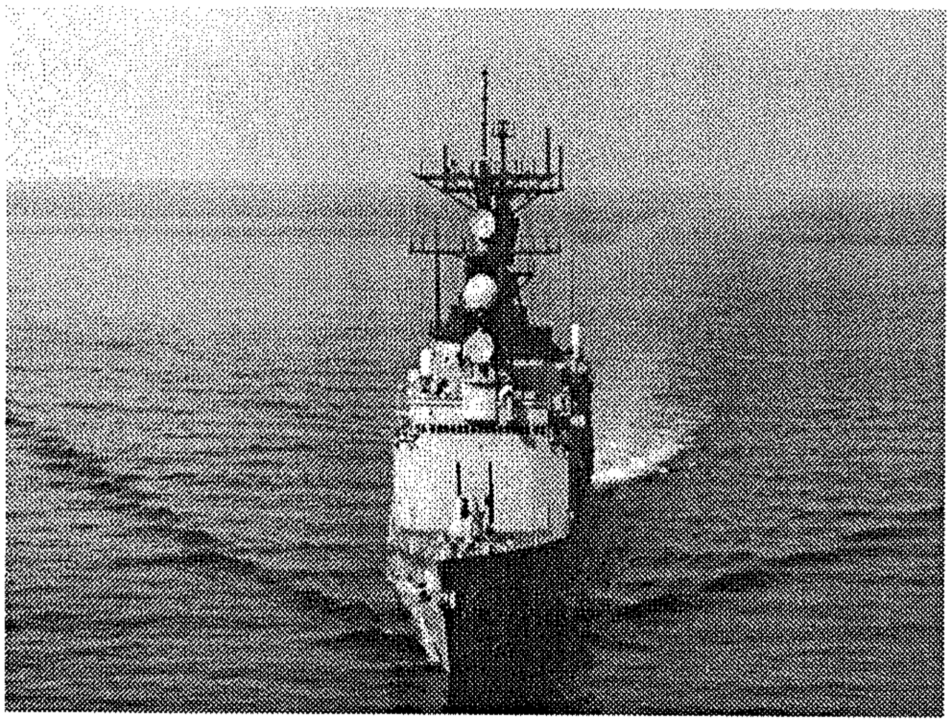


After Cleaning

International



"HMAS Collins"



"USS Scott"

Overheads used during presentation 7C

Presentation of available products

Stefan Andreasson[1)]

Hempel

[1)]Presentation not given due to acute illness during the workshop

HEMPEL'S ANTIFOULING GLOBIC SP-ECO 8190 Series*

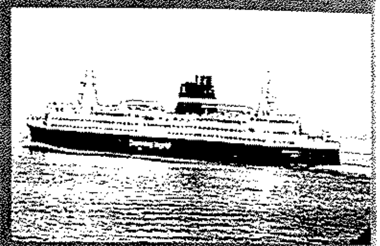
8190

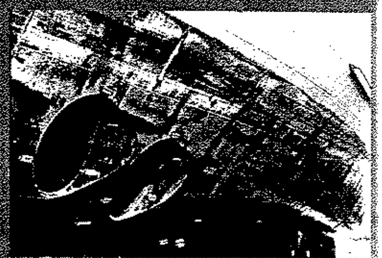
Self-polishing Antifouling
Tin-free
Newbuilding
Maintenance and repair
Coastal Vessels

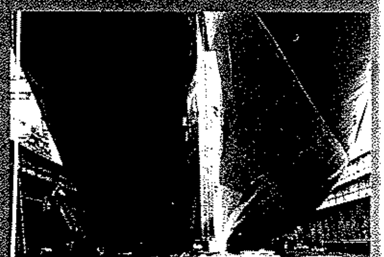
GLOBIC SP-ECO is a big step forward in tin-free technology. It makes up part of a new generation of high performance self-smoothing antifoulings. It has a unique fibre composite formulation with enhanced mechanical properties, developed and engineered to manage the severe fouling conditions found in coastal waters.
It has been extensively tested on a range of vessel types. Succesful performance has resulted from its fast polishing rate, controlled release of powerful antifouling biocides and efficient self-smoothing.

Specific Profile:
- **Low to medium speed vessels**
- **Low to medium activity**
- **Medium to long idle periods**
- **Coastal trade**

Engineered for:
- **General Cargo Vessels**
- **Ferries**
- **Fishing Vessels**
- **Tugs**
- **Coastal Tankers**
- **Navy Vessels**







Features	Benefits
Tri-butyl tin-free.	Comply with tri-butyl tin regulations.
Especially formulated for coastal vessels.	Fouling control in severe fouling conditions of coastal waters.
Hydrolysable zinc carboxylate polymer salt binder technology.	Excellent polishing properties.
Fibre composite technology (Patent pending)	Better mechanical properties.
Technically matched polishing rate and release rate of biocides.	High performance fouling control for coastal vessels.
Self-smoothing product.	Optimum hull performance with roughness control and resulting fuel economy.
Reduced formation of leached layer (only HPFW needed).	Safe, fast and easy overcoating, reducing time in dry-dock and maintenance costs.
No sealer coat needed on subsequent applications.	Saves time and paint in dry-dock.
Up to 36 months' fouling protection.	Prolonged in-service periods for coastal vessels.
High solids antifouling, high build coating.	Low VOC, Reduced solvent emission.

GLOBIC SP-ECO 8190 Product Data

Colours:	Red 51110, Reddish Brown 50220
Volume Solids:	61%
Specific Gravity:	1.9 kg/litre - 15.9 lbs/US gallon
VOC:	380 g/litre - 3.2 lbs/US gallon
Theoretical Spreading Rate:	4.9 m^2/litre - 125 micron
Dry Film Thickness:	125 micron - 5.0 mils
Recoat Interval:	Min: 10 hours at 20°C/68°F Max: See Product Data Sheet
Exposure time before undocking:	Min: 12 hours (2 x 125 micron 20°C) Max: 6 months depending on exposure conditions

For further details see Product Data Sheet

***GLOBIC SP-ECO exists in C, H and O versions representing different biocide compositions according to local regulations.**
Note: This product should not be used without reference to the relevant Product Data Sheet and Safety Data Sheet, copies of which are available from HEMPEL upon request.

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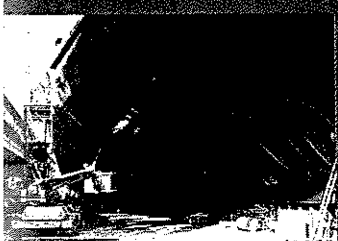
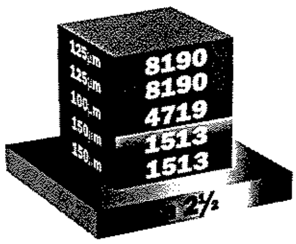
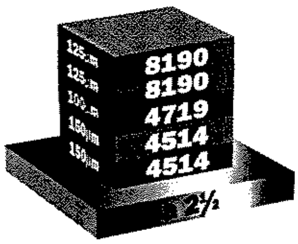


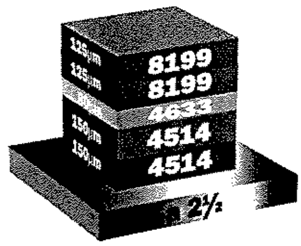
HEMPEL'S ANTIFOULING GLOBIC SP-ECO 8190 Series

Newbuilding

Typical coating systems





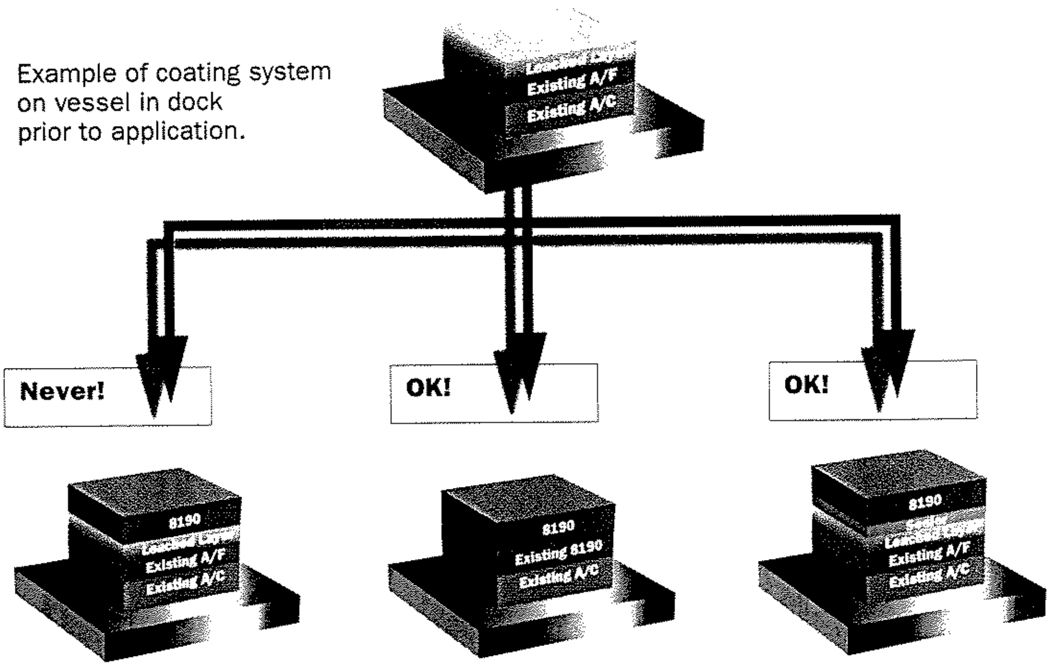


Products:
- HEMPADUR 1513 (Coal Tar Epoxy)
- HEMPADUR 4514 (Epoxy Coating)
- HEMPADUR 4719 (Epoxy Sealer)
- HEMPATEX 4633 (Sealer)
- GLOBIC SP-ECO 8190

Maintenance

- Conversion to GLOBIC SP-ECO 8190 Series
- Recoating of GLOBIC SP-ECO 8190 Series requires no sealer

Example of coating system on vessel in dock prior to application.



- Application directly on leached layer

- High Pressure Fresh Water Hosing
- Removal of leached layer
- Application of 8190

- High Pressure Fresh Water Hosing
- Application of sealer*
- Application of 8190

* The generic type and the condition of the existing antifouling determines if a sealer is needed. HEMPEL reserve the right to require the use of a sealer.

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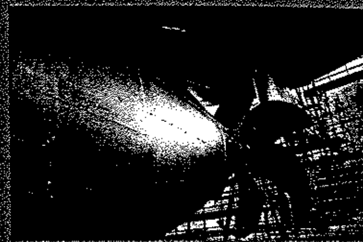
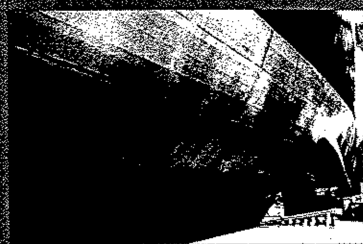
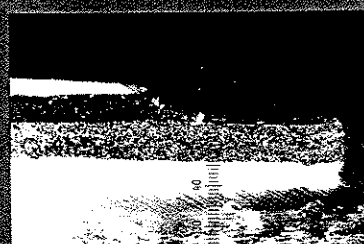
HEMPEL'S ANTIFOULING
GLOBIC SP-ECO 8199 Series*

8199

Self-polishing Antifouling
Tin-free
Newbuilding
Maintenance and repair
Deep Sea Vessels







GLOBIC SP-ECO 8199 is a major breakthrough in tin-free antifouling technology offering significantly improved fouling protection and self-smoothing properties compared to conventional tin-free antifoulings. It is part of a new generation of high performance self-polishing tin-free antifoulings with a fibre compo-site formulation and enhanced mechanical properties - developed for effective fouling control on vessels in global trade. It has been tested on a range of vessel types and has shown very promising antifouling performance. It is a low polishing rate product with a controlled release rate of powerful biocides and has excellent self-smoothing properties.

Specific Profile Vessels:
- **Medium to high speed vessels**
- **Moderate to high activity**
- **Short idle periods**
- **Global trade**

Engineered for:
- **Deep Sea Vessels**
- **Tankers**
- **Container Vessels**
- **Bulk Carriers**
- **General Cargo Vessels**
- **Reefers**
- **Car Carriers**

Features	Benefits
Tri-butyl tin-free	Comply with tri-butyl tin regulations
Very effective low polishing rate and balanced release rate of biocides	High performance fouling control - significantly higher than conventional tin-free systems
Hydrolysable zinc carboxylate polymer salt binder technology.	Excellent polishing properties
Excellent self-polishing properties	Extra fuel savings
Reduced formation of leached layer compared to conventional tin-free	Safe, fast and easy overcoating, reducing time in dry-dock and maintenance costs
Fibre composite technology (Patent pending)	Very good mechanical properties
No sealer coat needed on future applications	Saves time and paint in subsequent dry-dockings
High solids antifouling, high build coating	Lower VOC, reduced solvent emission

GLOBIC SP-ECO 8199 Product Data

Colours:	Red 51110, Reddish Brown 50220
Volume Solids:	61%
Specific Gravity:	1.9 Kg/litre - 15.9 lbs/US gallon
VOC:	380 g/litre - 3.2 lbs/US gallon
Theoretical Spreading Rate:	4.9 m^2/litre - 125 micron
Dry Film Thickness:	125 mm - 5.0 mils
Recoat Interval:	Min: 10 hours at 20°C/68°F Max: See Product Data Sheet
Exposure time before floating:	Min: 12 hours (2 x 125 micron at 20°C) Max: 6 months depending on exposure conditions

For further details see Product Data Sheet

***GLOBIC SP-ECO exists in D, F and 0 versions representing different biocide compositions according to local regulations.**
Note: This product should not be used without reference to the relevant Product Data Sheet and Safety Data Sheet, copies of which are available from HEMPEL upon request.

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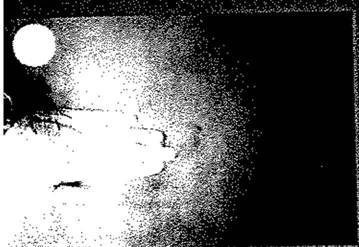
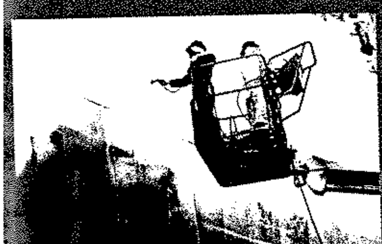
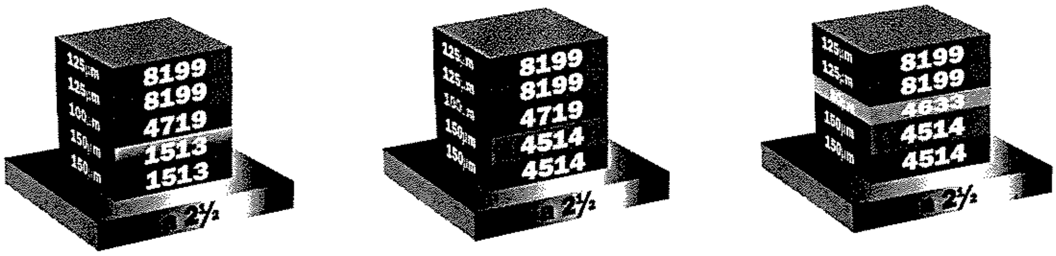


HEMPEL'S ANTIFOULING GLOBIC SP-ECO 8199 Series

Newbuilding

Typical coating systems

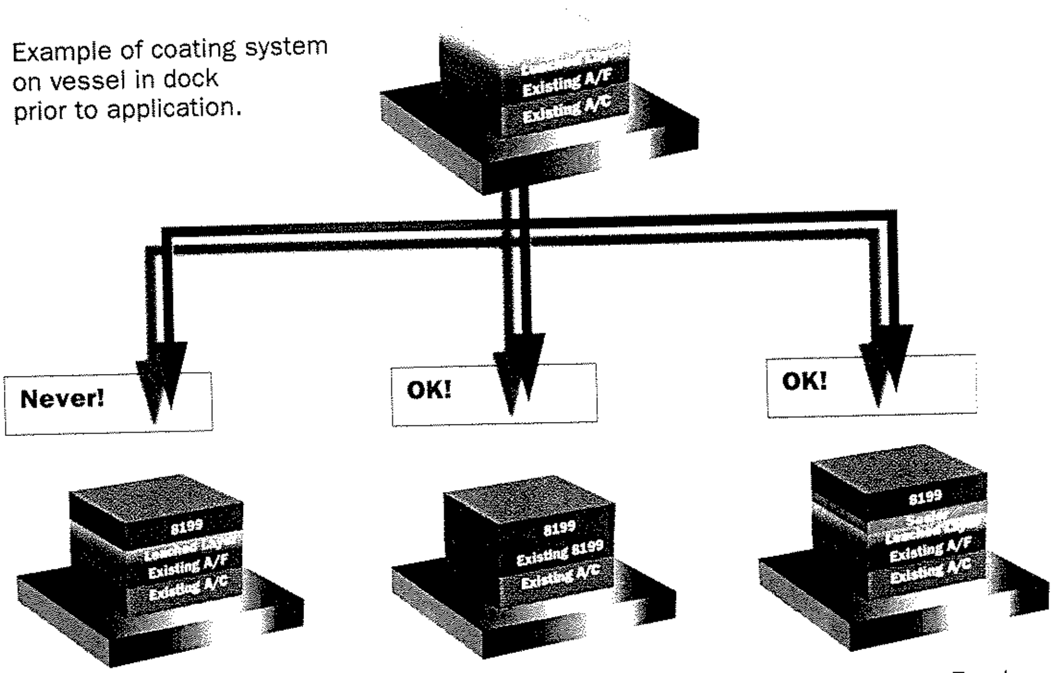


Products:
- HEMPADUR 1513 (Coal Tar Epoxy)
- HEMPADUR 4514 (Epoxy Coating)
- HEMPADUR 4719 (Epoxy Sealer)
- HEMPATEX 4633 (Sealer)
- GLOBIC SP-ECO 8199

Maintenance

- Conversion to GLOBIC SP-ECO 8199 Series
- Recoating of GLOBIC SP-ECO 8199 Series requires no sealer

Example of coating system on vessel in dock prior to application.



- Application directly on leached layer

- High Pressure Fresh Water Hosing
- Removal of leached layer
- Application of 8199

- High Pressure Fresh Water Hosing
- Application of sealer*
- Application of 8199

* The generic type and the condition of the existing antifouling determines if a sealer is needed. HEMPEL reserve the right to require the use of a sealer.

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