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Paint systems for the marine industry

Synopsis

The first part of the paper presents a general overview of the different paint systems used in the marine industry. Different methods of surface preparation and paint application are summarised. In the second part, the attention is focused on antifouling systems. Fouling is shortly introduced in Section 1 and a brief history of antifouling is presented in Section 2. Section 3 and Section 4 discuss TBT-SPCs and the impending ban on TBT. Section 5 presents the antifouling alternatives to TBT-SPCs.

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Part 1. General resume of paints and ingredients

The notes in this Part 1 are taken and slightly edited from International Paint's Technical course on Marine Coatings, 1999. See also BMT (1986) for a good published overview.

1. Introduction

Paint can be described as a liquid material capable of being applied or spread over a solid surface on which it subsequently dries or hardens to form a continuous adherent, obliterating film.

In the past paint technology and paint making were arts or crafts developed over many years and supported by results of practical experience.

The performance limitations of the paints produced were basically attributable to the available raw materials. These were predominantly of natural origin. For example, oxides of iron were used as pigments and various blends of vegetable oils and natural resins used as binders. These traditional coatings however, did generally fulfil the accepted demands of the time.

Significant advances in paint technology came about with the demand for higher performance, longer life coatings. These were eventually realised by the progressive introduction and development of synthetic raw materials and intermediates helping not only to alleviate the restrictions imposed on the paint chemist by traditional technology but also to establish a much more scientifically based industry. Reproducible products with predictable performance resulted.

The modern surface coating industry provides many different generic types of coatings used in many different circumstances and applied by many different methods. These range from conventional liquid paints applied by brush and drying at ambient temperatures by oxidation, to powder coatings applied by electrostatic spray and cured by heat.

The following notes describe the principal components of paints, their functions and the properties they impart to the finished product.

2. Paint technology

Paints are mixtures of many raw materials, each of which in turn has been manufactured to give certain specific properties. Basically, however, paints consist of three major components and many additives which are included in minor proportions.

The major components are:

1. Binder (other terms used include: vehicle, medium, resin, film former, polymer).
2. Pigment or extender
3. Solvent.

Of these only the first two form the final dry paint film. Solvent is necessary purely to facilitate application and initial film formation, it leaves the film by evaporation and can therefore be considered an expensive waste product.

2.1. Binders

Binders are the film forming components of paint. They are predominant in determining the principal characteristics of the coating, both physical and chemical. Paints are generally named after their binder component, (e.g. epoxy paints, chlorinated rubber paints, alkyd paints ', etc). The function of the binder is to give a permanent continuous film which is responsible for adhesion to the surface and which will contribute to the overall resistance of the coating to the environment.

Binders used in the manufacture of paints fall into two classes, convertible and non-convertible. The classification is solely dependent upon how they, form a film. In the case of liquid paints, how they change state, i.e. from a liquid to a solid. This transformation in paint terms is known as drying.

It will be readily appreciated that a convertible coating when dry will be chemically quite different from the paint in the can. With a non-convertible coating the dry film and the wet paint differ only in solvent content but chemically these remain essentially similar.

2.1.1. Convertible coatings

In liquid paints where solvent is involved, drying is considered a two stage process. Both stages actually occur together but at different rates.

Stage One	Solvent is lost from the film by evaporation and the film becomes dry to the touch.
Stage Two	The film progressively becomes more chemically complex by one of the following methods: -

A Reaction with atmospheric oxygen, known as oxidation.
B Reaction with an added chemical curing agent.
C Reaction with water, (generally as moisture in the atmosphere).
D Artificial heating.
E Radiation curing (e.g. ultra violet).

The films formed by the above methods are chemically different to the original binders and will not re-dissolve in their original solvent.

Generic types of binders which are in this category include: -

Oleoresinous varnishes	
Oil modified alkyd resins	Dry by oxidation
Urethane oil/alkyd resins	(air drying resins)
Epoxy ester resins	
Two component epoxy resins	Dry by chemical curing
Two component polyurethane resins	
Moisture cured polyurethane resins	Dry by water absorption
Organic silicate resins	

2.1.2. Non-convertible coatings

These types of paint binders are simple solutions of various resins or polymers dissolved in suitable solvent(s). Drying is simply effected by the loss of the solvent by evaporation. This is termed physical drying as no chemical change takes place. The resulting film is therefore always readily soluble in the original solvent and can also be softened by heat (thermoplastic). Generic types of binders which are in this category include:

- Chlorinated Rubber Resins
- Vinyl Resins
- Bituminous Binders
- Cellulose Derivatives

2.2. Pigments and extenders

Pigments and extenders are used in paints in the form of fine powders. These are dispersed into the binder to particle sizes of about 5-10 microns for finishing paints and approximately 50 microns for primers.

These materials can be divided into the following types:

• Anticorrosive pigments	To prevent corrosion by chemical and electrochemical means. e.g. Red Lead, Zinc Chromate
• Barrier pigments	To increase impermeability of the paint film.
• Colouring pigments	To give permanent colour e.g. Titanium dioxide, iron oxides
• Extending pigments	To help give film properties required.

2.3. Solvents

Solvents are used in paints principally to facilitate application. Their function is to dissolve the binder and consequently reduce the viscosity of the paint to a level which is suitable for the various methods of application, i.e. brush, roller, conventional spray, airless spray, dipping etc. After application the solvent evaporates and plays no further part in the final paint film, the solvent therefore becomes a high cost waste material. Liquids used as solvents in paints can be described in one of three ways:

- True Solvents: A liquid which will dissolve the binder and is completely compatible with it.
- Latent_Solvent: A liquid which is not a true solvent. However, when mixed with a true solvent the mix has stronger dissolving properties than the true solvent alone.
- Diluent Solvent: A liquid which is not a true solvent. Normally used as a blend with true solvent/latent solvent nixes to reduce the cost. Binders will only tolerate a limited quantity of diluent.

There are numerous solvents used in the paint industry. This is partly due to the number of different properties which have to be considered when selecting a solvent or solvent mixture. In addition to commercial factors such as price and availability, these include toxicity, volatility, flammability, odour and suitability (in certain countries certain types of solvents are not allowed).

3. Surface preparation

Before paint can be effective as an anticorrosive, the steel substrate to which it is to be applied must be clean. Cleanliness is necessary in order that maximum adhesion of paint to steel is obtained. This can only be successfully achieved when the coating comes into contact with the steel surface. Contamination of any kind such as rust, millscale, grease, oil or dust will obviously not allow direct contact. Overcoating such contaminated surfaces will inevitably lead to poorer adhesion and premature breakdown of the coating. For successful paint performance therefore, it is essential to achieve the recommended surface preparation standards.

New steel used for construction is invariably hot formed. This results in the formation of a mixed oxide surface layer generally called millscale**.**

Initially the millscale layer is continuous but not necessarily uniform in thickness. The thinner areas are more susceptible to penetration by moisture, which, together with the cathodic nature of the millscale to steel creates an electrolytic cell allowing corrosion to occur at the steel surface, i.e. the anode. Millscale is therefore detrimental to steel and should always be removed before painting.

Shipbuilding yards are almost invariably situated in areas where industry is concentrated and the atmosphere heavily polluted by industrial gases. If new steel plate is allowed to 'weather' the rust layer formed from this process is easily penetrated by the sulphurous gases which subsequently form corrosion products with a highly reactive nature because of the soluble salt content. These salts do not lie on the surface of the rust but are found within the rust near to the interface of the steel and the rust layer. The compact rust layer forms a barrier which prevents removal of these salts simply by washing with fresh water, and even prolonged washing with hot water is ineffective. The weathering of steel is therefore not recommended and should be avoided.

The following notes describe briefly the various methods for preparing steel prior to painting:
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1. Hand Scraping and Wire Brushing

This method is virtually ineffective, and more often than not, serves only to remove loose material and gross contamination. It fails to remove compact rust scale which is often encountered. The large area presented by the outside hull of a vessel does not allow any method which depends completely on manual effort.

2. Rotary Wire Brushing

This method does have some value, depending upon the condition of the surface. Loose 'Powdery rust can be removed but hard scale will resist the abrasion of the wire bristles. When rust scale is intact and adherent to base metal, rotary wire brushing tends merely to burnish the surface of the rust scale but does not remove it. The burnished rust scale may have the appearance of a well-cleaned surface which is often misleading. This method only has some benefit when cleaning highly rusted surfaces.

3. Mechanical Descaling: Hammers and Pistols

These are normally pneumatic instruments and are effective to some degree in removing thick rust scale. The action of these types of instalments is dependent upon a cutting blade or point pounding the surface and breaking away the scale. Cleaning is only effective at the actual points of contact. The intermediate areas are only partially cleaned because the brittle scale disintegrates, but the lowermost layer remains attached to the surface.

Descaling implements can be divided into two main types; those used for breaking large flat surfaces and consist of a number of broad chisel-like blades which rotate and strike the surface, and those which are hand operated used for treating small irregular areas like welds.

4. Discing

For treatment of localised areas of fairly severe corrosion and more widespread light corrosion, discing is an effective method of preparation producing a surface suitable to receive most types of paint systems. Normally silicone carbide type discs are used and the grade selected to suit the conditions of surface to be abraded. The method has limited application because it is slow when dealing with rust-scaled surfaces and the degree of cleanliness can vary quite considerably. However, for local repair, particularly in tanks, the method is often used instead of grit blasting because the quantity of dust produced is much less than by the latter method.

5. Flame Cleaning

Millscale can be removed by raising the surface temperature of the plate by using an oxyacetylene flame. The differential expansion between scale and plate causes the scale to crack away, leaving bright steel. With heavy scale, it may be necessary to repeat the process and to rotary wire brush between heat treatments. Loose scale and dust must finally be removed by thorough brushing.

6. Pickling

Chemical cleaning of steel has been practised for many years but has declined in recent years due to the advent of abrasive blasting. There are numerous methods available but a typical method consists of removal of rust and millscale by immersion in hot sulphuric acid containing inhibiting agents followed by thorough rinsing with hot water and finally immersion in hot phosphoric acid. It is important that all traces of acid should be removed from the steel surface otherwise blistering of the paint system may occur on subsequent exposure or immersion.

7. Abrasive Cleaning

This is the most widely used surface preparation method in present day shipbuilding. New plates are blasted automatically, usually by wheelabrator where steel shot is impelled against the plate surface by wheels revolving at high speed. The abrasive within the enclosed unit can be changed to suit the particular paint system but in the UK usually round steel shot is used and this reduces wear on the impeller wheels. This is a recirculating system and the apparatus provides for the removal of worn shot and other debris from the blasting medium. After blasting, the surfaces are cleaned by vacuum or compressed air blowers and brushes.

The automatic methods of blasting are relevant only to new plates whilst for vessels in service, 'open' blasting is used. In this method, abrasives are not recirculated and the type can vary, according to the country or locality in which they are used; from silica, i.e. washed sand, to copper free mineral grit. If sand is used it must be washed to remove salts and dried thoroughly.

The grits are usually by-products of heavy industry, such as the steel smelting industry, and are produced as slags which are crushed and sieved to give various sizes or grades. Health regulations in UK stipulate that grits used in open blasting should not contain free silica but the use of silica types is still permitted in some countries. The cost of silaceous abrasives is much lower than that of the mineral grits but some of the cost difference is reduced by the more effective and rapid results which can be achieved with grit. This is due to the greater hardness and shatter resistance of the grits and they also have a rather higher specific gravity than silica which gives the grits greater energy than sand when propelled against a surface at the velocity (normal blasting pressure 6-7 bar at the nozzle). The particle size of the grit has been reported as having an appreciable effect on the rate and cost of blasting. For open blasting it has been estimated that a mixture of equal proportions of medium grade (0.5 - 1mm) and fine grade (0.2 - 0.5mm) allows a blasting rate approximately three times greater than when coarse grit (1 3mm) is used. This, of course, will also give a considerable saving in cost.

The standard of cleaning by grit and shot blasting has been the subject of an investigation by several authorities and the Swedish Standards Institute has produced a reference book of photographs showing the various grades. This shows the various states of the steel surface with respect to corrosion before cleaning and the results which can be obtained for each state by scraping and wire brushing and also by grit blasting. The most usual grade required in practice for the application of paint coatings is that which is designated as Sa2½. The highest degree of surface preparation is Sa3 and there are some paint systems that require this highest grade to be successful, (e.g. zinc silicate).

Vacublasting has been used for some time by means of small hand operated machines usually for cleaning welds and other small areas; it is often used in cargo tanks and other confined spaces where contamination by grit must be avoided. The method is rather slow but it is probably the most efficient way of cleaning rough welds to remove corrosion and other contamination.

There is no simple answer to the question 'how well must a surface be cleaned to receive a particular paint system?' Any paint system must be considered in conjunction with the various factors which will affect its life expectancy, e.g. is it intended for sea water immersion or atmospheric exposure; for the internal surfaces of cargo tanks or in, cargo holds; for accommodation or engine room? Will it suffer mechanical damage? Will it be required to be decorative? Experience can go some way to answering these questions and the tests which are carried out in the laboratory and in the field are invaluable in this respect.

Economic considerations, however, are often the overriding factors, but in many cases economy at one stage may lead to a far greater expense for maintenance later. In this respect there are several areas of particular importance, i.e. the outside hull below water and boottopping, cargo tanks, ballast and fresh water tanks and certain holds. Inaccessible places such as double bottoms, fore and aft peak tanks must also come within this category. All these places should receive special attention because remedial treatment in these areas is restricted to periods in drydock and any increase in the length of time that the vessel is out of service can cost many times the amount saved by inadequate surface preparation and insufficient paint in the first place.

4. Recommended cleaning and painting procedures for the maintenance of vessels in drydock

4.1. Introduction

The service life of any steel fabricated vessel is dependent upon many factors and one of the most critical is that of correct hull maintenance.

Painting ships is the most cost-effective way of controlling corrosion and fouling and regular maintenance is essential to keep operating costs to a minimum.

Maintenance and repair schemes make recommendations regarding the type of recoating materials which are considered suitable. It is advisable to continue with the same type of materials as the existing scheme. If that is not possible, then the compatibility of alternative schemes must be very carefully considered.

Conventional antifoulings often present a rather powdery texture and are unsuitable to recoat without the application of a sealer coat. The selection of the sealer depends, not onlv on the antifouling but also on the type of anticorrosive system beneath it. When repairing damaged coatings a suitable method of preparation for those areas has to be selected.

The following notes outline the different procedures considered necessary for effective maintenance of vessels in drydock.

4.2. Vessel in drydock

Before any maintenance painting can be done the surface to be coated must be free from contamination.
The surface preparation can be divided into two sections:

1. General surface cleaning of the areas where existing coatings are intact but require recoating to improve protection, antifouling properties or cosmetic appeal.

2. The treatment of specific types of breakdown such as damaged corroded areas. paint detachment or blistering.

4.2.1. General surface cleaning

(a) Oil and Grease Removal

The presence of even a very thin layer of oil or grease can destroy or seriously impair adhesion of paint coatings.

Solvents such as white spirit can be used to dissolve the grease, but the problem then becomes one of completely removing the solution of oil in solvent. Drying with rags or cloths invariably means spreading the solvent/grease solution over a larger area and unless repeated washing with solvent is carried out total removal of the contamination is not achieved.

A more effective method is to apply a proprietary water soluble oil and grease removing fluid and brush it into the surface then to fresh water hose until all contamination is removed.

(b) Dried Sea Salts and Weed Fouling

The removal of both sea salts and weed fouling should be done by high pressure fresh water washing preferably using a fanjet with a minimum pressure of 210 kg/cm^2 (21 MPa). With this method salt deposits are relatively easily removed, however, weed fouling can be more difficult particularly if dry. Traces of slime residues must also be removed and this is best confirmed by rubbing the flat palm of the hand over the substrate. Slime contaminated areas feel greasy whilst clean areas are not. If done correctly high pressure cleaning will also remove loose paint coatings.

If high pressure equipment is not available then normal fresh water hosing together with thorough hand scrubbing should be used. This method, whilst removing most soluble deposits does not remove any offending layers of poorly adhering coatings.

(c) Shell Fouling

Shell organisms are much more difficult to dislodge from a surface than weed fouling. Quite often high pressure water washing will not remove acorn barnacles although other species such as goose-necked barnacles, tube worms and hydrozoa may be removed. Those organisms which resist removal by high pressure washing should be manually scraped ensuring that the adhering bases are also removed.

4.2.2. Treatment of surface defects, corrosion, detachment, etc

The surface preparation techniques to deal with surface defects are the same as discussed in Section 3 for the treatment of bare steel.

5. Paint application

5.1. Application conditions

Normal Conditions

When applying marine paints, the most important factors to consider are the state of the surface, the surface temperature and the atmospheric conditions at the time of painting. When a vessel enters drydock, the hull temperature up to the floating line will be that of the sea water. Above the floating line, the steel temperature will be closer to atmospheric.

During the night steel temperatures fall. They rise again during the day but there is always a lag in movement of steel temperature compared to the atmospheric condition, so condensation on the steel surface is possible. Condensation will occur if the steel temperature is below the dew point of the atmosphere. If this is likely to be a problem, the ship should be totally emptied of ballast water to reduce its thermal mass as soon as it enters drydock.

Bad weather is a familiar problem to those using marine paints. Relative humidity itself rarely creates a problem. Most paints will tolerate high humidities, but humidity should not be permitted to lead to condensation on the surface being painted. In order to determine whether or not a surface is wet, the steel temperature should be measured using a surface temperature thermometer and the dew point calculated after measurement of humidity with a hygrometer. Paint application should not take place when steel temperature is less than 3°C above the dew point.

Paint should not be applied when surfaces are affected by rain or ice. Some two-pack paints, e.g. epoxies, should not be applied at low temperatures as full cure will not be achieved.

Borderline Conditions

When a vessel enters drydock, conditions may not be entirely suitable for painting, but nevertheless painting must proceed if the vessel is to undock on schedule.

If the steel temperature is close to the dew point, i.e. within 3ºC, better adhesion can be achieved by applying paint by brush or roller. This physically disturbs any moisture on the surface. Application by spray causes the paint film to lie over the moisture.

Extreme Conditions

Generally extreme conditions refers to temperatures below 5ºC or above 30ºC.

Below 5ºC, the curing of paints such as epoxies slows down dramatically and for some paints curing stops altogether. Other marine paints are not so severely aflected. Chlorinated rubbers and vinyls are quite suitable for use at temperatures below 0ºC provided that the surface is clean and free from ice or frost.

At the other extreme 30ºC and above, the drying and curing of paints is rather rapid and care should be taken to avoid dry spray. This is caused by the too rapid loss of solvent from paint droplets between the spray nozzle and the surface. It can be minimised by holding the spray gun at a minimum suitable distance from the surface and spraying at right angles to the surface to be painted. If problems are still encountered then additional thinners will help but not more than 5% by volume should be added.

5.2. Application methods

The objects in applying paint coatings are to provide films which will give protection and, normally to a lesser extent, decoration to the structure being painted. The variables which govern the success of an application are:

(i) Surface preparation.
(ii) Film build and total thickness of system.
(iii) Method of application.
(iv) Atmospheric conditions during application.

The normal methods of application of paint coatings are by:

- Brush
- Roller
- Conventional Spray
- Airless Spray

Other methods may also be encountered, such as dipping and pouring, and more sophisticated adaptations of spraying such as electrostatic, powder coatings application, and automatic plants.

5.2.1. Brush Application

The oldest method of paint application is not as fast as spraying or rollering and is generally used for the coating of small complicated or complex areas or where the need for ‘clean’' working with no overspray precludes the use of spray application.

When painting it is important to dip the brush in paint frequently and not to 'over-brush' the surface as this will result in large variations in film thickness, the inherent problem with brush application. Choice of brush, both size, length and type of bristle, and shape, are important, and the type of paint being applied will modify the selection. Thus large flat brushes are normally used for the majority of purposes, but round brushes are better for painting bolt-heads and 'difficult' areas. Special brushes are available with offset heads and long handles to facilitate painting the 'backs' of strictures and inaccessible areas.

Brush application is most suited to the slower drying, normal build type of coatings, and will not always be suitable for more sophisticated 'fast-drying' or 'high-build' materials. It is often not possible to achieve the required film thickness in the same number of coats as with spray application, and multi-coat applications are necessary to give the specified film build.

5.2.2. Roller Application

Roller application is faster than brush on large, flat surfaces, such as tank sides and tops and walkways and deck areas, but is not so good for 'difficult' areas. It is hard to control film thickness, however, and care must always be taken that the coating is not 'over-rolled' in the same manner that it can be 'over-brushed'. Choice of roller pile - short or long hair, sponge or lambswool - is dependent on type of coating and roughness and irregularity of surface being coated.

5.2.3. Conventional spray

This is a widely accepted, rapid method of applying paint to large surfaces. The equipment is relatively simple and is usually confined to fairly low-viscosity paints, although newer techniques using 'pressure-pot' or 'hot spray' apparatus allow application of some of the ‘higher build’ type coatings. Whatever type of equipment is used, the mechanism is the same. Paint and air are fed separately to the spray gun and mixed at the nozzle, where the paint is atomised and air is mixed with these droplets forming a fine mist of paint which is carried by-the air pressure to the work surface. The pattern of the 'fan' so produced is controlled by adjusting the air and fluid pressures, and major changes in paint type can be accommodated by different sizes of nozzle.

It is important to have only sufficient air to provide good atomisation, as excess air gives rise to overspray and 'rebound' from the work surface. The gun should be held at right-angles to the work surface with the nozzle some 15-18cm away. Normal air pressure is from 2.8 - 5.6 kg/cm^2 (0.28 – 0.56 MPa).

5.2.4. Airless spray

By far the most important and efficient method for the application of heavy duty marine coatings.

As the name implies. it is a technique of spray application which does not rely on the mixing of the paint with air to provide atomisation, which is achieved by, forcing the paint through a specially designed nozzle or 'tip' at very high pressures (176-246 kg/cm^2 or ca. 17-24 MPa).

This very high pressure is provided by a hydraulic pump driven by an air motor, which explains why the pump unit requires a supply of compressed air, a fact which often confuses the newcomer to the industry when told it is ‘airless spray’

Pumps are available with compression ratios from 20:1 up to 60:1, which means that with an input air pressure to the motor of 5.6 kg/cm^2, the maximum paint pressure at the gun would be 1 12 kg/cm^2 and 338 kg/cm^2 respectively. These are very high pressures, and it is imperative that stringent safety precautions are taken when using airless spray equipment. A paint jet at this pressure can easily penetrate the skin and necessitate a painful operation to cut open the tissue and thoroughly clean out the wound to prevent gangrene. The loss of a finger is not unknown among sprayers.

The major advantages of airless spray over conventional spray are the reduction of overspray and the ability to apply high build coatings at higher film thicknesses. This leads to savings in number of coats and loss of paint, with the added bonus of reduction of toxicity, and the lessened explosion risk. A typical airless spray set-up would comprise:

1. Compressor

It should be capable of providing the required volume of air - fitted with an oil/water separator to ensure this is clean and dry.

2. Pump Unit

The unit should have a suitable 'ratio' that can readily handle the paints being applied. A high ratio pump working at half capacity will last much longer than a lower ratio unit working 'flat-out' all of the time. The 'packings' used in the pump should be solvent resistant. The unit should always be earthed when in use.

3. Fluid Line and spraygun

it is important that the line is in good condition and has been tested and approved for operation under high pressure. Long lengths of line will lead to pressure drops at the gun. It should also have a built-in earthing line to ensure no static build-up.

4. Tips - reversible type

These are precisely constructed from tungsten carbide, and consist of an orifice, into the front of which is cut a V-groove or slot. Tips can be obtained with different orifice diameters and slot angles, and the tip must be chosen according to the properties of the paint, the required wet film thickness per coat and the shape and contours of the job.

Because of their small size there are often problems with the tips becoming blocked. In the past this necessitated taking the tip off the gun and cleaning it out, but now it is possible to use a 'reversible' tip. This is a device which allows the tip to be turned around through 180º' whilst still attached to the gun. A 'burst' of paint then forces out the obstruction through the back of the tip, which is quickly 'reversed' and spraying can continue.

Tips will wear, especially when using abrasive paints, such as zinc silicates or micaceous iron oxide pigmented materials, and it is important to check that wear is not excessive. High paint usage or poor atomisation can often be due to a badly worn tip.

Part 2. Antifouling

The notes for Section 1 and 2 are based on **V. Bertram (2000)**, Past, present and prospects of antifouling methods, *32nd WEGEMT Summer School on Marine Coatings*, Plymouth, July 2000

1. Fouling

Fouling is the undesirable growth of organisms on artificial structures immersed in seawater. The most visible form of such fouling are barnacles and seaweed which degrade the performance of ships considerably. Worldwide, the cost of keeping marine fouling at bay is estimated to at least 1.4 billion dollars a year, Clare (1995).

For conventional ships, 50-80% of the resistance is caused by friction between the water and the wetted surface of the ship. The smooth, wetted surface of a newly built ship has a roughness of about 80-130 µm. However, the roughness of a surface fouled with for example green algae can easily exceed 1000 µm.

The process of fouling can be divided into four stages, as illustrated in Figure 1 (Davis and Williamson, 1995).

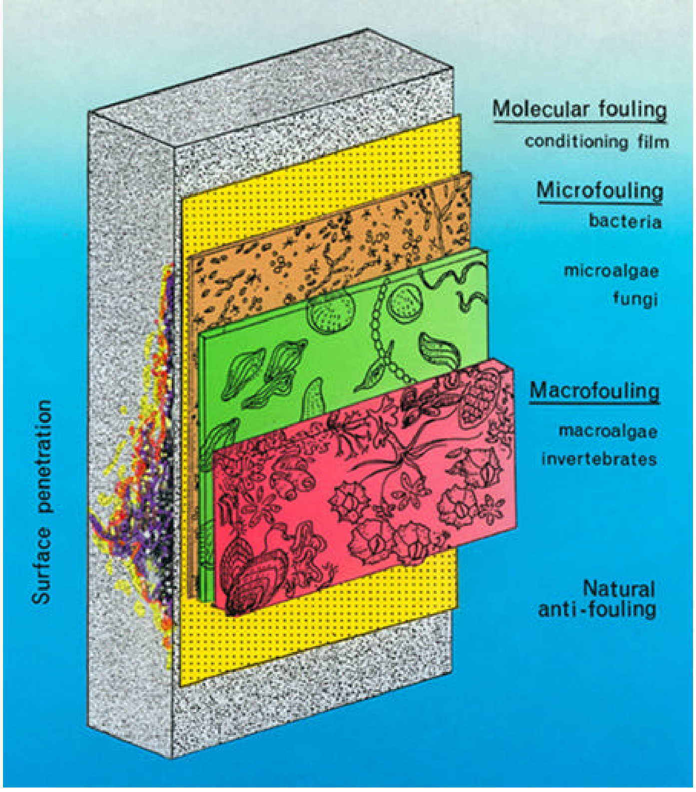

Figure 1. Build-up of marine biofouling (from Davis and Williamson, 1995).

1. Fouling starts from the moment the ship is immersed in seawater. The hull rapidly accumulates dissolved organic matter and molecules such as polysaccharides, proteins and

protein fragments. This conditioning process is regarded as the first stage of fouling. It begins within seconds, stabilises within hours, and sets the scene for later fouling stages.

2. Bacteria and unicellular organisms then sense the surface and settle on it, forming a microbial film. This second stage of fouling involves the secretion of sticky muco-polysaccharides. This slime already reduces the ship's performance:
   - the 'Lucy Ashton' had 3 -5 % added resistance after 40 days of immersion
   - Watanabe et al. (1969) report 8-14% added resistance due to slime.
   - Bohlander (1991) reports 8-18% added power for a frigate

3. The presence of adhesive exudates and roughness of irregular microbial colonies enables the settling of more particles and organisms. These are likely to include algal spores, marine fungi and protozoa. The transition from a microbial film to a more complex community that typically includes multicellular primary producers, grazers and decomposers is regarded as the third stage of fouling.

4. The final stage involves settlement and growth of shell fouling and seaweeds. Green weed can grow up to 15cm long in a band a few meters wide at the waterline. It grows rapidly and scrubbing it off triggers an even more vigorous growth within a few weeks. Shell fouling may consist of barnacles, mussels, polyzoans, and tubeworms. Weed and shell fouling decrease the ship's performance drastically.

Figure 2. Fouling green algae (NERC, 1995)

Figure 3. Massive shell fouling (Clare, 1995)

Ship fouling is most commonly prevented by the use of antifouling paints. These usually contain biocides that are release during the lifetime of the coatings, creating a concentration of biocide within a surface micro-layer of water adjacent to the paint surface, thus preventing settlement of juvenile fouling organisms. There are over 4000 marine fouling species, therefore the biocides used in antifouling paints must have a wide spectrum of activity to cover such a diversity of organisms (Anderson, 2000).

2. Historical development of antifouling

The history of antifouling methods dates back to ancient times, but the topic remains an important issue for research until today. In the middle of the 19th century, antifouling paints were developed to prevent marine growth on ship hulls. The basic principle was the same as in today's antifouling paints: some toxic substance was mixed with the paint and killed by some kind of leaching mechanism marine organisms.

In the 5th century BC, historians report that coatings of arsenic, sulphur, and oil were used to combat shipworms. In the 3rd century BC, the ancient Greeks used tar and wax. From the 13th to 15th century, pitch, oil, resin, and tallow were used to protect ships.

The first record about antifouling paints is in the British patent of William Beale in 1625. Beale used a mixture of cement, copper compound, and powdered iron. In 1670, Philip Howard and Francis Watson patented a paint consisting of tar, resin, and beeswax. In 1791, William Murdock patented a varnish mixed with iron sulphide and zinc powder, using arsenic as antifoulant. Until 1865, more than 300 such 'patent paints' were registered. All of them were quite ineffective. In 1860, James Mclnness used copper sulphate as antifoulant in a metallic soap composition. This 'hot plastic paint' was very similar to the 'Italian Moravian' paint, which was a rosin and copper compound developed at the same time in Italy. This was the best paint at the time. In 1863, James Tarr and Augustus Wonson were given a US patent for antifouling paint using copper oxide and tar. In 1885, Zuisho Hotta was given the first Japanese patent for an antifouling paint made of lacquer, powdered iron, red lead, persimmon tannin, and other ingredients. A variety of paints was developed in this era. Copper, arsenic, or mercury were popular antifoulants. Binder included turpentine oil, naphtha, and benzene. Linseed oil, shellac, tar, and various kinds of resin were used as matrix. At the end of the 19th century, 'Italian Moravian' and McInness' hot plastic paint were widely used, but these paint were expensive and their life-span short.

In 1906, the US Navy tested hot plastic and other antifouling paints at Norfolk Navy Yard. From 1911 to 1921 many more experiments were performed. From 1908 to 1926 ceramic-type paints were tested but they lasted only 9 months. In 1926, the US Navy developed hot plastic paint, using tar or rosin as binder and copper or mercuric oxides as toxics. Hot plastic paint required some heating facility for the paint at the ship's site which made application difficult. So 'cold plastic paints' were developed which were easier to apply. These paints already effectively decreased fouling and the periods between dry-dock times (for re-painting) was extended to 18 months.

In the 1960s organotin paints were commercialised. Initially organotins were used as co-toxicants for high performance copper paints. Later all-organotin systems emerged which did not contribute at all to corrosion on steel or aluminium. Organotin polymer-based (“self-polishing”) antifoulants were hailed as a “wonder weapon” at the end of the 1970s because these systems could provide up to 5 years fouling-free performance, kept the hull smooth and low-resistant, and were easy to apply. The antifouling problem seemed to be solved at last.

Table 1. Historical development of antifouling methods (from Bertram, 2000)

Ancient	Resistant wooden ship - coating of coal tar, oil, and wax - wooden and metallic (lead, copper) sheathing
1850 - 1900	Resistant wood and iron ship copper sheathing, galvanic action for iron "patent paints", almost Ineffective "Italian Moravian" hot plastic paint, fairly effective
1900 - 1950	Antifouling paint - various binders and copper oxide - hot plastic paint, followed by cold plastic paint
1950 - present	Antifouling paint - Insoluble or soluble matrix used, containing copper oxide and mercuric oxide as toxics - organotin and copper oxide combinations - organotin polymer antifoulant (self-polishing co-polymer)
present - future	Paint and system - low and non toxic paint - electrolysis technology of seawater by electro-conductive coating system - use of copper alloy etc. - Low surface-energy paint

3. Self-polishing co-polymers

The industry 'benchmark standard', against which performance of all antifouling paints is now measured, is that of the tributyltin self-polishing co-polymer (TBT SPC) products. TBT SPC products contain an acrylic co-polymer as the film-forming component of the paint, with the TBT biocide chemically bonded to the polymer. In the finished paint other biocides are included, usually copper compounds and 'booster biocides', along with additives and solvent.

On immersion, a reaction occurs between seawater and the TBT copolymer which. releases the TBT and the other biocides present. The reaction is confined to the top few nanometers of the paint surface. This chemical reaction results in the formation of a water-soluble reaction product, which is then able to dissolve away, resulting in the surface 'polishing' away with time, and so releasing the other biocides in a steady controlled way. The biocide release is controlled by this chemical reaction, and it has been finely tuned over the past 25 years in order to minimise cost and to maximise lifetime. The lifetime itself is directly related to the thickness of coating applied, and in-service lifetimes of up to 5 years are easily achievable.

The fact that the reaction only occurs at the surface, and not in the bulk film, is of major importance. Since it is purely a surface reaction, the depleted “leached layer”, from which the biocides have been leached out, is very thin (usually less than 20 μm) and this means that biocide release is not impaired, and it can be easily overcoated without the need for extensive pre-treatment. Simple high pressure fresh water washing is all that is required. This keeps maintenance and repair costs down to a minimum.

The paint film of TBT SPC products is also mechanically strong, and is able to withstand extreme environmental conditions. This makes it ideal for use during the long periods of exposure to the atmosphere which can occur during new construction.

The biocidal potency and wide spectrum activity against fouling organisms of the [TBT+Copper+Booster] biocide combination, coupled with the precisely controlled release rate, allows vessels coated with TBT SPC products to maintain a high level of fouling control for long periods. Typical records show that over 90% of vessels with high performance TBT SPC products return to dry-dock in a satisfactory condition, at the end of the specified lifetime of the paint scheme applied.

4. The TBT ban

In the early 1980s it became clear that organotin (TBT) not only killed fouling organisms, but its slow release into the water had toxic effects at concentrations of parts per billion on a wide range of other marine species, particularly molluscs such as whelks and oysters. In marine harbours that were contaminated with the TBT, whelks were starting to show sex-changing disorders, and oysters developed abnormally thick shells. Within a few years, some whelk species had disappeared from many harbours and marinas along the North Sea. Environmental concerns grew as poisoning of marine organisms including fish had risen to alarming levels (Bertram 2000)

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The effects have also been detected in the vicinity of maintenance and repair drydocks where repair TBT contaminated washdown water is released untreated into the marine environment.

Current situation

As a consequence of these observations, the use of TBT in all antifouling products used on vessels < 25m length overall (L_{OA}) was banned in 1989 in the European Union and similar bans have been introduced throughout the world. A summary of antifouling regulations worldwide (Hunter and Cain, 1996) implies furthermore that in most countries:

- all antifoulings used require registration
- TBT antifoulings must have a release rate of less than 4 μg TBT/cm^2 per day
- in certain countries washing water and blasting abrasive used to prepare TBT antifoulings should be collected and treated as a hazardous waste

The guidelines in Japan effectively mean application of antifoulings containing TBT is no longer allowed. In 1990 the International Maritime Organisation Marine Environment Protection Committee’s (IMO-MEPC) report included recommendations (that TBT antifoulants on vessels < 25m L_{OA} should be banned and dockyard practices should be improved to minimise discharge of TBT in contaminated washdown water.

Overall, the legislation appears to have had a positive environmental effect with falling TBT levels (indicated by assessments of water, sediments and shellfish taken from areas where TBT had previously been detected). Biological recovery has also been observed in coastal dogwhelk and oyster populations. “Elevated levels of TBT and biological effects are now reported to specific localised ‘hotspots’, i.e. coastal areas adjacent to drydocking operations or within busy commercial harbours and ports. In these hotspots where concentrations are relatively high, implementation of the legislation reducing the release of contaminated water washings from drydocks will further reduce TBT levels” (Hunter and Cain, 1996).

Nevertheless, the real problem with TBT is not its toxicity as such - this is in fact its biggest asset - but the fact that it is too stable in sea water (Milne, 1991), retaining its biocidal potency when it is no longer needed.

The IMO Regulations for 2003/2008:

Because of the environmental concerns, the International Maritime Organisation Marine Environment Protection Committee's (IMO-MEPC) published mandatory regulations to ban the use of toxic antifouling paints containing organotins such as TBT. A draft resolution has been submitted to IMO in 2000, urging the MEPC to ensure global prohibition on the application of organotin compounds by 2003 and a complete prohibition of these biocides in antifouling on ships by 2008. The resolution will now be presented to a full plenary session of the Committee and looks likely to be approved shortly, despite much debate.

The objections to approval of the ban not only comes from shipowners (who will have to pay more for tin-free antifouling alternatives) but also from biologists and environmentalists. The argument centres on the viability of the alternatives to TBT, assuming that the systems currently do not deliver the same satisfactory antifouling performance. If the performance is not as good, fouling will cause the resistance of a ship will rise sharply (cf. Section 2) and increase fuel consumption and air pollution.
"Deep-sea vessel owners derive the greatest benefit from TBT-SPC products as fuel costs represent the major component of total operating costs. The relative economic importance of effective antifouling coating performance varies for different ship types. Tankers and fast ships such as container vessels are particularly sensitive to increases in fuel consumption and thus have an essential need for high performance antifouling coatings. The economic penalty associated with minor fouling on coasters is relatively small compared to deep-sea vessels, since other components of their total operating costs represent a greater proportion of the total cost (crew costs, harbour dues, etc.). The excellent performance delivered to deep-sea vessels from TBT-SPC antifouling products provides major economic benefits, but also environmental benefits in less fuel burned and associated reductions in air pollution" (Hunter and Cain, 1996). "There is a case for the continued use of TBT-SPCs for deep-sea vessels, and a ban for coastal vessels would greatly reduce TBT inputs into coastal environments" (Hunter and Cain, 1996).

The discussion about the TBT ban thus currently centres on the central argument that the negative biological effects of TBT would be preferable to the increased fuel consumption and air pollution implied with the use of tin-free alternatives.

However, as will be seen in Section 5, the tin-free alternatives do give up to 5 years satisfactory performance and with that, the whole argument loses ground.

The decision is of great importance to the marine industry and is currently extensively commented on. In 1993 (Anderson, 1993), the established antifouling volumes sold excluding Japan (where there already was a switch to TBT-free products), was made up of 69 % TBT systems, 16 % TBT-free, and 15 % conventional (see Section 5). It is certain that these volumes will have changed significantly by 2008.

A topic of concern now is the treatment of dockyard wastewater and the practical logistics involved in removing all of the TBT-SPC coatings by 2008.

5. Whither antifouling paints after TBT?

The notes in this Section are slightly edited from **C.D. Anderson (2000),** Whither antifoulings after TBT?, *NAV2000 Conference Proceedings*, Venice, September 2000.

A wide variety of new TBT-free products have been introduced over recent years in order to replace the TBT-SPCs effectively. In general, two main generic routes have been followed: a biocidal route, based principally on the use of copper and boosting biocides, and a non-biocidal route, using foul-release technology (Anderson, 2000).

5.1. Copper-based antifouling paints

When seeking a biocidal route to replace TBT-SPCs, most formulators have developed antifoulings based on copper, which has been used since the late 1700s for fouling control on ships. “Two main technology routes have been followed for these copper-based antifoulings:

(i) Upgrading conventional “soluble matrix” technology, using modern reinforcing resins. This is referred to as “Controlled Depletion Polymer” (CDP) technology.
(ii) Synthesis of completely new acrylic polymers which react with seawater in the same way as the TBT co-polymers. This is referred to as “TBT-free SPC” technology.

Both these technologies achieve their overall antifouling effectiveness by including boosting biocides to work alongside the copper compounds used. These boosting biocides have been selected to have minimal environmental impact, in particular by having shorter half-lives in seawater than TBT” (Anderson, 2000).

5.1.1. Controlled depletion polymers

“Controlled Depletion Polymer (CDP) antifoulings are derived from traditional or conventional “soluble matrix” antifoulings, and are formulated using a substance obtained from trees: Rosin. This material has been used for well over a century by antifouling paint chemists, and is used because it is slightly soluble in sea-water. This enables the paint film to slowly dissolve or “solubilise” and thus release the biocides contained in the coating matrix. Rosin is a cheap renewable resource, but it does have some drawbacks. It is a brittle material, and if too much is used in the coating it can cause cracking and detachment. In order to overcome this, CDP systems include modern reinforcing polymer resins, such as acrylics, vinyls, polyesters or polyamides. Care has to be taken not to include these polymers at too high a level since they are water insoluble, and addition of too much would retard the solubilisation process and so prevent biocide release (Milne, 1991).
Another drawback of Rosin arises from the fact that, unlike the TBT SPC polymers, it cannot prevent seawater penetration into the depth of the coating. As the seawater penetrates further and further into the bulk of the CDP film, a large leached layer can develop, slowing down biocide release, which eventually leads to the attachment of fouling. In CDP systems, this is most commonly seen as green weed on the vertical sides. Prior to the advent of TBT SPC systems, it was well known that the leached layer was the rate-controlling and lifetime-limiting step in all antifouling formulation work. Once it is formed, the only way to remove it

is either by in-water scrubbing, or by high pressure fresh water washing in drydock. If it is not removed prior to overcoating, it can lead to detachment and increased roughness at subsequent dockings.

Given the above disadvantages inherent to Rosin, CDP systems based on it cannot match the longevity and fouling control performance of TBT SPC systems" (Anderson, 2000).

5.1.2. TBT-free SPCs

"The main developments in TBT-free SPC antifoulings have been pioneered by Japanese paint companies, in response to the TBT application ban which was introduced in Japan in the early 1990s. A series of new acrylic polymers have been synthesized which attempt to mimic the chemistry of TBT in seawater. There are three main types:

- Copper Acrylate
- Silyl Acrylate
- Zinc Acrylate

The first of these to be introduced was the copper acrylate system, launched in 1990 under the brand name "Ecoloflex SPC", by Nippon Paint Marine Coatings. The copper acrylate polymer reacts with seawater in exactly the same way as the TBT SPC co-polymer, producing a soluble micro-layer at the paint surface, resulting in the gradual "polishing away" of the coating. This mechanism ensures that there is no leached layer build up over time, and that the biocides in the system are released in a controlled way, to give long-term fouling protection, and with lifetime proportional to the thickness applied.

The biocides in the Ecoloflex SPC products are copper oxide and zinc pyrithione. Copper itself is safe to man and the environment when used in antifouling paints for ships, and is registered for use as an antifouling biocide in products for commercial vessels with government authorities around the world. It is clearly accepted that its use in antifouling paints is much safer to the environment than TBT. Zinc pyrithione is degraded and becomes non-toxic quickly after release from the coating. It is not persistent and will result in minimal impact on the marine environment. The other major use of zinc pyrithione is as an anti-dandruff agent in shampoos. As many thousands of tonnes of this substance is applied to human hair each morning and subsequently discharged into the environment via sewage treatment works without incident, its safety to humans and the environment is proven.

Ecoloflex SPC products have been applied to the complete underwater hull of over 1,350 commercial vessels greater than 4,000 dwt.

At present there are more than a dozen ships currently in-service with five year Ecoloflex SPC systems applied to the entire underwater hull. One of these has now completed 53 months in-service and a recent underwater inspection showed that performance was good. The Royal Australian Navy has also been carrying out long-term testing of Ecoloflex SPC on Patrol Boats, and after 64 months Ecoloflex SPC showed exactly equivalent performance to the standard TBT-SPC product used. This was far superior to the other tin-free products tested, which were all of the CDP type" (Anderson, 2000).

5.2. Foul-release systems

“From an environmental perspective the most desirable approach to fouling control is one which does not rely on the release of biocides to achieve its effect. One of the first patents in this area was filed in January 1975, which was less than a year after the launch of the first TBT SPC system (April 1974). This patent describes a biocide-free fouling control coating which is based on silicone elastomer technology, and which works on a “non-stick” principle.

This technology was largely dormant for the years 1975 to 1990, during which time the TBT SPC systems came to dominate the antifouling market. It has only been since 1990, as the environmental problems associated with TBT SPC have arisen, that the technology has re-emerged in the marine market. There are now silicone-based foul release products available for both high speed specialist vessels (such as fast ferries, trading at over 30 knots) and for high activity deep sea scheduled ships, which operate at speeds between 15 and 30 knots (< 10% of the world fleet by dwt)” (Anderson, 2000).

These foul-release coatings rely partly on their smoothness and partly on their low surface energy for their efficacy (Candries et al., 2000). Fouling organisms have difficulty adhering to the smooth, hydrophobic surfaces, and so either move away to find another, more favourable, site for settlement, or they are removed by the action of the seawater over the hull during voyaging (Kovach and Swain, 1998). A force of less than 0.7MPa is required to remove most types of fouling off these surfaces. The only type of fouling that can adhere, even at speeds in excess of 35 knots, is slime fouling. The effect of this slime fouling has not been fully evaluated. Operators such as Tropical Shipping, Norwegian Cruise Line and Leif Hoegh/Cool Carriers, who have compared fuel consumption and speed before and after full ship applications of a commercial foul release system Intersleek, report that little difference can be seen between the previously used TBT systems and the foul-release (even with slime). It would appear that, although the foul-release is initially smoother and has less drag (Candries et al., 1998, 2000), this is then off-set by the slime fouling that inevitably occurs, resulting in an overall drag which is similar to that of the previous TBT SPC system, which was less smooth originally.

When compared to CDP systems on the other hand, there have been reports of significant speed increases and fuel savings achieved with Intersleek. On one 36m high speed catamaran the operating crew reported an increase in speed of 3 knots after the Intersleek was first installed, and with an overall fuel consumption reduction of 12% (Millett and Anderson, 1997).

Given their very attractive environmental profile, it can be anticipated that even without any speed or fuel saving benefits, foul release systems such as Intersleek will become increasingly important in the 21st century for control of marine fouling. At present, their use is restricted to a small sector of the marine market where the vessels are fast and active enough.

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