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SCHOOL

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Mechanical &
Marine Engineering

Marine Coatings

WEGEMT

UNIVERSITY OF PLYMOUTH

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Training and Mobility of Researchers

32nd WEGEMT School
on

Marine Coatings

Papers from the course held on the 10-14 July 2000

at the

University of Plymouth
Department of Mechanical & Marine Engineering

Edited by David Short BSc(Eng) MSc CEng MIMechE MIM

ABOUT WEGEMT

WEGEMT is a European Association of 43 Universities in 18 countries. It was formed in 1978 with the aim of increasing the knowledge base and updating and extending the skills and competence of engineers and postgraduate students working at an advanced level in marine technology and related sciences.

WEGEMT achieves this aim by encouraging universities to be associated with it, to operate as a network and therefore actively collaborate in initiatives relevant to this aim.

WEGEMT considers collaborative research, education and training at an advanced level, and the exchange and dissemination of information, as activities which further the aim of the Association.

NB For marine technology and related sciences, WEGEMT includes all aspects of offshore oil and gas exploration and production, shipping and shipbuilding, underwater technologies and other interdisciplinary areas concerned with the oceans and seas.

ABOUT THE PUBLICATION

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Chapter 1

Setting the Scene
An Introduction to the School

Dr R L Townsin

Setting the Scene - An Introduction to the School.

Dr RL Townsin - Consultant.

Abstract.

The introduction raises the issues which will be addressed during the School and provides a checklist of questions to be answered.

1. Points of view.

There are a number of standpoints from which to view marine coatings: here are some examples.

The *naval architect* can see them as the products to prevent the corrosion of the designed steel structure. Above water appearance may be an issue, especially for a cruise ship, say. Underwater, the *submariner* may accept any hull colour as long as it is black!

The *shipbuilder* is concerned to plan the coating work so as not seriously to impede the production flow. Some of the issues which are of concern to the builder are:

- where should coating take place? In paint cells; outside; after assembly; afloat?
- the environmental problems of industrial use of toxic substances.
- scheduling of construction in relation to curing times.
- guarantees.

The paint supplier, viz. the *marine coatings company*, may possibly have little understanding of a ship, other than as thin films of paint held in place by a steel structure. One of their major concerns is the competitors' products vis-a-vis their own. Of course, the struggle for business inevitably leads to an interest in all the foregoing issues, some of which drive the research of the paint chemist. Whilst at new building the customer is usually the builder, subsequently, for in-service maintenance, it is usually the ship operator who chooses the supplier. For long term coating success, should the operator always be the customer?

Ship operators vary in their expertise in choice of coating and coating strategy. The larger companies are likely to have the greater understanding of coating technology and the techno-economic issues at stake. Recoating of an antifouled bottom is very expensive. Restoration of a failed ballast tank coating is not only expensive, but difficult and time consuming and off-hire time equates to money.

The *Classification Societies'* core roles are the surveying and classification of ships, particularly with regard to their structural integrity. The effects of corrosion on the steel structure are well understood by the societies, not least through the experience and reports of surveyors of ships in service. Their rules and surveys are directed to the maintenance of reliability. However, the specification of coatings themselves and the procedures used in application, are issues which have only recently attracted close attention by the societies.

2. Issues of particular importance.

Although the points of view indicated above have differences, there are common concerns affecting marine coatings and one of them is, most importantly, safety. Pressure is brought to bear by governments worldwide, particularly, for example, the USA in the 1990's. The International Maritime Organisation (IMO), then promulgates cooperative regulations. These pressures are transferred to the shipbuilders and operators through the classification societies, helped by ISO standards where appropriate. The principal societies, although commercial entities, cooperate closely through the International Association of Classification Societies, IACS, which cooperatively issues Unified Requirements. An example is the detail in 'UR Z9 (1992) - Corrosion protection coatings for cargo hold spaces on bulk carriers', which requires all structural steelwork exposed to cargoes to be coated, and the application to follow 'manufacturer's recommendations', with the 'owner's selection of coating giving due consideration to intended cargo conditions expected in service'.

There has been debate in IACS circles between those who think that the societies should involve themselves as much as possible in corrosion and coating matters, and those who consider that the choice and application of a corrosion protection paint is, and should remain, a private matter for the shipowner. We can see, in UR Z9 (1992), a half way position. As this School proceeds, it will be borne in upon us that not only the coating but also its manner of application is critical to the defence against corrosion. Also, the detail design of steelwork, particularly in cargo and ballast tanks, is esential for coating integrity. Additionally, structures should be designed to facilitate inspection and application.

In addition to antifouling technology, the developing catalogue of IACS Unified Requirements is as good an indicator as any, of the coatings issues of principal current concern to the maritime industries. It follows that these are the ones that we should pay particular attention to in this WEGEMT School. The principal issues seem to be :

- The US Pollution Act (OPA '90), has led to double hull tankers with inter-hull spaces dedicated to water ballast use. The confined spaces are difficult to coat, to inspect and even more difficult to recoat. The extra skin means that the area to be coated is greatly increased. Greater edge lengths are introduced, increasing the risk of coating breakdown. Water ballast tank areas, which may now be three times the cargo tank areas, must be coated to the same quality standards as the cargo tanks.

- Coating condition is to be graded at survey under the IACS Harmonisation System of Survey and Classification, HSSC. Presently, the categories are *good, fair or poor*. How is this system working? Inevitably, this closer inspection is leading to a demand for higher quality coating at new building to reduce subsequent maintenance costs. Anticipation of these developments has led manufacturers to design new products for longer life and which are safer to apply.

- The frequency and nature of surveys has changed markedly (HSSC) and is influencing not only product development but also ship steelwork detail design, eg.

permanent ladders, walkways and general access design as well as such details as the minimal inclusion of horizontal surfaces.

- Corrosion control strategies are required and these include ensured quality of surface preparation and paint application. How should this best be assured? Should classification surveyors also become 'inspectors'? Whilst societies may issue guidance notes for surface preparation, application and maintenance of coatings, they have, so far, set their face against acting as 'inspectors', principally because of potential contractual and legal problems.

- Stress concentration and fatigue cracks eg. at joints, holes and welds, are clearly linked to corrosion problems. Whilst the societies have issued guidance, there is also a requirement for awareness and supervision engendered by training, for naval architects, shipbuilders and ship operators. (Perhaps this School helps !).

- Antifouling provision is undergoing major development due to environmental legislation. No organotin application will be permitted after January 2003, with a complete prohibition of the presence of these systems by 2008. Whilst copper in an ablative matrix is allowable (except for small craft in parts of Scandinavia), it is less effective as a toxin. Meanwhile, toxin-free, low surface energy, 'non-stick' products are being developed, marketed and tested at sea.

- Ship operators, since ancient times, have been well aware that hull fouling can involve a severe performance penalty, although no one has offered a correlation between a measure of fouling and its penalty. Some ship operators seem less concerned about the roughness penalties of their antifouled hull surfaces, even though roughness can be measured and the penalty calculated, which can also be punitive. Quality of application and maintenance are the key factors to ensure smooth hulls.

- In the quest for quality of coating in the context of efficient ship production, the conflicts can be resolved in a number of ways. Two sessions of the School will be devoted to this topic which is of growing importance to shipbuilders.

It is important that these topics and views from various standpoints are mutually understood, which today is not always the case, although there have been some advances in recent years, for example, by way of international conferences. This WEGEMT School has as its mission, the furthering of mutual understanding of these marine coatings issues.

3. A checklist of questions.

Until the School meets, the background and current expertise of participants will not be known. The Introductory session itself, will explore this, in order to tailor the emphases of presentation. However, in this written Introduction, it may be helpful to itemise the questions which one professional may ask of another, across the disciplines. The items may then be used as a checklist throughout the School, so that each

participant can see what remains to be understood. The list could also be seen as an open book (self) examination paper!

Corrosion.

- What is corrosion and what causes it?
- What is micro-biological corrosion?
- How do coatings inhibit corrosion?
- How do they fail?
- How do other methods prevent corrosion, especially cathodic protection?
- How is steel cleared of mill-scale?

Fouling.

- What are the fouling organisms?
- Which ones apply to a ship?
- How does the ship become infected?
- What are the mechanisms for attachment?
- What toxins are effective?
- How are antifouling coatings tested?
- What current and impending legislation is relevant to antifouling toxins?

Hydromechanics.

- In fluid flow, what is the boundary layer?
- How does fluid friction arise?
- What is the roughness function?
- Does the roughness function correlate with roughness measures?

Roughness.

- What is meant by the roughness of a surface?
- In what circumstances is it important in engineering?
- How can roughness be defined and how can it be measured?
- How is ship hull roughness measured?
- How is it analysed?
- What is its importance?
- How are the effects of hull roughness calculated?
- What causes a hull surface to become rough?

Coatings.

- What is paint; what is a coating?
- How are paints designed, manufactured and tested?
- What other types of coating are available for marine use?
- How are surfaces prepared for coating?
- How are paints applied?
- What special application problems arise for marine coating, including safety?
- What problems arise in the design of a primer and of an anti corrosive?
- How are coatings removed or prepared for overcoating?

- What are the compatability problems when overcoating?
- How do toxins leach from an antifouling?
- What is an ablative coating?
- What determines the cost of a coating?
- What special problems arise in ballast and cargo tank coating?
- How can quality be assured?

New antifouling technology.

- What is meant by surface energy?
- What is a low surface energy coating?
- How effective are such coatings as antifoulants and what might their future be?

Ship production.

- How are ships put together?
- How does the coating process integrate with ship production?
- What problems for overcoating arise from welding?
- How can steelwork detail design improve coating integrity and quality?
- What issues arise in coating specification and quality control at new building?
- Is there a possibility for robotic inspection, cleaning and coating application at new building and for in-service maintenance?

Underwater maintenance.

- What are the prospects for the underwater maintenance of hull coatings?
- How are the roughnesses of the hull (and propeller) measured underwater?

Classification societies.

- What are the active interests of Classification Societies in marine coatings?
- How will IACS develop the societies involvement with coating issues?

It is anticipated that these, and some other questions, will be answered during the School. No doubt, some answers will be more detailed than others. Participants are likely to formulate many questions from their own viewpoints and it is anticipated that they will seek the answers before the end of this WEGEMT School.

For a comprehensive review of many of the topics alluded to above, the reader is referred to :

Marine Corrosion Prevention - a re-appraisal for the next decade. *Int. Conf.* RINA London. Oct. 1994.

Chapter 2

The Physics and Chemistry of Surfaces
An Introduction

Dr Roy Lowry

The Physics and Chemistry of Surfaces – An Introduction

Dr. Roy Lowry

Department of Environmental Sciences, University of Plymouth, Plymouth, United Kingdom
e-mail: R.Lowry@plym.ac.uk

Abstract

The aim of this lecture is to provide an introduction to the study of surfaces. A model for a "perfect" (simple) surface will be given which will then be further refined to include both atomic scale features and surface roughness. The subject of the energetics of surfaces will then described. The adsorption of material onto surfaces is considered, initially as the formation of monolayers. Both physisorption and chemisorption processes are considered.

Keywords

Topography, surface irregularities and defects, roughness, surface energy, adsorption, physisorption, chemisorption.

What is a surface?

The word "surface" is used in common speech without much concern because we all know what we mean. However, when considering the processes that occur at an atomic or molecular scale, the term is not so easy to define. A common definition is "the boundary at the edge of a solid". This definition is not helpful as to study a surface would be to study nothing. To enclose all of the atoms of a solid, the boundary itself could not include any matter. Indeed, a single 2-dimentional surface cannot include any volume – hence any material. For the purposes of scientific analysis, a surface must include a slim volume that is worthy of inspection.

When we see the surface of an object, the light is scattered by the layers of material nearest the light source. Visible light can penetrate to a considerable depth and is dependent upon the wavelength. This distance can be in the order of microns. This means that the information carried by "reflected" light is from over 1000 atom layers – hardly surface specific. Surface analysis techniques therefore use energy sources with shorter wavelengths to minimise penetration into the bulk of the material, or use processes that sample only the outermost layers of material (e.g. electrochemical methods).

For the purposes of this lecture, the "surface" of a material will be defined as that region between two phases that includes all structures that are not characteristic of the bulk. In this way, we can consider defects caused by the presence of a boundary, the first (outermost) layer of atoms that are open to attack, the initial covering of another substance and any other layers that may form. The "surface" may therefore be anything from a few nanometers to several microns in depth, depending upon the complexity of the structures in the interfacial region.

Surface topography

From the point of view of simplicity, the "perfect" surface would consist of a 2-dimentional array of atoms of a single material in a regular arrangement (see Figure 1). This situation is possible to manufacture, but it is far from straightforward. In addition, the processes necessary to promote such a smooth surface would also affect the bulk. For example, for metals, long periods at high temperatures are required, followed by slow cooling. This also affects bulk properties (such as strength and ductility) by promoting large grains.

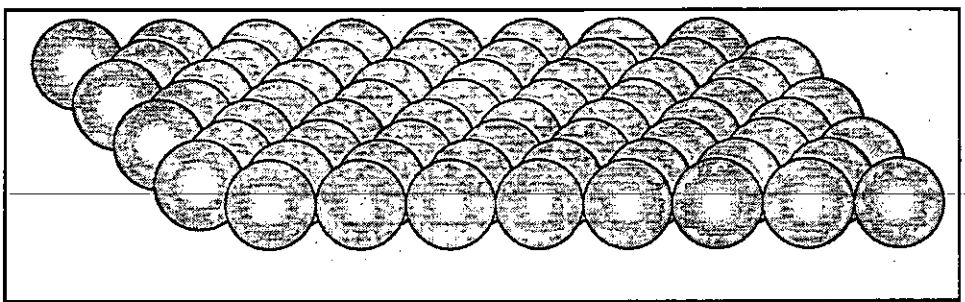


Figure 1: A "perfect" surface

Surface defects

At the atomic scale, there is a range of surface irregularities. The flat areas of a surface are called terraces that are separated by steps. These steps are rarely continuous, but usually contain changes of direction called kinks or kink sites. These kinks are usually represented as right angles in the surface of the step, but the angle will depend upon the crystalline structure of the material. Single atoms can appear on the surface of a terrace (Adatom). If two terraces are growing (due to the addition of new material) then the collision of these (or a series of kink sites) can result in a vacancy (see figure 2).

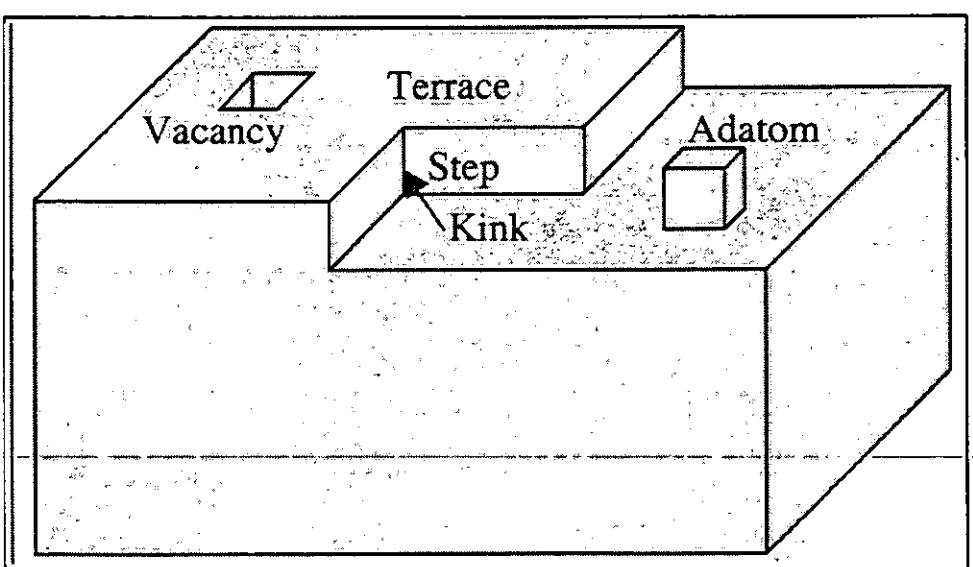


Figure 2: Atomic scale surface defects

If we assume the co-ordination number of the substrate to be 6 (a cubic lattice), then each of these sites has a different number of atoms next to it as follows:

Site	Adjacent atoms
Terrace	1
Step	2
Kink	3
Vacancy	5

Table 1: Number of atoms adjacent to sites

If there is a positive interaction between the surface and the deposited material then the vacancies will be filled preferentially followed by the kink sites, etc. However, this preferential behaviour will only occur if the following criteria are fulfilled:

- The interaction with the surface is not so strong that inter-site "hopping" is prevented (this usually means that a chemical bond is not formed between the adsorbent and the surface)
- There is sufficient energy to allow the material to migrate across the surface.
- The deposition rate is sufficiently low.

Surface roughness

The finish provided on modern materials may look smooth but does not even approach the model of a surface that we have constructed so far. The polishing techniques used are based upon replacing large-scale surface blemishes with smaller ones (e.g. glasspaper or grinding pastes). These smaller blemishes are then replaced by even smaller ones, and so on. However, there is a limit. Most processes don't go to the extreme of using 5μm alumina or diamond powder as an abrasive, but for the sake of this illustration, we will assume that this was the final stage of the process.

A reasonable approximation for the size of an atom is 0.1nm (1×10^{-10}m). This means that across the diameter of a 5μm particle there are 50000 atoms. These particles are used to erode the surface. Thus, the "mirror finish" created contains gullies 50000 atoms wide and just as deep.

Irregularities such as these, together with atomic scale irregularities, create extra surface area. The true area of a surface can be measured by methods involving electrochemical or gas adsorption processes. The ratio of this to the measured "geometric area" is called the roughness factor:

$$\text{Roughness factor} = \frac{\text{true surface area}}{\text{geometric area}}$$

Roughness factors vary enormously depending upon the history and finishing of the material. Indeed, the method chosen to measure the "true" surface area will affect the roughness factor as any technique has a limit of spatial resolution and this is different for different techniques. However, the use of the same technique for a range of samples allows comparisons to be made.

If a material is porous then the roughness factor will increase dramatically. Figure 3 shows an image of a conducting polymer obtained by scanning electron microscopy. To the eye, this appears as a smooth film of shiny transparent polymer, much like a layer of varnish. It is clear that when considered at a smaller scale, the roughness of this surface is considerable.

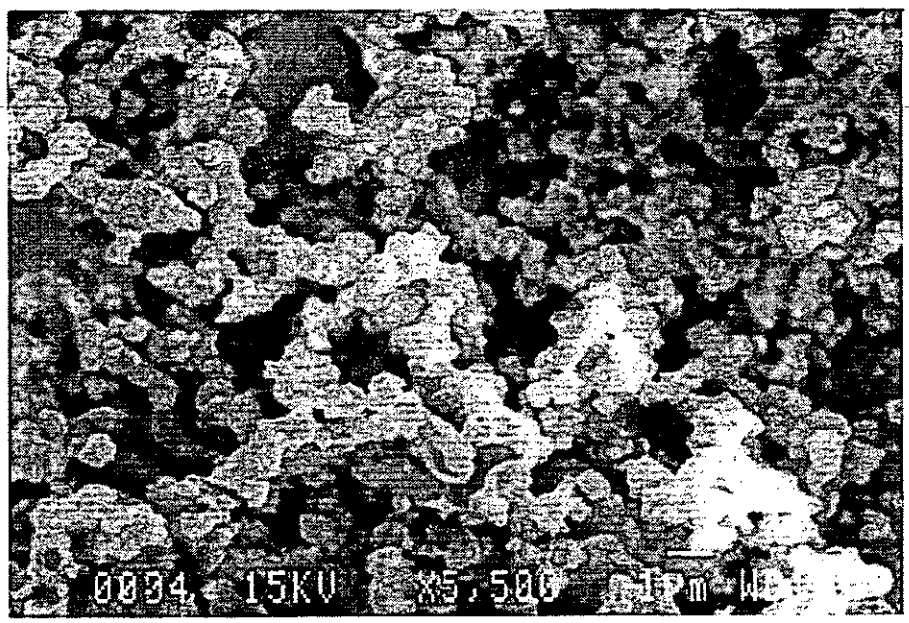


Figure 3: SEM of a conducting polymer

Surface roughness can be both a blessing and a curse. The excellent adhesion of modern paints is dependent upon surface roughness to provide a "key". However, rough surfaces are by nature not uniform and thus can contain sites which are more prone to corrosion attack.

The energetics of surfaces

Within the bulk of any material, atoms experience a balance of forces from directions. This is not true at a surface and leads to a variety of effects:

Surface energy

Cleaving a crystal of material creates a new surface and this process must be accompanied by the breaking of bonds. This requires energy. The energy required to do this can be measured and quoted per unit area (J/m^2) and is called the surface energy. This is a function of both the number of bonds per unit area and also the strength of these bonds. Thus, the surface energy is also a function of the plane down which the crystal has been cleaved. However, except for

exceptionally accurate studies an average figure derived from polycrystalline samples is sufficient for macroscopic work.

Since surface energy (more correctly: surface free energy) is the energy required to increase the surface, it also can be applied to liquid surfaces. Under these conditions the term surface tension is used with the units Newtons per metre (N/m). These two terms both describe the same process and the units are completely interchangeable as 1 J = 1 N m.

Work has to be done to create a new surface and therefore, the surface energy is always a positive quantity. Another way of expressing this is to say that surfaces are highly energetic. This also leads to the conclusion that anything that leads to the lowering of the energy of the surface (e.g. adsorption onto the surface) will be favoured.

Metals and non-metals

In a non-metal, discrete bonds between individual atoms hold the material together. Hence when a new surface in created, the surface contains numerous unfulfilled bonding sites. However, in metals, positive ions of the element are bonded together by mobile electrons that are free to move randomly or in response to events. This results in an additional effect.

Consider a crystal (grain) of a metal. Positive ions are held in a regular array by electrostatic forces generated by the "sea" of electrons, which moves between the ions. If this crystal is now cleaved to generate a new surface, this will leave some electrons with a positive ion to one side, but no balancing force on the opposite side. Under these conditions, the electrons are drawn back into the metal (see figure 4). This is equivalent to reducing the number of bonds per unit area (to be exact it is reducing the electron density which *was* used in bonding). Thus, the surface energy of a metal is less than would be expected from the simple model given above.

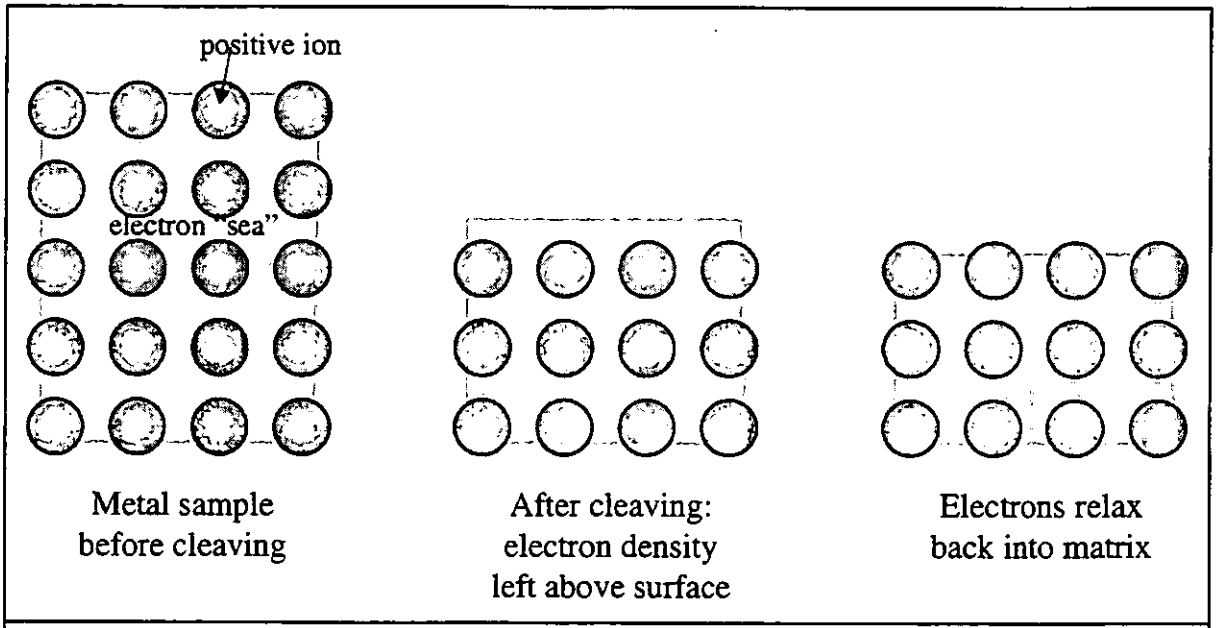


Figure 4: Processes that occur as new surfaces are created in a metal.

Adsorption at surfaces

Since surfaces are highly energetic, any process that lowers the energy will be favoured. This can be achieved by the adsorption of other materials onto the surface. Virtually any surface will become contaminated as molecules become attached to the surface. Under normal conditions (i.e. room temperature and atmospheric pressure) the collision frequency for molecules from the air hitting a surface is 3×10^{25} cm^{-2} s^{-1}. This means that each atom at the surface will be struck about 10^{10} times per second. Even if only a small fraction of these collisions result in a molecule adsorbing onto the surface, the surface will not remain uncontaminated for long.

The adsorption of compounds is the first step in any process that would alter the surface. There are two main mechanisms for this: physisorption and chemisorption.

Physisorption

The term physisorption is a contraction of the phrase "physical adsorption". In physisorption, no chemical bond is made between the adsorbed molecule and the surface. The adsorbed material is only held onto the surface by weak electrostatic interactions. These interactions can be measured and typically are about 3×10^{-20} J per molecule. Since there is no formal bond between the adsorbed material and the surface, the adsorption step is easily reversed. Therefore, a constant concentration is required above the surface (or in solution) to maintain the equilibrium and therefore the surface coverage. For adsorption phenomena, this equilibrium is best expressed in terms of an adsorption equilibrium constant:

$$k_{(ads)} = \frac{[surface]}{[bulk]}$$

Where [surface] is the concentration of the adsorbing material at the surface (which is a measure of the surface coverage) and [bulk] is the concentration in the gas phase or in solution.

If the conditions at or above the surface change, this will affect the equilibrium. An example of this adsorption mechanism is the use of the corrosion inhibitor benzotriazole, which is used widely for preventing corrosion in central heating systems, on tools, etc. A constant concentration of this compound above the surface must be maintained if it is to be effective as this affects the coverage of the surface (and hence the blocking of the surface to attack). Benzotriazole is also ineffective in solutions of low pH. Under these conditions it gains a positive charge due to reacting with a hydrogen ion (H^+). This interferes with the electrostatic forces that would hold it onto the surface and thus it desorbs allowing the metal to be attacked.

Chemisorption

In chemisorption (a shortening of the phrase "chemical adsorption"), the adsorbing molecule is held to the surface by the formation of a chemical bond. The bond energy is typically about 3×10^{-19} J per molecule and some of this energy comes from the highly energetic unfulfilled bonding sites. This interaction with the surface may be so strong that it causes the adsorbing

molecule to be torn apart or undergo gross distortions. Equally, strong chemisorption can result in the surface layers of a metal substrate undergoing rearrangement to accommodate the structure of the adsorbed material. This will occur only when a critical surface coverage has been reached.

It is still possible to calculate an adsorption equilibrium constant for chemisorbed species. However, for many cases, the strength of the bond is such that the adsorbed species will not desorb, except under exceptional conditions. The coverage of the adsorbed species will depend upon the concentration of adsorbate that the surface was been exposed to and the length of time of the exposure. The chemical nature of the adsorbate will also influence this, as different compounds will have different energetics for the process of adsorption. Coverage can range from very small fractions to complete monolayer coverage.

Multiple layers

Once a new surface is created by the adsorption of a material, it too can be capable of undergoing adsorption. If the adsorbate to this new surface is yet another material, then the processes and mechanisms already described occur. If there are appreciable interactions between atoms or molecules of the original adsorbate, then the formation of multiple layers is possible. If these interactions do not exist (or cannot be induced due to the nature of the substrate) then multiple layers will not form.

If there are considerable inter-molecular forces due to electrostatic interactions, multiple layers of regularly stacked molecules are possible. The presence of the surface may modify these interactions, making them more likely. In this situation, there will be a limit to the number of layers formed, as each succeeding layer becomes further away from the initial surface. Since the presence of these layers is due to physical forces (as opposed to chemical bonds) the molecules will desorb if the conditions away from the surface change. Whether the initial monolayer remains intact will depend upon the conditions and whether this layer is physisorbed or chemisorbed.

The formation of chemical bonds between adsorbed layers is not really a surface phenomenon. The chemical reaction between the molecules would occur anyway (although the presence of the substrate may alter the energetics). Indeed, since the "layers" are chemically bonded, the process becomes one where the size of the molecule increases and thus the number of layers remains one, but the thickness of this monolayer increases.

The plating of multiple layers of a metal on a surface is conceptually identical to the process described above. However, the initial layer of metal atoms may not align in the usual (bulk) packing arrangement due to distortions caused by the surface below. These distortions may lead to further dislocations within the plated metal, or be accommodated and made negligible over several atom layers.

Adhesion

Once a component has been constructed that consists of two materials, the strength of this depends not only upon the strength of the two compounds, but also the strength of the interaction between them. The work required to separate a unit area of interface is called the work of adhesion and is measured in J/m^2. It is analogous to the surface energy, but here the

two faces created are of different materials. The work of adhesion will not be the average of the surface energies of the two materials as specific interactions between then will occur.

The complete picture

To illustrate how these separate topics interrelate, consider the plating of a metallic component as part of corrosion prevention measures. From the issues discussed so far, it is clear that:

- More material will be required than expected from simple measurements due to surface roughness.
- Highly energetic sites such as vacancies, kinks and steps will preferentially take part in adsorption.
- Once a critical surface coverage has been reached, rearrangement of the crystal structure of the substrate is possible.
- Adsorption can continue until a complete monolayer is formed.
- Further deposition creates multiple layers.

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Chapter 3

Science of Electrolytic Corrosion

Dr David Plane

Science of Electrolytic Corrosion

D. C. Plane

Department of Mechanical and Marine Engineering, University of Plymouth, Plymouth, United Kingdom.

e-mail: D.Plane@plymouth.ac.uk

Abstract

This lecture covers the fundamentals of oxidation, passivation and the electrochemical corrosion of metals in electrolytic solutions such as seawater. The different forms of corrosion will be discussed and the importance of the electrochemical series and galvanic series will be covered. The causes of localised corrosion, such as pitting, will be outlined with its relevance to surface coatings. Corrosion mapping using Pourbaix diagrams will also be considered.

Keywords

Corrosion, Oxidation, Oxide growth rate, Spalling, Pilling-Bedworth ratio, Diffusion coefficient, Arrhenius law, Activation energy, Fick's law, Active, Passive, Electrochemical series, Galvanic series, Electrolyte, Equilibrium, Anode, Cathode, pH, Faraday law, Nernst equation, Standard electrode potentials, Standard reference electrodes, Composition cells, Concentration cells, Pitting, Crevice corrosion, Intergranular corrosion, Pourbaix diagrams.

1. Introduction

With the exception of a few very 'noble' materials like gold, most engineering materials are susceptible to corrosion. Corrosion, from the Latin word 'corrodere', meaning 'to gnaw away', is a process by which materials, which have been obtained from ores in nature, will revert back to a form similar to that in which they were originally found. The consequences of corrosion can be serious, even life threatening, and include deterioration of the strength and operational reliability of structures, loss of hard won materials, environmental damage, loss of aesthetic appearance and not least the high costs associated with repair or replacement. About 3.5% of the annual GNP of the UK, or around £2000 million, is one estimate of the cost of corrosion to the UK economy. Much is now understood about the causes of corrosion, and many methods are used to combat or reduce corrosion, including of course the application of corrosion resistant coatings. It is important, however to appreciate the underlying mechanisms of corrosion for any particular material in order to apply effective surface pre-treatments and appropriate coatings. One of the earliest recorded examples of a lack of understanding of the corrosion mechanism causing problems with coatings is the case of the Royal Naval Frigate HMS Alarm, reported on in 1763 (Trethewey and Chamberlain, 1988). The wooden hull of the ship had been coated in thin copper strip to avoid damage by teredo woodworm and to reduce barnacle growth, which could lower speed. After two years at sea it was found that much of the sheathing had become detached because the iron nails that had been used to attach it had corroded away. The copper had originally been delivered coated in brown paper, and where this insulating layer still existed beneath the nail heads, the nails were less corroded. Corrosion by two dissimilar metals in electrical contact in an

electrolyte like seawater is known as galvanic corrosion. Unfortunately the lessons of history are often ignored, and there have been many examples of galvanic or dissimilar metal corrosion causing service failures right up to the present. In the early 1960's, a copper alloy end plate fell off a seawater evaporator on a submarine because of severe corrosion of the steel securing bolts. Another example, in the 1980's after the Falklands conflict, is the collapse of two Royal Navy Sea Harrier nose wheels because of galvanic action between the magnesium alloy hub and stainless steel bearing. In such situations, one material forms an Anode, and corrodes, while the other material forms a Cathode and is protected. Coatings, which are applied to a material requiring protection, may be either Anodic or Cathodic to the substrate material. Clearly an understanding of the fundamentals of corrosion should help to design the correct form of coatings and hopefully avoid a situation where a damaged coating may actually enhance corrosion rather than slow it down.

2. Oxidation of Metals and Passive Films

2.1 Mechanism and Energy of Oxidation

Dry corrosion processes occur when gases attack the surface of a metal, for example, sulphur dioxide gas that attacks nickel alloys at high temperatures, causes intercrystalline corrosion. Oxygen is responsible for most atmospheric attack on metals, and some metals such as sodium react with oxygen very quickly, while others such as gold and silver hardly react at all. In the surface of a metal the atoms are not completely surrounded by other atoms, as they are in the interior, and they therefore have spare bonds which will attract oxygen onto the surface. The oxidation reaction can be written in two stages, firstly the metal atom M, loses two electrons e^-, to become a metal ion, M^{++}, the number of electrons lost, in this case two, being the valency of the metal.

$$M \rightarrow M^{2+} + 2e^- \qquad (1)$$

The electrons are then taken by the oxygen, which requires two electrons to fill up the outer electron orbital, and therefore has a valency of two, to form an oxygen ion.

$$O + 2e^- \rightarrow O^{--} \qquad (2)$$

The overall reaction is then:

$$M^{2+} + O^{2-} \rightarrow MO + \Delta H \qquad (3)$$

The energy or heat of the reaction, ΔH, can be either positive (endothermic reaction), in which case the metal is stable, or negative (exothermic reaction), in which case the metal will oxidise. The ionic molecule that forms then rearranges itself by diffusion to form the structure of the oxide layer.

As the oxide film grows, the attraction between the metal and oxygen decreases and oxide film growth rate slows as metal or oxygen atoms have to diffuse through the thickening oxide film. Electron flow is also involved, as the continuing reaction may take place at the oxide-air interface or at the metal-oxide interface. Table 1 gives energy of formation of a selection of oxides.

2.2 Rates of Oxidation

There is generally not a very good correlation between rates of oxide film growth and the energy of formation of oxides, as shown in Table 1. The metal aluminium is quite reactive but takes a long time to oxidise, whereas tungsten is less reactive but oxidises to the same

depth in a very short time. The reason for these differences is due to the nature of the oxide formed. Some oxide films are porous, while others may form a passive protective film on the surface. This is determined in part by the Pilling-Bedworth Ratio: $P-B, Ratio = \frac{M_o \rho_m}{n M_m \rho_o}$ (4), where M_o and M_m are the molecular mass numbers of the oxide and metal, and ρ_0 and ρ_m are the densities of oxide and metal, and n is the number of metal atoms in the oxide molecule. This is effectively the ratio of the volume of oxide to the volume of metal forming that oxide. If this is much less than one, tensile stresses in the film may crack the oxide and a porous oxide may be produced, which allows easy access to further oxygen attack. If much greater than 1, the oxide film (or oxide scale if over 10^{-3} mm thick) will experience compressive stresses which may buckle and spring away or spall as it breaks the adhesion between oxide and metal, and again allow access to oxygen. There is not a good correlation between Pilling-Bedworth Ratio and the type of behaviour seen because of other factors such as oxide properties, metal reactivity, etc.

Metal	Melting point /^{0}K	Oxide	Energy /kJmol^{-1} of O_2	Time to oxidise to a depth 0.1mm at 0.7T_m in air ** Hours
Magnesium	923	MgO	-1162	$> 10^5$
Aluminium	933	Al_2O_3	-1045	Very long
Titanium	1943	TiO	-848	<6
Chromium	2148	Cr_2O_3	-701	1600
Zinc	692	ZnO	-636	$> 10^4$
Molybdenum	2880	MoO_2	-534	Very short
Tungsten	3680	WO_3	-510	Very short
Iron	1809	Fe_3O_4	-508	24
Tin	505	SnO	-500	Very long
Nickel	1726	NiO	-439	600
Copper	1356	CuO	-254	25
Silver	1234	Ag_2O	-5	Very long
Gold	1336	Au_2O_3	+80	Infinite

Table 1 Energies of Formation of oxides at 273K, and Times to oxidise to a depth of 0.1mm at 0.7 T_M in air. (Times could vary with metal purity, surface treatment, atmospheric impurities etc.)**

If the oxide film remains coherent with the metal surface, an impervious, limiting film thickness, may result and the metal is rendered passive to its environment. This is the case with aluminium, the oxide of which has a high melting point and low diffusion rate for oxygen. Another factor is the electrical resistivity of aluminium oxide is 10^9 times that of iron oxide, thus limiting the rate of electron diffusion across the oxide and hence the rate of film growth. These types of film are illustrated in Figure 1.

There are, therefore, three commonly observed rates of oxide growth, usually measured by mass gain, but expressed below as film thickness (x), which mass is proportional to, as a function of time (t). Figure 2 shows these growth rates graphically.

(i) Parabolic Growth: $x^2 = k_p t$ (5) where k_p is a constant.
This occurs where the rate of growth is limited by diffusion rates at a particular temperature, and is determined by Fick's 1st Law, i.e. the atomic flux, and also film growth rate, is proportional to the diffusion coefficient (D) times the concentration gradient $\left(\frac{\Delta c}{x}\right)$, so that:

$\left(\frac{dx}{dt}\right) = CD\left(\frac{\Delta c}{x}\right)$ (6), where C is a constant. Integrating with respect to time gives:

$x^2 = k_p t$ (7), where $k_p = C_o D \Delta c = C_o D_o \exp^{\frac{-Q}{RT}} \Delta c$ (8) C_o is a constant. Metals showing this growth rate include iron, nickel, cobalt and copper at room temperature. Note that film growth rates show an Arrhenius Law increase with temperature, Q is the activation energy, R the gas constant and T the absolute temperature.

(ii) Linear Growth: $x = k_L t$ (9) where k_L is a constant.

This occurs where the oxide film is porous due to cracking or spalling and allows continuous access of oxygen to the metal, i.e. not dependent on solid diffusion rates. Examples include sodium and potassium, and iron above 1000°C. The rate of growth may start off in a parabolic way but spall away, and after several repetitions the overall rate is linear.

(iii) Logarithmic Growth: $x = k_c \log(c_1 t + c_2)$ (10) where k_c, c_1 and c_2 are constants.

This occurs where the oxide film is completely impervious due to high melting point coherent oxides that have low diffusion rates and high resistivity, such that oxide growth ceases after a limiting thickness. In aluminium this limiting thickness is about 20.10^{-10} m at 293 °K. Other examples are chromium, magnesium below 200°C and beryllium.

In a few cases the oxides formed at high temperature are volatile and weight loss is observed at a linear rate. Examples are tungsten, and molybdenum above 300°C, which explains why they oxidise rapidly as shown in Table 1.

Oxides, which form on metal surfaces under dry conditions at room temperature, do not usually result in the loss of significant material, and in fact may protect from further attack. The oxides may also make joining difficult and may require removal prior to coatings being applied.

3. Electrochemical Corrosion

3.1 Electrolytic action

Electrolytic or 'wet' corrosion can result in a much more rapid material loss than 'dry' oxidation . It occurs wherever two different metals are in electrical contact with each other and an electrolyte. An electrolyte is any solution that can conduct an electric current, e.g. an aqueous solution of salt or a molten salt. All except noble metals dissolve as ions when placed in a dilute electrolyte, and this is essentially the same as the oxidation reaction described earlier, and is called the anodic reaction..

e.g. $Zn \rightarrow Zn^{2+} + 2e^-$ (11) or $Cu \rightarrow Cu^{2+} + 2e^-$ (12)

The ions go into solution and leave the electrons in the metal, which becomes negatively charged. This continues until a state of equilibrium is reached between the rate of ions dissolving and the rate of ions being attracted back and plated onto the surface due to the negative charge. The metal then has an equilibrium potential with respect to its ions in solution. If the electrons are conducted away, or the ions removed, equilibrium would be lost and the metal would carry on dissolving. Other possible anodic reactions, depending on conditions, are:

$2M + 2(OH)^- \rightarrow M_2O + H_2O + 2e^-$ (13)

$M + (OH)^- \rightarrow MOH + e^-$ (14)

$M + X^- \rightarrow MX + e^-$ (15)

In all cases free electrons are generated, and oxides, hydroxides or insoluble salts are formed which may passively coat the surface and slow metal dissolution.

If electrons flow into a region, the metal does not need to dissolve to establish equilibrium with the environment, and a cathode is formed, which is cathodically protected. Several cathode reactions are possible, depending on conditions, for example:

$M^+ + e^- \rightarrow M$ (16) metal is deposited.

$2H^+ + 2e^- \rightarrow H_2$ (17) hydrogen may be evolved, usually in acid conditions.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (18) oxygen may be reduced, usually in alkaline conditions.

In each case, electrons are absorbed.

3.2 Definition of pH and Thermodynamics of Corrosion

Water undergoes limited dissociation into hydrogen and hydroxyl ions:

$H_2O \Leftrightarrow H^+ + OH^-$ (19)

This is a reversible reaction as indicated by $\Leftrightarrow$, and at a given temperature and pressure this degree of dissociation is a constant and can be expressed mathematically by the Law of Mass Action. For the equilibrium process: $A + B \Leftrightarrow C + D$, where A and B are reactants, C and D are products, constant, $K = \frac{[C][D]}{[A][B]} = \frac{[H^+][OH^-]}{[H_2O]}$. (20) The symbols in square brackets represent concentrations. At one atmosphere and 25° C, $K = 10^{-14}$. This means that both the hydrogen ion, and hydroxyl ion concentration are 1 in 10^7 or 10^{-7}. Since pH is defined by: $pH = -\log_{10}[H^+]$ (21), then the pH of neutral pure water is 7, and the pH for acids, which contain a lot of hydrogen ions, will be less than 7, while the pH of alkalis will be more than 7.

For any reaction to occur there must be a decrease in free energy, i.e. ΔG is negative, though this is not the only condition, since activation energy must often be available to initiate a reaction. The change in free energy is affected by temperature:

$\Delta G = \Delta G^0 + RT \ln K_n$ (22), where K_n is obtained as above for K, but represents any non-equilibrium values, ΔG and ΔG^0 are the non-equilibrium and equilibrium values of the free energy change respectively, R is the gas constant and T is absolute temperature. At equilibrium $\Delta G = 0$, $K_n = K$, so $\Delta G^0 = -RT \ln K$ (23). Since electrical energy is given by (charge x potential), these equations can be expressed in terms of the electrochemical potential E and charge F, using Faraday's Law: $\Delta G = -nFE$ (24), where n is the number of electrons or equivalents exchanged in the reaction, F is Faraday's constant (96,494 coulombs of charge needed to liberate the chemical equivalent in grams, chemical equivalent being molecular mass ÷valency). For Standard conditions, $\Delta G^0 = -nFE^0$ (25). Substituting (24) and (25) into equation (22) we get: $-nFE = -nFE^0 + RT \ln K_n$ (26). This

can be written more generally as shown and is called the Nernst Equation: $E = E^0 - \frac{RT}{nF} \ln \frac{[products]}{[reac\tan ts]}$ (27). Substituting numerical values, R = 8.31 J.mol^{-1}.K^{-1} and T = 298 K and using logarithms to base 10, gives: $E = E^0 - \frac{0.059}{n} \log \frac{[products]}{[reac\tan ts]}$ (28). E is then the non-equilibrium potential generated by performing the reaction, and if the concentrations are equilibrium values, there would be no driving force, $\Delta G = 0$ and E = 0.

3.3 The Electrochemical Series and Galvanic series

Different metals ionise to different extents and will possess different values of the equilibrium voltage. Measurement of the voltage between two electrodes will only give the difference in potential, not the absolute values of equilibrium potential. Since hydrogen is frequently liberated at cathodes (Equation 17), Standard Electrode Potentials (E^0) are measured with respect to a hydrogen coated platinum electrode at standard temperature and pressure in standard solution. Potentials are measured using high input resistance voltmeters or potentiometers that draw negligible current, since current flow would upset the equilibrium conditions. A list of SEP's is called the Electrochemical Series, shown in Table 3. If two metals are connected electrically and have an electrolyte between them, then the more anodic metal will go into solution and electrons will flow around the external circuit into the more cathodic metal and metal ions or hydrogen will be liberated at the cathode. If hydrogen bubbles form an insulating film on the cathode, the cell resistance increases, there is a larger potential drop across the cell, the cell is polarised and the corrosion current reduces. Measurement of voltages in the field is not practicable using hydrogen electrodes, so other Standard Electrodes have been devised which are more robust and stable. The Saturated Calomel Electrode (SCE), or unsaturated variations, and the Silver/silver chloride (SSC) reference electrodes are two examples, and their voltages relative to the Standard Hydrogen Electrode (SHE) are shown in Table 2. Converting from one scale to another is just a case of adding or subtracting the appropriate value. For example, a potential of –0.600 volts (SHE) is the same as a potential of -0.8224 volts on the Silver/silver chloride scale.

Electrode	Electrolyte	Potential (SHE) volts
Calomel (SCE)	Saturated KCl	+0.2420
Calomel	0.1 M KCl	+0.3335
Silver/silver chloride (SSC)	1.0 M KCl	+0.2224
Silver/silver chloride	Sea water	≈ +0.25
Copper/copper sulphate	Sea water	≈ +0.30
Zinc	Sea water	≈ -0.79

Table 2 Potentials of Standard Reference Electrodes

	Metal-metal ion equilibrium (unit activity)		Electrode potential versus normal hydrogen electrode at 25°C, volts
Noble Metals ↑	Gold	Au^{3+}	+1.498
Cathodic	Platinum	Pt^{2+}	+1.20
	Palladium	Pd^{2+}	+0.987
	Silver	Ag^{+}	+0.799
	Mercury	Hg^{2+}	+0.788
	Carbon		+0.74
	Copper	Cu^{2+}	+0.337
	Hydrogen	H^{+}	0.000
	Lead	Pb^{2+}	-0.126
	Tin	Sn^{2+}	-0.136
	Nickel	Ni^{2+}	-0.250
	Cobalt	Co^{2+}	-0.277
	Cadmium	Cd^{2+}	-0.403
	Iron	Fe^{2+}	-0.440
	Chromium	Cr^{3+}	-0.744
	Zinc	Zn^{2+}	-0.763
	Aluminium	Al^{3+}	-1.662
	Magnesium	Mg^{2+}	-2.363
Base Metals ↓	Sodium	Na^{+}	-2.714
Anodic	Potassium	K^{+}	-2.925

Table 3 The Electrochemical Series

The electrochemical series shows the relative reactivity of pure elements. More electropositive metals will replace more electronegative metals in solution; e.g. iron will replace copper in a copper sulphate solution, $\{Cu^{2+} + SO_4^-\} + Fe \rightarrow \{Fe^{2+} + SO_4^-\} + Cu \downarrow$ (29). A Galvanic series differs from the electrochemical series in that it shows relative reactivity in non-standard electrolytes such as seawater under non-standard conditions. Instead of pure metals, practical alloys are listed and alloys may appear in two places in the

list depending on whether they are active or corroding, or are passive and non-corroding due to a passive film having formed on the surface. Table 4 shows a galvanic series for seawater.

Cathodic End: Noble Metals	
Graphite	Silicon Bronze:96%Cu:2%Si
Platinum	Manganese Bronze:66%Cu:23%Zn:4.5%Al:3%Fe:4%Mn
Gold	Aluminium Brass:76%Cu;22%Zn:2%Al
Hastelloy C: 55%Ni:15%Cr:17%Mo:5%Fe:5%W.	Lead:Tin solder:50:50
Titanium	Copper
Inconel 825:40%Ni:21%Cr:30%Fe:2%Cu:3Mo.(Passive)	Tin
Alloy20:Stainless Steel:20%Cr:29%Ni:2%Mo(Passive)	Naval Brass:62%Cu:37%Zn:1%Sn
Type 316,317:Stainless Steel: 18%Cr:10%Ni:3Mo:(Passive)	Red Brass:85%Cu:15%Zn
Monel:70%Ni:30%Cu:	Yellow Brass, Muntz Metal:60%Cu;40%Zn
Types 302, 304: Stainless Steels:18Cr:8Ni: (Passive)	Aluminium Bronze:88%Cu:9%Al:3%Fe
Silver	Type 316/7: Stainless Steels: 18%Cr:10%Ni:3Mo: (Active)
Nickel (Passive)	Inconel Alloy 600: 76%Ni:15Cr:8%Fe (Active)
Inconel Alloy 600: 76%Ni:15Cr:8%Fe(Passive)	Nickel(Active)
Nickel-Aluminium-Bronze:80%Cu:10%Al:5%Ni:5%Fe.	Aust. Nickel Cast Iron:73%Fe:21%Ni:2.8%C:1.3%Si:2%Cr
Monel: Copper-Nickel 70:30	Types 302, 304: Stainless Steels:18%Cr:8%Ni (Active)
Lead	Type 430 Stainless Steel:17% Cr: Bal.Fe(Active)
Type 430 Stainless Steel:17% Cr: Bal.Fe(Passive)	Low Alloy Steel
Cupronickel: 80%Cu:20%Ni	Mild Steel, Cast Iron
Cupronickel: 90%Cu:10%Ni	Cadmium
Gunmetal:83%Cu:5%Zn:5%Sn:2%Ni:5%Pb	Aluminium Alloys
Nickel Silver:(10-30)%Ni:(55-63)%Cu: Bal.Zn	Beryllium
Type 410 Stainless Steel:11-14% Cr:1-2%Ni:Bal.Fe (Passive)	Zinc, Zinc Alloys, Galvanised Steel
Tin Bronze:88%Cu:(5-10)%Sn	Magnesium Alloys
	Anodic End: Base Metals

Table 4 Galvanic Series in sea water: (compositions are approximate and potential ranges for types of alloys may overlap)

3.4 Forms of Corrosion

Corrosion can be classified under various headings, for example:
Uniform Corrosion, Galvanic Corrosion, Crevice Corrosion, Pitting Corrosion, Environmentally Induced Cracking, Hydrogen Embrittlement, Intergranular Corrosion, Dealloying, Erosion Corrosion, Biological Corrosion, Stray Current Corrosion, etc. Alternatively, the nature of corrosion cells and the origin of corrosion currents may be considered, and examples of where these may occur in practice can be listed.

3.4.1 Composition Cells

Composition cells are galvanic cells where two dissimilar metals or materials, with differing electrode potentials, may be in contact with each other and an electrolyte. The scale of the cells may vary from the microscopic to the macroscopic, as illustrated in the following examples.

(a) **Strengthening or Impurity Phase:** Alloys often contain second phase particles for strengthening purposes, or as a residual oxide or other compound resulting from the purification process. Though these particles may be anodic to the metal, they are more likely to be cathodic, with the metal forming an anode and dissolving if water is present. Steel contains iron carbide in the pearlite phase, making mild steel more prone to corrosion than pure iron. In unstabilised stainless steels, prolonged heating in the temperature range 600°C to 800°C can result in the formation of chromium carbide on the grain boundaries, thus resulting in a depletion of the protective chromium oxide passive layer. This can cause a corrosion cell between the chromium carbide and the iron. When this occurs in the heat affected zone as a result of welding, it is known as 'weld decay'.

(b) **Two metals joined:** If two different metals or alloys are joined, either by mechanical fasteners or, for example, welding, one will become an anode and dissolve, while the other will be protected. Examples might include connecting a copper pipe to a steel water tank, or an aluminium superstructure on a steel hulled ship. In general this would be considered bad practice, but where it is unavoidable, an insulating layer should be introduced between the two metals in order to reduce the corrosion current.

(c) **Rusting of Mild Steel:** Iron is anodic with respect to iron oxide. When the oxide scale is broken and becomes covered in an electrolyte (e.g. rain water with dissolved CO_2 or SO_2 giving carbonic or sulphurous acids respectively), the iron dissolves:

$$Fe \Leftrightarrow Fe^{2+} + 2e^- \quad (30)$$

The electrons flow to the cathodic oxide where, in the absence of dissolved oxygen, hydrogen is formed: $2H^+ + 2e^- \rightarrow H_2$ (31)
This hydrogen would cling to the cathode and produce a polarising layer, which would stop further electrolysis. However, in the presence of dissolved oxygen, a depolarising reaction occurs: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (32)
There are several steps involved in the reaction, but the net effect is that ferric iron ions drift to the cathode and combine with hydroxyl ions to form reddish brown rust, ferric hydroxide: $Fe^{3+} + 3(OH)^- \rightarrow Fe(OH)_3$ (33). This is illustrated in figure 3.

(d) **Coatings on Steel:** Both zinc and tin are commonly used to coat steel. If a zinc coating becomes damaged, the zinc will act as an anode and will sacrificially dissolve, thus making the steel a cathode, which will be protected. In the case of a tin coating becoming damaged, because the coating is only a direct coating (as opposed to a

sacrificial one), the tin will be the cathode but the underlying steel will dissolve anodically. The same situation exists with paint and other surface films, that are cathodic to steel, the underlying corrosion revealing itself as blistering of the paint. This is illustrated in figure 4.

3.4.2 Concentration Cells

Concentration Cells can arise where there are differences in oxygen or ion concentration in contact with a metal. It is not necessary for there to be differences in composition, since the cells are driven by varying conditions and therefore varying thermodynamic potentials.

(a) Differences in Oxygen Concentration: The reaction:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (34) can occur when oxygen is present. It follows that if regions exist in contact with a metal, that have different oxygen concentrations, then the above reaction occurs to a greater or lesser extent i.e. high oxygen areas give more OH^- ions in solution and absorb electrons from the metal. These electrons are supplied from the area with the lower oxygen concentration, since this area acts as an anode and the metal dissolves at this point. $M \rightarrow M^{2+} + 2e^-$ (35)
Electrons therefore flow from regions of low oxygen concentration to regions of high oxygen concentration and this means that positive metal ions pass into solution in order to supply these electrons. Metals, therefore, in contact with moisture and oxygen, corrode at a greater rate where the oxygen content is lowest.

e.g (1) At the bottom of a water tank.
(2) Along the shank of a nail in moist wood (not the head).
(3) Underneath loose rust, bolt heads, washers, barnacles, paint etc.
(4) At the bottom of pits in a metal surface (Pitting and Crevice corrosion).

(b) Differences in Ion Concentration: The more concentrated in metal ions that a solution is, the less likely that a metal in contact with the solution will ionise. If there is a difference in concentration of solution in contact with a metal, more metal ions will go into solution, in an attempt to reach equilibrium, and create more electrons where the solution is weakest. Current will therefore flow from regions of low ion concentration to region of high ion concentration and the metal will corrode more at the low ion concentration position.

e.g. (1) Steel piling in stagnant (no oxygen) water will corrode faster near the top where there are likely to be fewer dissolved salts. Note that this may oppose an oxygen concentration cell !
(2) Rotating propellers or impellers will corrode more at the tip where rapid movement does not allow high ion concentrations to build up.
(3) Liquids travelling at various velocities in pipes e.g. on corners, set up corrosion currents, with the fastest flow areas on the outside of the bend producing the worst corrosion.(There may additionally be abrasion due to suspended particles).

3.4.3 Influence of Stress:

Corrosion is often accelerated in regions of high mechanical stress due to the stored energy of cold work.

(a) **Stress-Corrosion**: Pile-ups of dislocations at grain boundaries in a cold worked metal leads to a stress concentration at the grain boundary. The boundaries became anodic with respect to the metal in the presence of an electrolyte and preferentially corrode. This occurs in hard-drawn brass and is called "Season Cracking". Hydrogen Embrittlement occurs where atomic hydrogen is in contact with metals under applied stresses or where there is an internal stress. Cracking occurs at the grain boundaries. Specific metals are usually susceptible to particular chemicals, e.g. brass and ammonia, steel and salt solution, stainless steel and hot chlorides etc.

(b) **Corrosion Fatigue:** Failure will occur more rapidly if fatigue takes place in a corrosive environment, due to crack growth at surface flaws which are attacked. The oscillating stress during fatigue helps to disrupt any passive film that might slow corrosion in a static load situation. The corrosion helps to initiate a fatigue crack by roughening the surface.

(c) **Fretting Corrosion:** This occurs where two moving metal surfaces are in close contact. Wear results in the formation of metal particles, which oxidise into abrasive oxide particles and cause roughening and can eventually lead to fatigue cracking.

(d) **Impingement Corrosion:** This occurs in pumps, turbines, pipelines, etc., where wear on surfaces, due to suspended abrasive particles in the fluid stream, can cause breaks in passive surface layers and accelerate corrosion due to enhanced surface roughness.

3.4.4 Other Types of Corrosion:

(a) **Long Line Corrosion:** This occurs where pipelines run through soils of differing pH (or acidity and alkalinity). Steels are generally passive in a very alkaline environment, but corrode in acid conditions.

(b) **Stray Current Corrosion:** This occurs where stray electric currents flow through metals e.g. near overhead power lines for trams, etc. The metal corrodes where the electron flow is away from the area.

(c) **Steel in Concrete:** Steel reinforcing bars develop a passive film in the normally very alkaline concrete mix. Over time the surface layers of concrete become more acid due to carbonation (CO_2 attack), leaching of alkalis by rain, chloride attack (from sea spray or road salting), or acid rain containing pollutants. If the steel is too close to the surface, it will begin to corrode and the attendant swelling will cause cracking and spalling of the concrete. To avoid this, a concrete cover over the steel of 50mm should provide protection for 50 years.

3.5 Localised Corrosion, Pitting and Crevice Corrosion:

Pitting and Crevice Corrosion are localised forms of attack, often resulting from the failure of a passive film. They can remain hidden from view until leaks are detected due to complete penetration through the metal. This is because the mechanism occurs under corrosion deposits or coatings, or within the crevices formed by gaskets, insulation, joints, bolts, washers, etc., in contact with a surface. Surface scratches, inclusions or even just water

droplets sitting on a surface, can act as initiation sites for pitting. See figures 7 and 8. Stainless steels are of the greatest practical interest, and most failures occur in neutral-to-acid solutions with, especially in marine locations, chloride ions playing a role in damaging the passive oxide film. Strongly oxidising conditions are necessary to favour passivity, but within a pit or under a film or crevice containing chloride ions, such conditions are lost. Once a pit has been established, it continues to grow by an autocatalytic process. The positively charged iron ions produced at the anodic bottom of the pit will attract negatively charged chlorine ions into the pit, which hydrolyse to ferrous hydroxide by the reaction:
$Fe^{2+} + 2H_2O + 2Cl^- \rightarrow Fe(OH)_2 + 2HCl$ (36). This produces local pH reductions, i.e. the solution inside the pit becomes more acid, which accelerates anodic dissolution, which further concentrates chloride ions in the pit, and so on. A cap of rust, the highest oxidation state ferric hydroxide, $Fe(OH)_3$, is soon seen at the surface of the pit, while the area around the pit remains uncorroded as it is still passive and cathodically protected. A cathodic reduction reaction such as shown in equation (18) is necessary to absorb the electrons flowing away from the anode region, so the local environment determines the spacing between pits. The pitting mechanism is illustrated in figure 5.

3.6 Effect of Microstructure on Corrosion:

Microstructure plays an important role in determining the corrosion resistance of alloys. Impurity inclusions and segregation of impurities or alloy elements at grain boundaries worsen corrosion resistance, as does structures such as martensite. A good example of the effect of microstructure is the dezincification of ($\alpha + \beta$) brasses or strongly cored α brasses in seawater. Other factors are crystallographic orientation, cold work, phase composition etc.

3.6.1 Intergranular Corrosion of Stainless Steels:

When stainless steels are heated in the temperature range 425°C to 815°C (800° to 1500°F) chromium carbides, $(Fe,Cr)_{23}C_6$), are insoluble and precipitate at grain boundaries. Above 815°C the carbides are soluble, while below 425°C the diffusion rate of carbon is too low to permit formation of carbides. The precipitates deplete the region near the grain boundaries of chromium and thus locally remove the passive chromium oxide film that normally protects stainless steels from corrosion. The unpassivated grain boundary region is then anodic to the passivated grains and carbide particles, so that in the presence of moisture, severe intergranular corrosion (IGC) results.
Stainless steels, which are put in this condition by thermal treatments, are said to be sensitized to IGC. As the carbon content is reduced, longer times are required to sensitize austenitic stainless steels. (See figure 6, from Jones, 1992). Other alloying ingredients also have an effect. Nickel increases the activity of carbon in solid solution thus enhancing sensitization, while increasing chromium or molybdenum is beneficial. One of the most corrosion resistant grade is type 316L, where the "L" refers to a low carbon content. Stabilised stainless steels (types 347 and 321) have about 1% niobium or titanium added. These are strong carbide formers and tend to react with the carbon, thus leaving the chromium in solution.
'Weld decay' results when stainless steels become sensitized during welding. The classic form results in intergranular corrosion in the heat affected zone (HAZ) on either side of the weld. The thermal transients produced during welding at various locations determine the degree of sensitization. At points that are close to the weld the alloy is not in the critical

temperature range for long enough to produce sensitization, but it is at points a little further from the weld. At points remote from the weld the alloy does not reach the critical temperature range. Various factors affect the position of the sensitized region, such as plate thickness, heat input, cooling rate etc. Pitting close to a weld in stainless steel, revealed by accelerated corrosion testing in ferric chloride solution, is shown in figure 7(a).
When a stainless steel has been sensitized to intergranular corrosion, it is also more susceptible to intergranular stress corrosion cracking (IGSCC) in stressed components.

3.6.2 Prevention of weld decay and sensitization.

There are three broad strategies for preventing weld decay:
(a) Solution Annealing: This involves heating the alloy above 815°C where all chromium carbides are dissolved, followed by rapid quenching to retain chromium and carbon in solution. This allows the passive chromium oxide film to remain in place.
(b) Low Carbon Alloy Modifications: This involves selecting low carbon alloys with insufficient carbon to precipitate chromium carbide, such as Type 304L which contains a maximum of 0.03% carbon. This was developed for nuclear applications where IGSCC was a potential problem, but is now widely used.
(c) Stabilized Alloys: These contain small additions of niobium or titanium, which react with carbon above 815°C to precipitate the respective carbides randomly throughout the grains, thus avoiding the depletion of chromium. 'Knifeline Attack' (KLA) is a very localised attack a few grains in from the weld bead which can occur in stabilized steels which have been rapidly cooled from above 1230°C where the titanium or niobium carbides have been dissolved. Subsequent heating in the sensitization range produces chromium carbide particles because the Ti or Nb has not had time to react with the carbon. Heating above 815°C can prevent KLA where the chromium carbide once again dissolves and the Ti or Nb carbide re-precipitates.

3.7 Pourbaix Diagrams:

Pourbaix Diagrams are a compact summary of thermodynamic data in the form of potential versus pH diagrams. They represent the various electrochemical and chemical behaviour of a metal in water and are available for most metals. The curves divide the diagram into regions of 'immunity' (where the metal does not react because it is cathodically protected; 'corrosion' (where it does react) and 'passivation' (where it reacts to form a passive or protective firm which then prevents further reaction once the film has formed, usually quite quickly).
No information is given concerning the rates of reactions nor the effectiveness or chemical formula of passive films in environments containing specific anions such as SO_4^- or Cl^-. Only the thermodynamically stable equilibrium films are shown and which result from metals immersed in acids and alkalis with various impressed potentials. Each line represents a condition of equilibrium. For the iron diagram, figure 9, (from Jones, 1992) horizontal lines represent equilibrium for a reaction involving electrons but not OH^- or H^+ ions, for example: $Fe \Leftrightarrow Fe^{2+} + 2e^-$ (37). Vertical lines represent reactions involving H^+ and/or OH^- ions but not electrons e.g. $Fe^{3+} + H_2O \Leftrightarrow Fe(OH)_2^{2+} + H^+$ (38). Sloping lines represent reactions involving both H^+, OH^- ions and electrons, e.g. $2Fe^{2+} + 3H_2O \Leftrightarrow Fe_2O_3 + 6H^+ + 2e^-$ (39). Oxygen is evolved only at potentials above the upper dotted sloping line (a), by the reaction: $2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^-$ (40), and hydrogen is evolved only at potentials below the lower

dotted sloping line (b), by the reaction: $2H^+ + 2e^- \Leftrightarrow H_2$ (41). Soluble hypoferrites $HFeO_2^-$ form in high pH, alkaline environments at low potential, hence corrosion of cathodically protected reinforcing bars in concrete could occur, when passivation might have been expected. Corrosion is impossible below a certain potential, when the concentration of Fe^{2+} ions in solution is in equilibrium with iron metal, or when the potential is lowered by an external applied voltage. The exact potential depends on temperature and the concentration of iron ions in solution, (known as the activity). The horizontal line at –0.62 volts on the iron diagram, means that iron will not corrode below this value to form a solution of greater concentration than 10^{-6} M Fe^{2+} i.e. with such a low concentration as 10^{-6} M Fe^{2+} in solution one assumes corrosion is negligible. If one assumes a lower value still, the line is lowered according to the Nernst equation: $E = E^0 - \frac{0.059}{n}\log\frac{[a_C][a_D]}{[a_A][a_B]}$ (42), where E^0 is the equilibrium potential of reactants (A,B) in contact with products (C,D) of unit activity (a), in other words this is the Standard Electrode Potential with respect to a hydrogen electrode, which is – 0.44 volts for iron when expressed as a reduction potential, or + 0.44 volts when expressed as an oxidation potential. The activity a_A of a substance 'A' is its concentration in moles per thousand grams of water (called the molality), times a correction factor.

For the reaction: $Fe \Leftrightarrow Fe^{2+} + 2e^-$ (43) at 25°C (298°K), $n = 2$, therefore: $E_{Fe} = E_{Fe}^{\ 0} - \frac{0.059}{2}\log\frac{[F_e^{2+}]}{[F_e]}$ (44). So, substituting $E^0 = 0.44$ volts and the concentration as 10^{-6}, gives $E_{Fe} = 0.44 - \frac{0.059}{2}\log 10^{-6} = 0.44 + 0.18 = 0.62$ (45). Expressed as a reduction potential, this is –0.62 volts with respect to a Standard Hydrogen Electrode. When steel requires cathodic protection in seawater, the potential applied to the steel must, therefore, be below - 0.62 volts with respect to the Standard Hydrogen Electrode, or below about - 0.87 volts with respect to a silver/silver chloride reference electrode. In practice the potential needs to be lower still to allow for the potential drop due to electrical resistance between the attachment point and the area to be protected. This is achieved by attaching zinc blocks (anodes) at regular intervals, or by an impressed current system. The zinc has a potential of about - 1.01 volts to silver/silver chloride, but needless to say, should not be painted or coated in any way.

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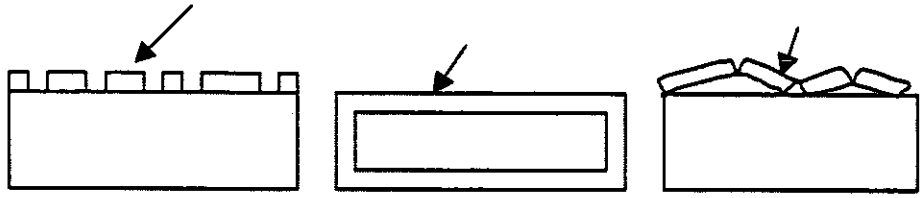
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Figures for Science of Electrolytic Corrosion:



(a) Magnesium **(b) Aluminium** **(c) Iron**

Figure 1: Types of oxide: (a) Porous, non-protecting. (b) Coherent and protective. (c) Oxide spalls due to volume being too large.

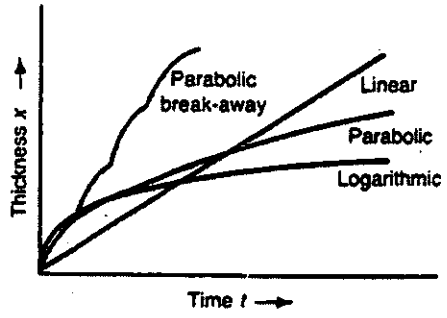


Figure 2: Rates of oxide film thickness growth.

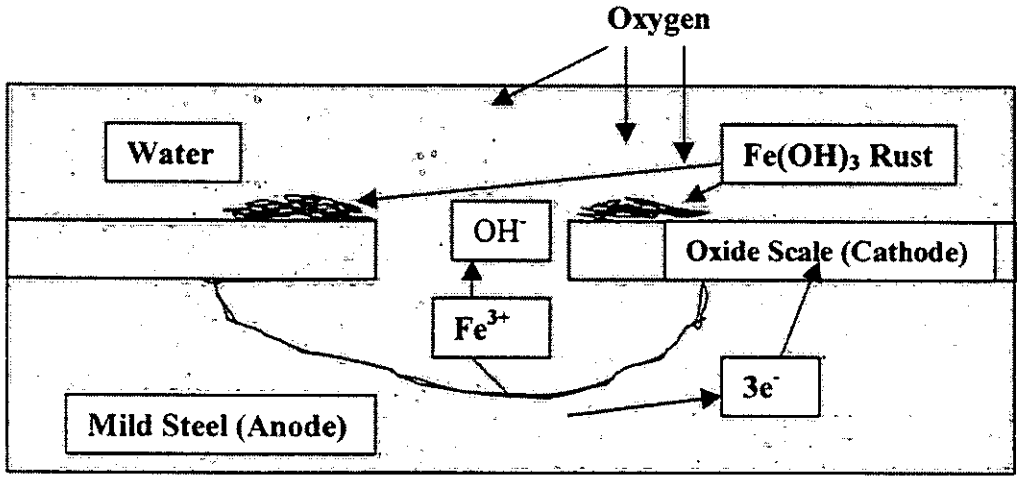
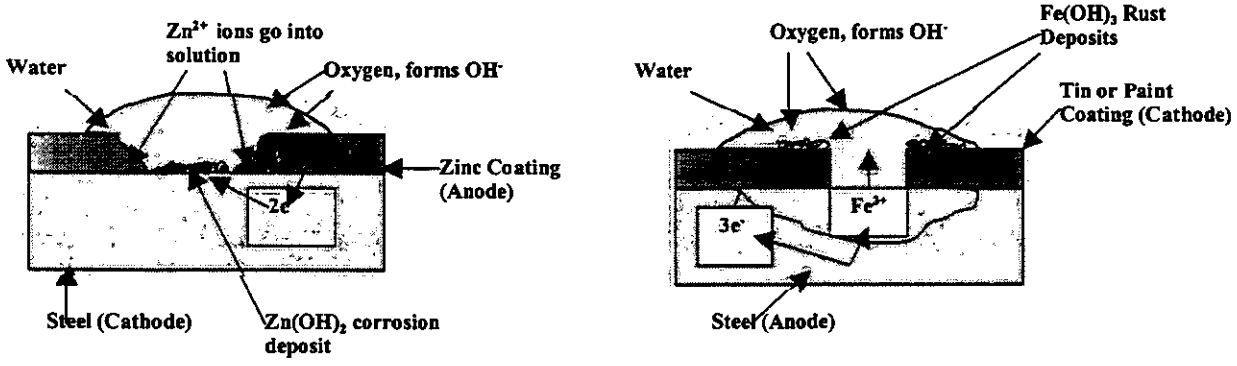


Figure 3: The rusting of steel.



(a) (b)

Figure 4: The effect of defective coatings on steel: (a) Zinc forms a sacrificial coating, so the steel is cathodically protected. (b) Tin or polymer based paints are cathodic, so the steel corrodes away beneath the coating.

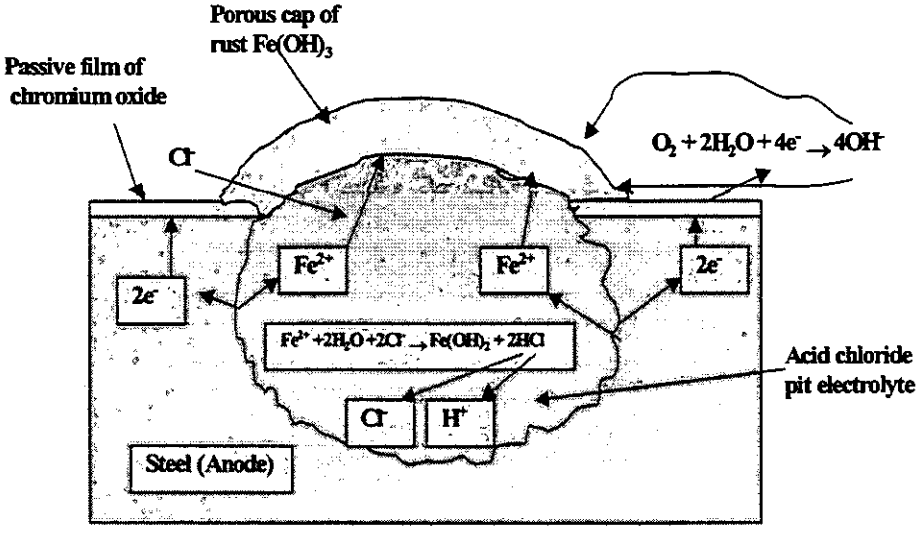


Figure 5: Processes occurring in a pit developing in stainless steel.

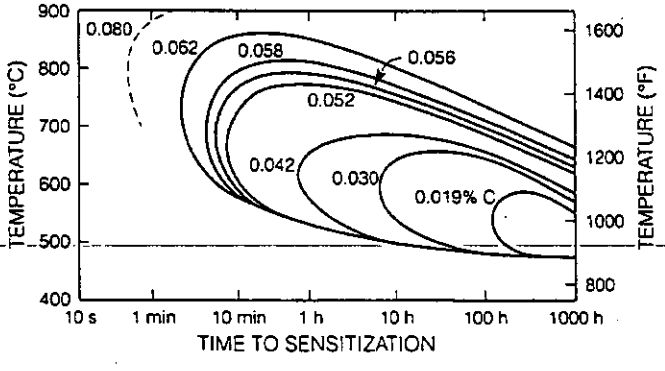
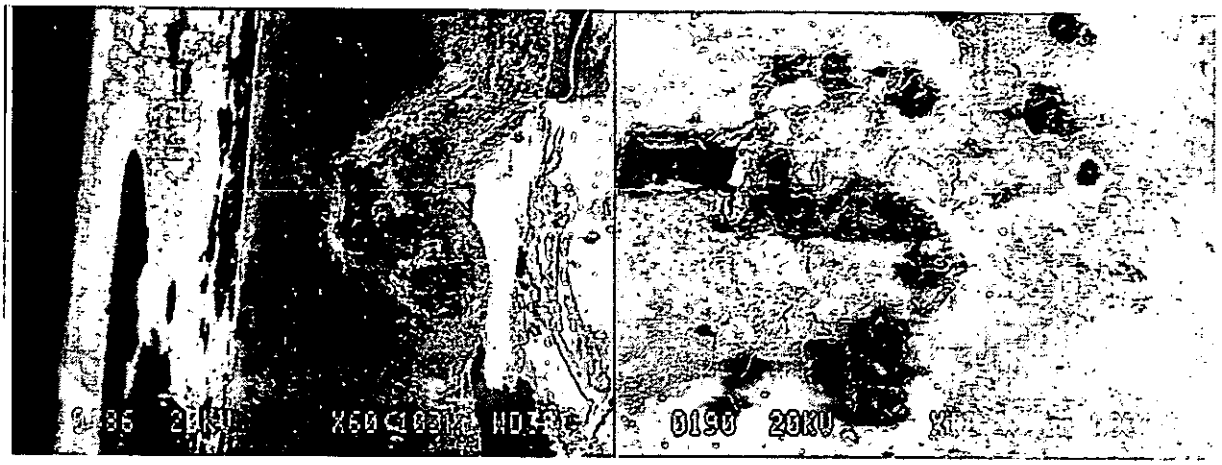
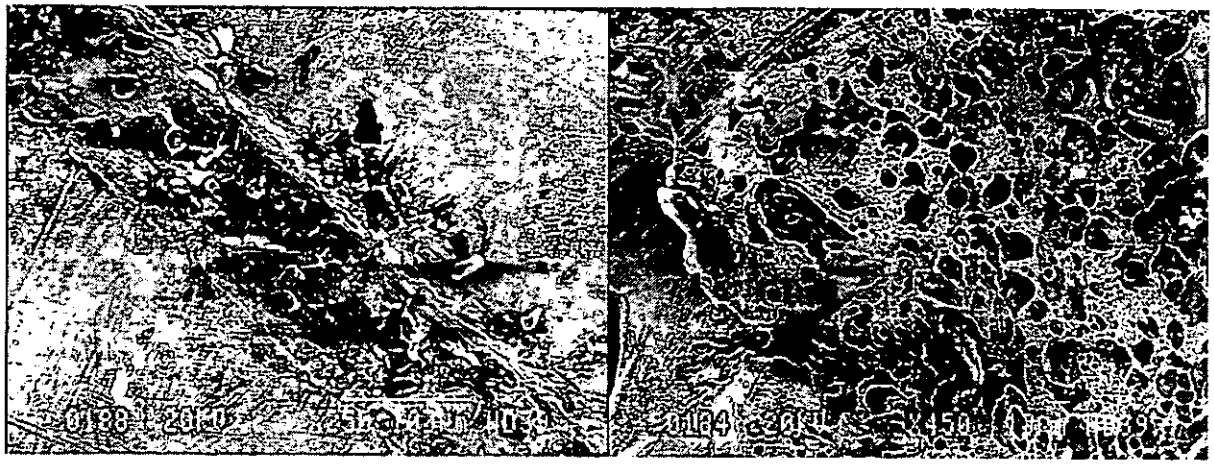


Figure 6: Sensitization diagram for 18Cr-8Ni stainless steel of varying carbon content.



(a) (b)

Figure 7: (a) Pitting damage close to a weld in stainless steel.
(b) Pitting under lettering written in black ink on stainless steel.
All examples in figures 7 and 8 revealed by accelerated corrosion testing in ferric chloride solution.



(a) (b)

Figure 8: (a) Pitting under a scratch on the surface of stainless steel.
(b) Close up of pitting damage in stainless steel.

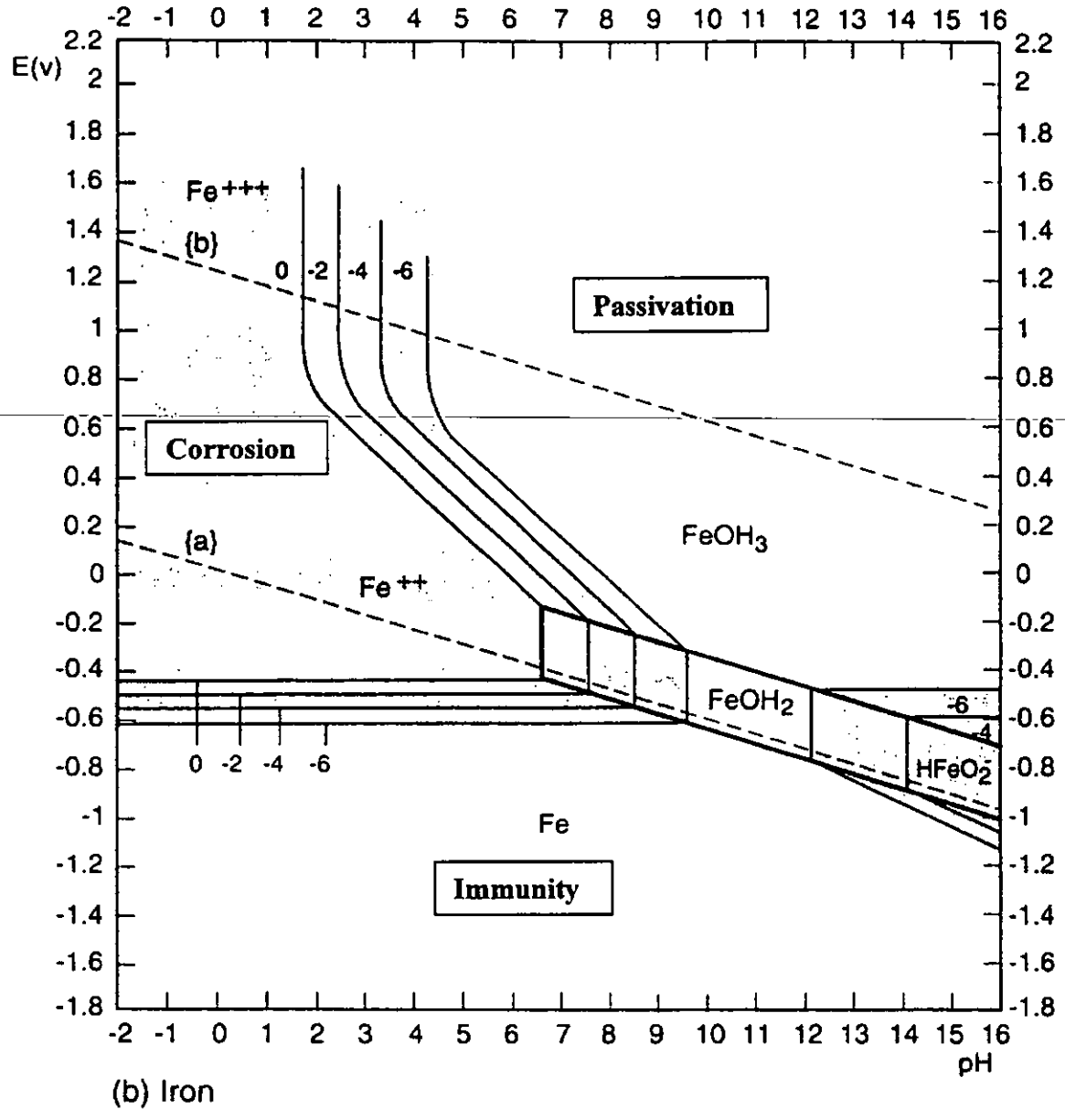


Figure 9: Pourbaix diagram for iron.

Chapter 4

Hydrodynamics of Near Surface Flow

Dr Peter Dyson

Hydrodynamics of Near Surface Flow

Peter Dyson

Department for Mechanical and Marine Engineering, University of Plymouth

Plymouth, United Kingdom

e-mail: pkdyson@plymouth.ac.uk

Abstract

This lecture will cover the fundamentals of fluid flow in the vicinity of a surface. Little prior knowledge of fluid dynamics will be assumed. The basic concepts associated with viscous flow will first be developed, before moving on to key factors which influence the surface, such as turbulence and impingement effects, wall shear stress and molecular diffusion. Examples will be given of current fluid flow modelling capabilities.

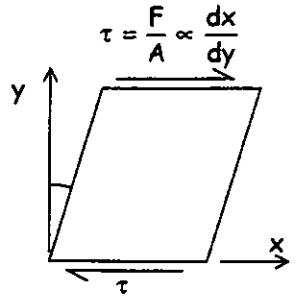
Keywords

Viscosity, Shear Stress, Turbulent Flow, Laminar Flow, Disturbed Flow, Boundary Layer, Reynolds Number, Nusselt Number, Prand tl Number.

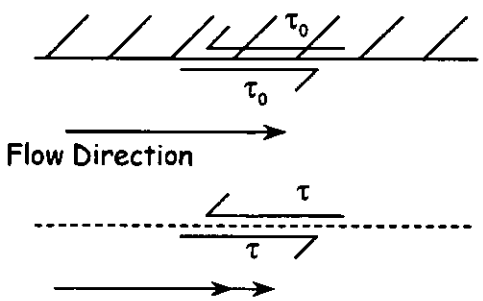
1. Fluid viscosity and its effects

1.1 Viscosity And Shear Stress

- shear stress induced in solids as a result of shear forces producing displacement gradient.
- shear stress induced in fluids as a result of pressure differences producing a flow in which



there is a velocity gradient.



- Newton's Law of Viscosity

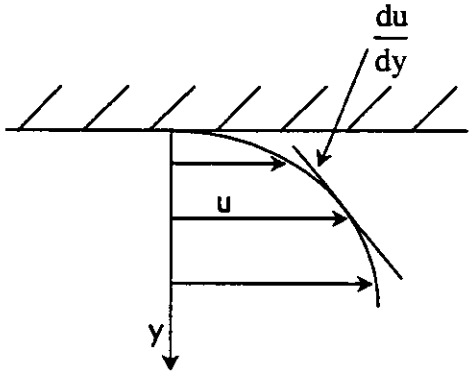
$$\tau = \mu \frac{du}{dy}$$

where μ is the kinematic viscosity. This:

- arises because of molecular interaction
- is temperature dependant
- is constant at constant temperature for Newtonian fluids
- depends on velocity gradient for non-Newtonian fluids
- has units Ns/m^2 or kg/ms; sometimes the Poise(P) is used (1 P = 0.1kg/ms)
- has value for water of 1.520×10^{-3} Ns/m^2 at 5^0C, falling to 0.798×10^{-3} Ns/m^2 at 30^0C.

1.2 The Momentum Boundary Layer

- region of fluid flow affected by solid boundary.

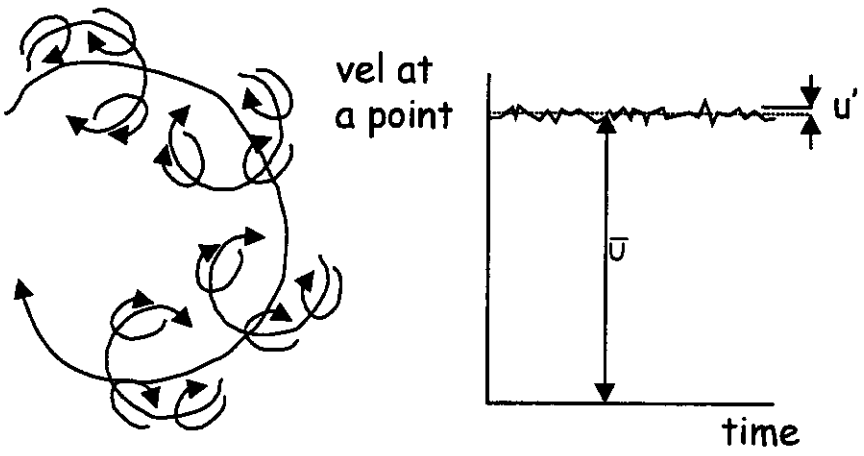


- often taken to be that region in which velocity is less than 99% of free stream velocity.
- may be viewed as a region in which momentum is diffused (similar to heat diffusion under influence of temperature gradient).
- viscous action takes place within the boundary layer; outside, velocity gradient is zero, so shear stress is also zero.
- maximum shear stress occur at the wall; this leads to viscous drag (for external flow) and pressure drop (for internal flow).

2. Laminar And Turbulent Flow

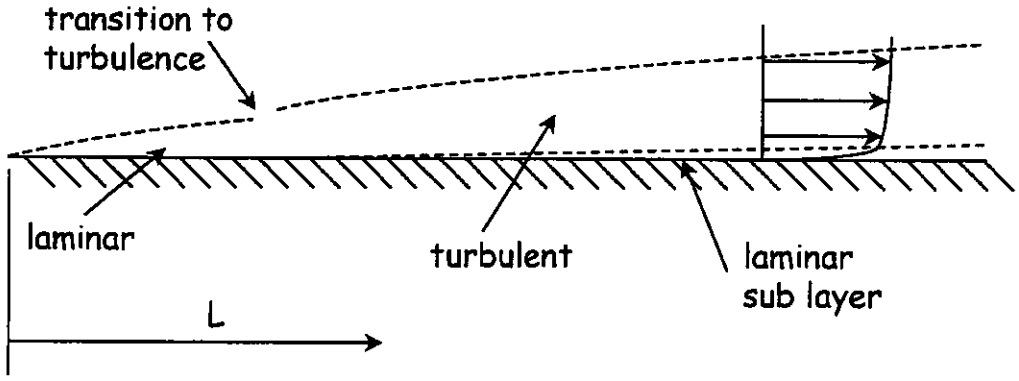
2.1 Nature Of Laminar & Turbulent Flow

- laminar flow characterised by smooth linear motion.
- turbulent flow characterised by erratic eddying motion superimposed on the mean flow

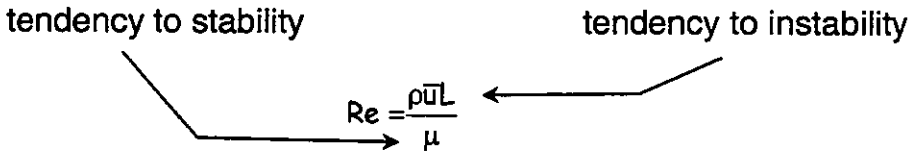


2.2 Transition

- transition from laminar to turbulence is determined by the relative magnitudes of inertia and viscous (damping) forces for the fluid particles.



2.3 Reynolds number



- dimensionless number describing ratio of inertia to damping forces.
- for flow over flat plate, in absence of pressure gradient, transition occurs within the limits $2x10^5 < Re_L < 3x10^6$.

2.4 Impact On Boundary Layer Thickness, Velocity Profile And Wall Shear Stress

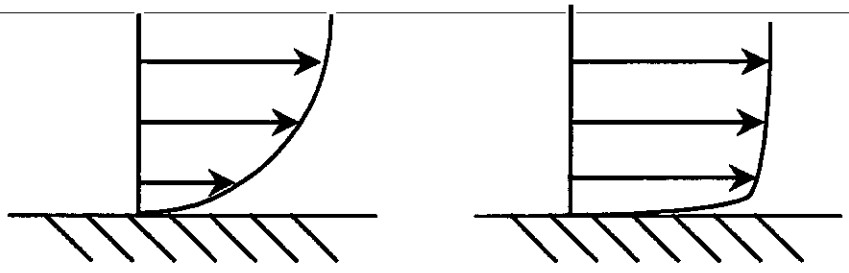
- boundary layer thickness (δ) may be determined from the following:

$$\text{laminar}: \frac{\delta}{L} = \frac{5}{\sqrt{Re_L}}$$

$$\text{turbulent}: \frac{\delta}{L} \approx \frac{0.376}{\sqrt[5]{Re_L}}$$

(assuming turbulent flow exists from leading edge)

- thus the turbulent boundary layer thickens more rapidly.
- velocity gradient at the wall is significantly higher for turbulent flow.



- this leads to higher shear stress, given by the following local (at a point x from leading edge) skin friction coefficients:

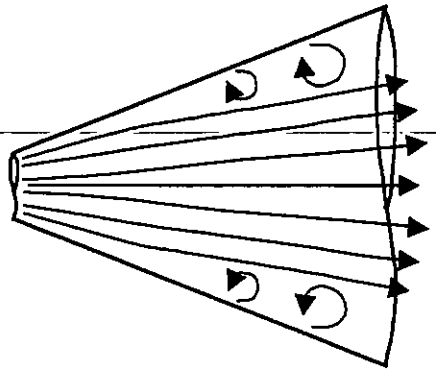
$$\text{laminar}: C_{fx} = \frac{0.664}{\sqrt{Re_x}}$$

$$\text{turbulent}: C_{fx} \approx \frac{0.0576}{\sqrt[5]{Re_x}}$$

$$\text{where } C_{fx} = \frac{\tau_0}{\frac{1}{2}\rho v_\infty^2}$$

2.5 Effect Of Pressure Gradients

- falling pressure in direction of flow tends to thin the boundary later.
- adverse pressure gradient causes thickening of the boundary layer and may lead to separation of low energy fluid in the boundary layer, and thus to loss producing eddying flow.



2.6 Modelling Effects

- when carrying out model scale tests, if $C_f = f(\text{Re})$, then provided

$$Re_{model} = Re_{full\ size}$$

then

$$C_{f\ model} = C_{f\ full\ size}$$

- however, care must be taken to ensure that the flow regimes are similar (both laminar, or both turbulent).
- similar principles apply in any modelling situation, whether for momentum transfer, heat transfer or mass transfer.

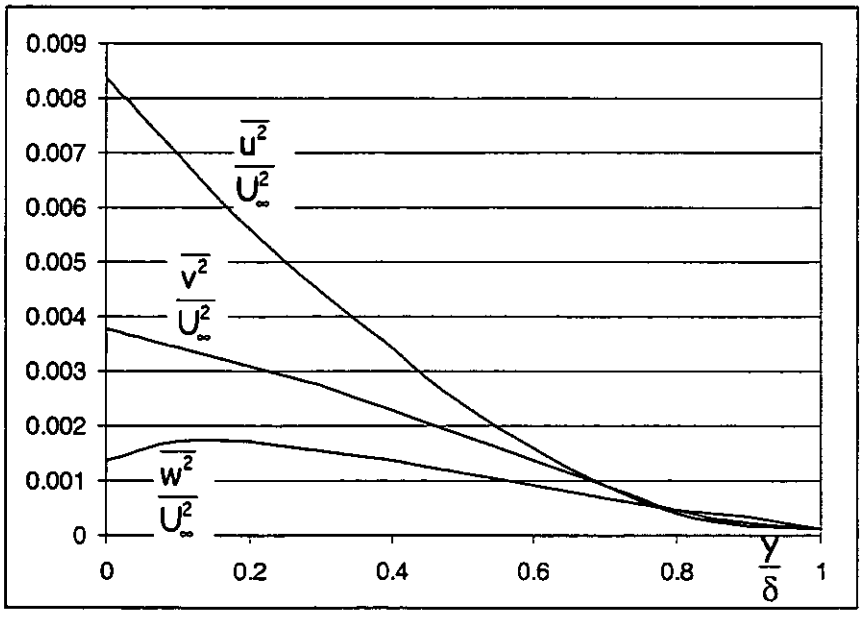
3. Disturbed Flow

3.1 Effect Of Eddies On Flow

- increased eddying in a flow leads to increased momentum, heat and mass transfer.
- eddying flow occurs
  - in turbulent boundary layers
  - as a result of an upstream flow disturbance
  - in separated flows
  - as a result of high shear stress (eg jet flow).

3.2 Length Scales And Intensity

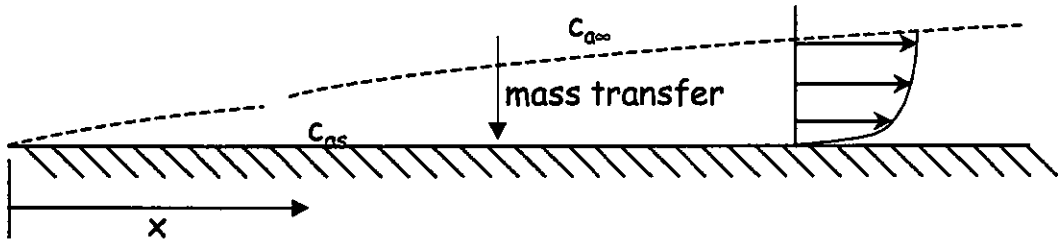
- eddying flow may be viewed as an energy cascade, in which large scale, energy transporting eddies pass energy down though smaller and smaller eddies until velocity gradients are so large that it is dissipated.
- the length scale of the largest eddies is governed by the physical dimensions of the flow field; the ratio of energy containing to energy dissipating eddies is generally much greater than 10.
- turbulence intensity may be measured as the mean square (or rms) of the turbulent fluctuations; typical values for a constant pressure boundary layer are shown below (from Bradshaw (1971)).



4. Molecular Diffusion Through Fluids In Motion

4.1 Mass Transfer, Concentration Gradients And The Concentration Boundary Layer

- momentum, heat and mass are transferred in fluids by similar mechanisms, by velocity, temperature and concentration gradients respectively; for each there is a similar analysis leading to similar non-dimensional equations.
- there are also equivalent boundary layers (though not necessarily the same thickness); of particular relevance is the concentration boundary layer.



4.2 Effect Of Free Stream Velocity, Turbulence

- since turbulence modifies the flow field, it also modifies mass transfer, as this now takes place largely by the eddying fluid moving from regions of high concentration to low and vice-versa, rather than by molecular diffusion which is the case for a stationary fluid or laminar flow. However, since, in turbulent flow, there is a laminar sub-layer, molecular diffusion still plays a role in the mass transfer from the surface to the free stream.
- as in heat transfer, we seek the convective heat transfer coefficient

$$h = \frac{q_A}{\Delta T}$$

and h is expressed functionally in non-dimesional form as

$$Nu = f(Re, Pr)$$

where

$$Nu = \text{Nusselt number} = \frac{hL}{k}$$

$$Re = \text{Reynold's number} = \frac{\rho u L}{\mu}$$

$$Pr = \text{Prandtl number} = \frac{\mu C_p}{k}$$

so in mass transfer, we seek the convective mass transfer coefficient, k, given by

$$k = \frac{N_{ab}}{\Delta C_a}$$

where N_{ab} is mass flux of species a through species b

and k is expressed functionally

in non – dimesional form as

$Nu_{ab} = f(Re, Sc)$

where

Nu_{ab} = Mass transfer Nusselt number = $\frac{kL}{D_{ab}}$

D_{ab} = mass diffusivity of species a through species b

Sc = Schmidt number = $\frac{\mu}{\rho D_{ab}}$

5. Mathematical Modelling Of Flow And Diffusion Fields

- CFD is providing increasingly accurate analysis of fluid flow by solving the governing equations discretely.
- for 2-D steady, incompressible flow, the governing equations are the mass continuity equation and the momentum (Navier Stokes) equations:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$

$$\rho\left(u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right) = X - \frac{\partial P}{\partial x} + \mu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)$$

$$\rho\left(u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y}\right) = Y - \frac{\partial P}{\partial y} + \mu\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right)$$

- to these may be added further transport equations for turbulent kinetic energy and dissipation, and for heat and mass transfer of several species through the host medium.
- typical results are graphical representations of velocity vectors and contour plots of pressure, temperature and concentration of a given species.

6. Flow – Corrosion Interaction

6.1 Influence Of Shear Stress On Erosion-Corrosion

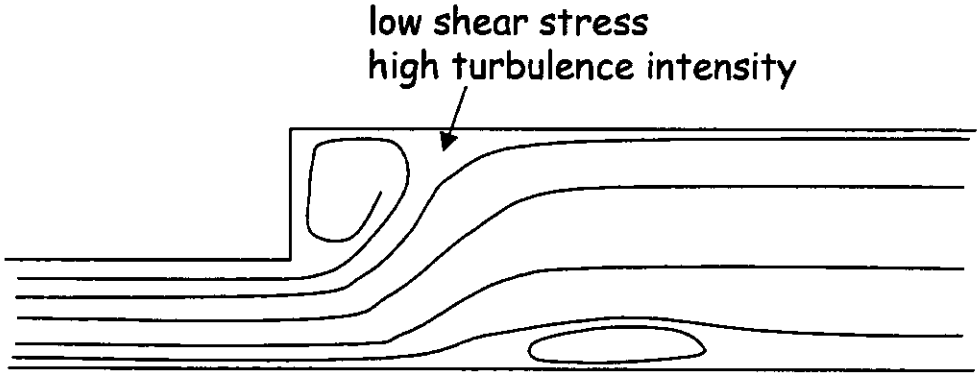
- **Lee (1983)** defined erosion-corrosion as " a conjoint action involving corrosion and erosion in the presence of a moving corrosive fluid". He reviewed several experimental methods for evaluating materials' behaviour in flowing seawater, including scale models, rotating discs, jet impingement and parallel flow tests.

- parallel flow tests are particularly relevant since they cover such things as hydrofoils, propellers and hull.
- he identifies the critical surface shear stress in seawater that exceeds the binding force of the corrosion product film, giving some values for copper alloys, and proposing a basis for extrapolation to service conditions.

- **Dawson et al (1991)** carried out similar tests to Lee, using a rotating cylinder electrode (RCE) and jet impingement, to establish the effect of hydrodynamic shear stress on a surface coated with both corrosion products and inhibitors. He evaluates several inhibitors, proposes the RCE as a potential standard evaluation procedure and identifies "turbulent bursts", impinging on the surface, as being instrumental in the erosion-corrosion process.

6.2 Effect Of Turbulence Intensity

- **Nesic & Postlethwaite (1990)** carried out physical analysis and CFD analysis of the turbulent flow through a sudden contraction followed by a sudden enlargement. Their interest was in oxygen mass-transfer-controlled corrosion. Their observations indicate that:
  - for single phase flow
    - regions of high turbulence intensity have high mass removal rates
    - turbulence intensity gives a better correlation than shear stress; these are often used interchangeably for flow in simple geometries such as smooth pipes, but this is not the case where there is separation and reattachment of the flow
      - high turbulence intensity is instrumental in removing protective corrosion



products from the wall, and allowed higher oxygen transport rates in the vicinity of the wall.

  - for two phase flow, with particles in suspension, particle-wall impacts provide a further mechanism for increased erosion-corrosion, particularly in regions of strong flow curvature.

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Chapter 5

Marine Biofouling

Dr Simon K Davy

Marine Biofouling

Simon K. Davy

Institute of Marine Studies, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK
E-mail: sdavy@plymouth.ac.uk

Abstract

Biofouling, the undesired colonisation of surfaces by sessile organisms, is a common feature of marine systems. Common biofouling organisms include invertebrates such as barnacles, sponges, sea mats and bivalve molluscs, as well as seaweeds. These organisms spread locally by asexual growth, but can spread over larger distances by producing planktonic offspring that are disseminated by waves and currents. At specific points in their lives, these offspring change their morphologies and/or behaviour, and select surfaces for colonisation. This selection is based upon a variety of physical and chemical cues that are used to identify favourable habitats. Physical cues include hydrodynamic regime, light regime, surface texture and surface contour. Chemical cues include protein or mucus secretions from a variety of organisms, and may either induce settlement (*e.g.* the 'settlement factor' of barnacles) or inhibit settlement (*e.g.* chemicals released by predators). Once a settlement site has been selected, organisms cement themselves to the surface and metamorphose into adults. This step is generally irreversible, though a small number of sessile organisms, such as sea anemones and goose barnacles can move slowly thereafter. Whether an organism then persists on a surface depends upon its competitiveness, with competitiveness afforded by rapid growth rates, massive growth forms, toxicity and active aggression. Only physical disturbance, resulting from storms, predation or grazing, prevents the strongest competitors from total domination of a surface. Once surfaces are colonised by dense populations of organisms, various problems may arise. For example, increased drag or weight, and anaerobic corrosion (in the case of metal surfaces). Understanding how these surfaces are selected and colonised by organisms is therefore fundamental to our understanding of how to regulate and prevent problems associated with biofouling.

Keywords: Biofouling; larval dispersal; site selection; surface properties; attachment; population development

What is biofouling?

Biofouling is defined as the undesired colonisation of a surface by sessile (permanently attached) organisms. These organisms include common marine animals such as sponges, sea anemones, barnacles and limpets, as well as bacteria and seaweeds. A more comprehensive list of biofouling marine animals is given in Table 1.

How do biofouling organisms disperse?

Sessile marine organisms can disperse in one of two ways: a) asexual division or b) production of planktonic larvae or spores. These two dispersal methods will be discussed in this section.

Table 1: Examples of common biofouling animals in UK seas

Phylum	Common Species	Common Name
Porifera	*Halichondria panicea*	Breadcrumb Sponge
	Cliona celata	Boring Sponge
Cnidaria	*Metridium senile*	Plumose Sea Anemone
	Corynactis viridis	Jewel Anemone
	Alcyonium digitatum	Dead Man's Fingers (a soft coral)
	Sertularia cupressina	White Weed (a hydroid)
Annelida	*Bispira volutacornis*	A fan worm
	Pomatoceros triqueter	A tube worm
Mollusca	*Lepidopleurus asellus*	Coat-of-mail Chiton
	Patella vulgata	Common Limpet
	Anomia ephippium	Saddle Oyster
	Mytilus edulis	Common Mussel
Arthropoda	*Semibalanus balanoides*	Acorn Barnacle
	Lepas anatifera	Goose Barnacle
Ectoprocta	*Membranipora membranacea*	Sea-Mat
	Flustra foliacea	Hornwrack
Chordata	*Botryllus schlosseri*	Star Ascidian
	Ciona intestinalis	A sea squirt

a) Asexual division

Many encrusting, sessile organisms spread via asexual division. That is, they grow and divide, to produce new individuals without the aid of sexual reproduction. Examples of animals that spread in this manner are clonal invertebrates, such as the sea anemones and sea mats. Sea anemones divide in a number of ways (Shick, 1991), with the most common methods being longitudinal fission (e.g. in the Snakelocks Anemone, *Anemonia viridis*) and basal laceration (e.g. in the Plumose Anemone, *Metridium senile*). Bacteria and microscopic algae also undergo asexual division, while some of the seaweeds can generate new individuals following fragmentation (Dring, 1986). Spreading in this manner can result in the overgrowth of less competitive species and the dominance of a particular habitat, though it does not facilitate the colonisation of distant habitats.

b) Production of planktonic larvae and spores

To colonise new regions, sessile organisms must release offspring or spores into the open sea, which are then free to disperse to other areas. Such organisms are at the mercy of oceanic currents and are termed planktonic. Fouling animals that rely solely on this method of dispersal include barnacles, tube worms and bivalve molluscs (*e.g.* mussels and oysters), all of which produce planktonic larvae. The morphology of the larvae differs between species (e.g. the

nauplius and cyprid larvae of barnacles, the veliger larva of molluscs, the trochophore larva of annelid worms), but all facilitate dissemination and the colonisation of new habitats. The planktonic spores of seaweeds serve the same function. All of these organisms can be termed 'meroplanktonic', as they only spend a portion of their lives in the plankton (as opposed to holoplanktonic organisms, which spend their whole lives in the plankton).

What factors determine settlement on a surface?

The transport, attraction and attachment of organisms to a particular surface depends upon a variety of biological, physical and chemical factors. These relate to the nature of the organism, the water column and the surface itself.

a) Transport to settlement sites

Though some larvae and spores have a rather restricted dispersal, a number (*e.g.* barnacle and mussel larvae) must navigate from the open ocean to find suitable settlement sites closer to shore. As mentioned previously, planktonic larvae are weak swimmers, but by careful positioning in the water column they can utilise ocean currents to 'navigate' their way to suitable settlement sites; the spores of some seaweeds do likewise (Rafaelli and Hawkins, 1996). Examples of this are the shoreward movement of crab larvae with tides (Zeldis and Jillett, 1982; Shanks, 1983), which peaks on a fortnightly basis, and the cross-Atlantic transport of mollusc larvae in major oceanic currents (Scheltema, 1966). This latter example illustrates how some marine organisms can potentially colonise new habitats even when the parent population is a considerable distance (>1000 km) away.

The migration of planktonic larvae to settlement sites usually occurs at a specific point in the organism's life-cycle, is often seasonal and is usually associated with a marked change in behaviour. For example, some larvae become negatively phototactic when they reach a surface, so that they settle in the shade away from the risk of desiccation (Chia and Bickell, 1978). Also, the final planktonic stage of the barnacle, known as the cyprid larva, is specialised entirely for site selection and settlement, and does not eat. The cyprid modifies its behaviour the moment it comes into contact with a surface, using its antennules to walk across the surface and assess its properties. Then, depending upon the surface properties, the cyprid either attaches or swims away (Anderson, 1994).

Exploratory behaviour and settlement is facilitated by reduced water velocity and turbulence close to the surface (the benthic boundary layer), which prevents larvae from being swept away by shear forces (Mann and Lazier, 1996). This means that flow regime is an important consideration, as the depth of the boundary layer (and hence the protection afforded by it) will lessen as flow rate increases. For example, larvae of the polychaete worm *Phragmatopoma lapidosa californica*, preferentially settle when flow rates are between 15-25 cm s^{-1}, but are carried away at higher flow rates (Pawlik and Butman, 1993). It should be noted, however, that the ability of different larval species to withstand shear forces differs. For example, the cyprids of open water barnacle species can tolerate greater shear forces than cyprids of estuarine barnacle species (Anderson, 1994).

b) Site selection for attachment

The factors that encourage settlement and attachment of larvae are of great interest in the field of biofouling, and have received considerable attention in recent years. It is now accepted that a large range of marine organisms (including marine worms, barnacles and molluscs) examine a site before selecting a suitable place for attachment (Chia, 1989; Raimondi, 1990; Pawlik, 1992). These organisms base their 'decisions' upon a range of physical and chemical cues.

Physical cues include light and hydrodynamic regime (Young, 1991; Anderson, 1994; Tait and Dipper, 1998). As mentioned above, larvae of the worm *P. lapidosa californica* preferentially settle in intermediate flow regimes, being swept away in fast currents and avoiding low velocity regimes (Pawlik and Butman, 1993). This avoidance of slow currents may be due to insufficient food being delivered, or the deposition of silty sediments that smother filter-feeding organisms such as *P. lapidosa californica*. Of course, other species may preferentially select habitats with faster or slower currents, and more of less turbulence, depending upon their habits and requirements.

Organisms also select certain sediment types, whether hard, stable substrates or soft, unstable substrates. Moreover, sessile organisms can determine the physical properties of a surface, with surface texture and topography (slope and contour) now known to be of great importance in site selection. In general, rough surfaces are preferred by settling organisms, as the various pits, crevices and concavities provide shelter from the forces imposed by passing currents (Raffaelli and Hawkins, 1996). Indeed, a preference for rough, heavily contoured surfaces is seen in barnacles (Barnes, 1956; Crisp, 1961; Rittschof *et al.* 1984) and sea mats (Mihm *et al.* 1981), while the sponge *Ophlitaspongia seriata* settles preferentially on overhanging surfaces (Tait and Dipper, 1998). Taken alone, this would suggest that one way to prevent fouling by such organisms would be to provide smooth, flat and so presumably unfavourable surfaces. However, the situation is not so simple, as larvae may become less selective with age, and ultimately settle on any available surface before perishing. This behaviour is seen in barnacle cyprids, which even settle upon glass if no preferable alternative is available (Rittschof *et al.* 1984).

The type of surface preferred for settlement may also be influenced by molecular and bacterial films. Macro-fouling (colonisation by macro-organisms such as barnacles) is often stimulated by micro-fouling (colonisation by micro-organisms such as bacteria), though the exopolymers of some bacteria may have an inhibitory effect (Maki *et al.* 1990). However, micro-fouling is not essential for macro-fouling to occur, as molecular films may be all that are required to condition a surface. Indeed the chemical properties of the surface are of great importance, with particular chemical cues known to either stimulate or inhibit settlement behaviour. The best known of these cues is the so-called "settlement factor" of barnacles, a specific protein recognised upon contact by the cyprid (Yule and Crisp, 1983; Gabbott and Larman, 1987; Tegtmeyer and Rittschoff, 1989). The protein is found both in the integument of adult barnacles and in the 'foot-prints' left by wandering cyprids, and is thought to promote the gregarious settlement of barnacles (Ritschoff *et al.* 1984; Walker and Yule, 1984; Anderson, 1994). Comparable settlement factors also occur in tube-worms and hydroids (Chia and Bickell, 1978; Eckelbarger, 1978), while some organisms even stimulate settlement by other species. For example, seaweeds may produce cues that induce settlement by sessile animals

(Chia and Bickell, 1978), and settlement of barnacles may be stimulated by other invertebrates that frequent similar habitats (Raimondi, 1988). Cues that inhibit barnacle settlement are produced by predatory species such as whelks, and also by some seaweed species (Johnson and Strathmann, 1989). Likewise, settlement of larvae of the Common Mussel (*Mytilus edulis*) is inhibited by the presence of adult mussels of a more competitive species (*Mytilus californianus*) (Petersen, 1984). It should be emphasised, however, that different species are likely to respond to these cues in different ways, with a cue that inhibits settlement of some species acting as an attractant for others.

Clearly therefore, larvae can respond to a variety of physical and chemical cues when selecting a settlement site, including surface topography, light regime, shear conditions, local microflora and molecular "settlement factors". The ability to respond to these cues has a number of advantages, including limiting larval losses and inducing gregariousness, which facilitates fertilization.

c) Attachment and metamorphosis

Once a suitable settlement site has been chosen, juveniles attach to the surface. This stage is often irreversible, with most sessile organisms being unable to move afterwards. Exceptions to this are the sea anemones and some lepadomorph barnacles (= goose barnacles) (Young *et al.* 1988; Kugele and Yule, 2000); goose barnacles may move at rates of only 10 $\mu m\ day^{-1}$, employing a variety of methods (Kugele and Yule, 2000).

The best-studied attachment mechanisms are those of barnacles, again reflecting the importance of barnacles in biofouling. Cyprids attach themselves to the surface during the investigation phase (see previous subsection) by means of their antennules, which secrete a visco-elastic protein (Walker and Yule, 1984). Then, when permanent settlement begins, the cyprid secretes 'cement'. This cement originates from specialised cement glands, which produce various proteins, phenol and phenoloxidase. Following release by the antennules, the cement hardens over 1-3 hours into a quinone-tanned protein, which is both rigid and biochemically stable. The barnacle is then adhered firmly to the surface (Nott, 1969; Walker, 1971; Anderson, 1994). Similar adhesion mechanisms, involving the glandular secretion of adhesives (proteinaceous cements or mucus coats), are also seen in other invertebrates, including ascidians (sea squirts) (Cloney, 1978), cnidarians (*e.g.* corals, sea anemones, hydroids, sea pens) (Chia and Bickell, 1978) and bryozoans (sea mats) (Reed, 1978).

Once attached to the surface by means of an adhesive, organisms undergo metamorphosis. The series of events associated with metamorphosis is complex and varies radically between different taxonomic groups. However, in all cases, metamorphosis marks the onset of the adult phase of the life-cycle. As mentioned earlier, the adult of most sessile organisms can move very little, if at all, with the major path of dispersion being the release of gametes and/or larvae. Therefore, once metamorphosis has occurred, sessile organisms must maintain their position in the face of environmental stress and competition from other organisms. This topic will be covered in the next section.

What factors determine the persistence of settled organisms?

Firm substrates are highly desirable habitats, as they afford long-term stability. Also, they are frequently associated with high-energy sites, where currents deliver abundant supplies of food and oxygen, and remove waste products. Consequently, there is tremendous competition for space in these habitats, and a variety of methods are employed to attain a competitive edge over other organisms. One of these methods is gregarious settlement (see earlier), which results in mass, simultaneous colonisation by generally opportunistic species. However, this does not guarantee long-term success, as other, more competitive species tend to displace the initial colonisers. Such displacement can occur due to differential growth rates, and associated undercutting or overgrowth. For example, when two competing barnacle species are considered, the fast growing *Semibalanus balanoides* undercuts, overgrows or laterally crushes the slower growing *Chthamalus montagui* (Boaden and Seed, 1985). Similarly, the soft coral *Alcyonium digitatum* (Dead Man's Fingers) grows rapidly after it first settles, making it highly competitive; growth rate decreases once a large size is achieved. Inter-specific aggression may not only be enabled by rapid growth, but some organisms also produce toxins with which to deter or kill competitors. Sea anemones are examples of actively aggressive sessile organisms, with many species having specialised batteries of stinging cells or toxic sweeper tentacles with which to attack neighbours (Shick, 1991). Likewise, many sponges are known to produce toxins that can convey a competitive advantage. Seaweeds can also be 'aggressive', either by overgrowing and smothering organisms, or by using their fronds to scour surrounding surfaces. Clearly therefore, the final community structure may be quite different from that during the early stages of colonisation, and could, if it remained unchecked, become dominated by only a small number of species. However, in reality, this rarely happens. This is because communities are disrupted by adverse environmental conditions (*e.g.* storms), or by predators and grazers. Such disruption clears surfaces, renders them suitable for re-colonisation by opportunistic species, and maintains community diversity (Rafaelli and Hawkins, 1996).

What problems are associated with biofouling?

While encrusting organisms can have a stabilising effect on structures, 'welding' them together or protecting them from mechanical abrasion (North and MacLeod, 1987), there are also a number of potentially serious problems associated with biofouling. Such problems include increased weight of structures, and increased drag and shear stress. A further problem is anaerobic corrosion of metal surfaces, which occurs when encrusting organisms create a barrier between the seawater and the surface. This barrier leads to a micro-environment, with an acidic pH and high Cl^- content, and an absence of oxygen. Such a micro-environment can enhance corrosion, especially when it encourages growth of sulphate-reducing bacteria. These bacteria generate sulphide ions and produce the enzyme hydrogenase, both of which accelerate the corrosion reaction (North and MacLeod, 1987). Clearly, therefore, the potential for hydrodynamic and structural problems is immense, highlighting the importance of understanding how and why marine animals and plants colonise surfaces. Indeed, only by having this understanding can effective measures be developed to inhibit biofouling.

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Chapter 6

What is Paint ?

Nigel Clegg

What is Paint?

Nigel Clegg
Consultant

Abstract

This chapter reviews the general consideration that needs to be borne in mind when using paints and the fundamental constitution of paint and the ways in which it can be modified.

Back to Basics

Before we start looking at paints in any detail, we should remind ourselves of some basic rules for safe and successful painting:-

1. A paint scheme is only as good as its weakest coat: painting over badly prepared surfaces, or over an old scheme which is unsound is a waste of both time and money.
2. Many marine substrates are better not painted at all than painted badly.
3. Always use the right material for the job: trying to cut corners by using cheaper alternatives will often result in failure, and will cost far more in the long term.
4. Don't try to save money by thinning the paint unnecessarily: if the manufacturers thought money could be saved in that way, they would have done it!
5. ***Always*** apply the number of coats specified by the manufacturer: reducing the number of coats will reduce both the performance and the lifespan of the coating scheme.
6. ***All*** organic coatings (including epoxies and polyurethanes) are slightly moisture permeable. This means that it is impossible to 'seal up' rot, corrosion, or a blistering fibreglass hull with paint.
7. Only use products specified for designated areas e.g. underwater use: some paints will fail if applied to permanently wet areas, so check to see that you are using the correct paint for the area to be painted.
8. ***Always*** read and follow the manufacturers instructions: they are there for a reason.
9. Paints are chemical compositions, and must be handled with care and respect: think about Health and Safety ***before*** you start work.
10. If in doubt, ***ask!***

The rationale for some of these points may not be immediately obvious, but as you read through this book, their importance will become increasingly clear.

It is important that we all speak the same language. Some of the more important terms that we shall be using: The word 'Coating' is now widely used to describe both paints and varnishes, especially where differences between the two types of material are not significant. The word 'Paint' is generally accepted to mean a pigmented or coloured coating, while a varnish is usually an unpigmented, clear coating.

The term 'conventional coating' usually describes a single component paint or varnish that dries by absorbing oxygen from the atmosphere, but can also include coatings which dry by solvent evaporation like antifoulings, and some keel primers.

'High performance' coatings are usually chemically cured, two component products like epoxies and polyurethanes, which provide much improved mechanical, chemical and cosmetic properties.

Once applied, each coat of paint or varnish is called a ***film***, and a series of films is called a ***coating scheme***. The thickness of both paint films and schemes is measured either in ***Microns*** (abbreviated μ or μM), or less commonly now, in thousandths of an inch (usually called ***Mil*** or ***Thou***)[1]. Unless stated otherwise, this measurement refers to the thickness of coatings when they are fully dried and cured (i.e. their ***dry film thickness*** or ***DFT***), rather than their w***et film thickness***.

A glossary of painting terms can be found at the back of the book.

[1] There are one million microns in a metre, and 2540 microns in an inch. One Mil is equivalent to 25.4 microns or μM, while one micron is equivalent to 0.000 039 37 inch.

Personal Hygiene and Safety

Paints are chemical compositions, and must be handled with care and respect. In particular, the following precautions should always be observed when using paint products:-

- Protect your eyes when mixing or using paints or solvents.
- Work in well ventilated conditions. Where this is not possible, the use of suitable respiratory protection is ***essential.***
- ***Never*** work alone or in isolation when carrying out hazardous operations or working in hazardous areas; you may need help in the event of an emergency.
- Protect your hands whenever mixing or using paints or solvents by wearing suitable protective gloves. A barrier cream is also recommended for added protection.
- Take care when opening paint tins, as the contents may be under pressure, (especially polyurethane curing agents and paints containing aluminium). If a tin appears to be under pressure, cover it with a rag before opening to avoid the risk of splashing.
- ***Never*** touch your mouth, eyes or other sensitive areas when wearing gloves, or without washing your hands. Always wash your hands ***before*** visiting the toilet.
- ***Never*** use solvents for hand washing. Remove paint by washing with tepid water and a hand suitable hand cleaner. A good hand cream should be applied after washing to maintain good skin condition.
- Wear protective overalls when handling, mixing or applying paint. Working clothes made from natural fibres are usually found best as they dissipate sweat better than man made materials. Elasticated cuffs and ankles are recommended when sanding to prevent the ingress of irritating dust.
- ***Never*** put solvent soaked or contaminated rags in overall pockets, as these can cause serious skin disorders, and pose a severe fire hazard. Remove contaminated overalls immediately for the same reasons.
- Wear respiratory protection whenever sanding or scraping paint to avoid inhaling harmful dusts. The dust from epoxy fillers can be particularly irritating.
- ***Antifoulings must never be dry sanded or burnt off*** as they contain toxic compounds.
- ***Never*** eat or smoke when working with paint.
- Wash your hands, and rinse your mouth with fresh water before eating, drinking or smoking. Overalls should be removed before eating.
- Wash protective equipment regularly with soap and water to remove irritating materials and to discourage bacteria.

Please note that the information given here is only a brief resume of the requirements for safe working conditions when painting, and is not intended to be exhaustive.

If you have any concerns about Health or Safety, you should contact the paint manufacturer for further advice. If you are a professional painter, your local Health and Safety Inspector will also be pleased to advise.

What is Paint?

Before looking at painting schemes or application details, we should first consider how paints are made; this will help our understanding of the properties and limitations of different coating types, and will also highlight some of the objectives and compromises involved in their formulation.

In its simplest form, a paint could be comprised of just a colouring pigment in water (like whitewash), although a coating like this would provide little protection in a marine environment, and would quickly be washed away by rain and sea water. But if we add a resin to bind the particles of pigment together, our paint can be made far more weatherproof, and will provide much better protection for the substrate.

Unfortunately, most resins are either solid or very viscous at normal temperatures, so a solvent must be added to reduce viscosity before the paint can be manufactured or applied. There are other problems too: many resins would take days or even weeks to dry by themselves, so 'dryers' have to be added to provide acceptable drying times. Similarly, many colouring pigments would have limited obliteration if used by themselves, so 'extenders' are added to improve opacity, and perhaps to give the paint a better 'feel' or 'body'.

While it is true that some excellent paint formulations have been dreamt up on a Friday afternoon, most are the results of years of painstaking work, usually involving hundreds of test panels and intensive exposure trials even before the first samples can be field tested. The diagram below give a basic idea of what a typical can of paint is likely to contain:-

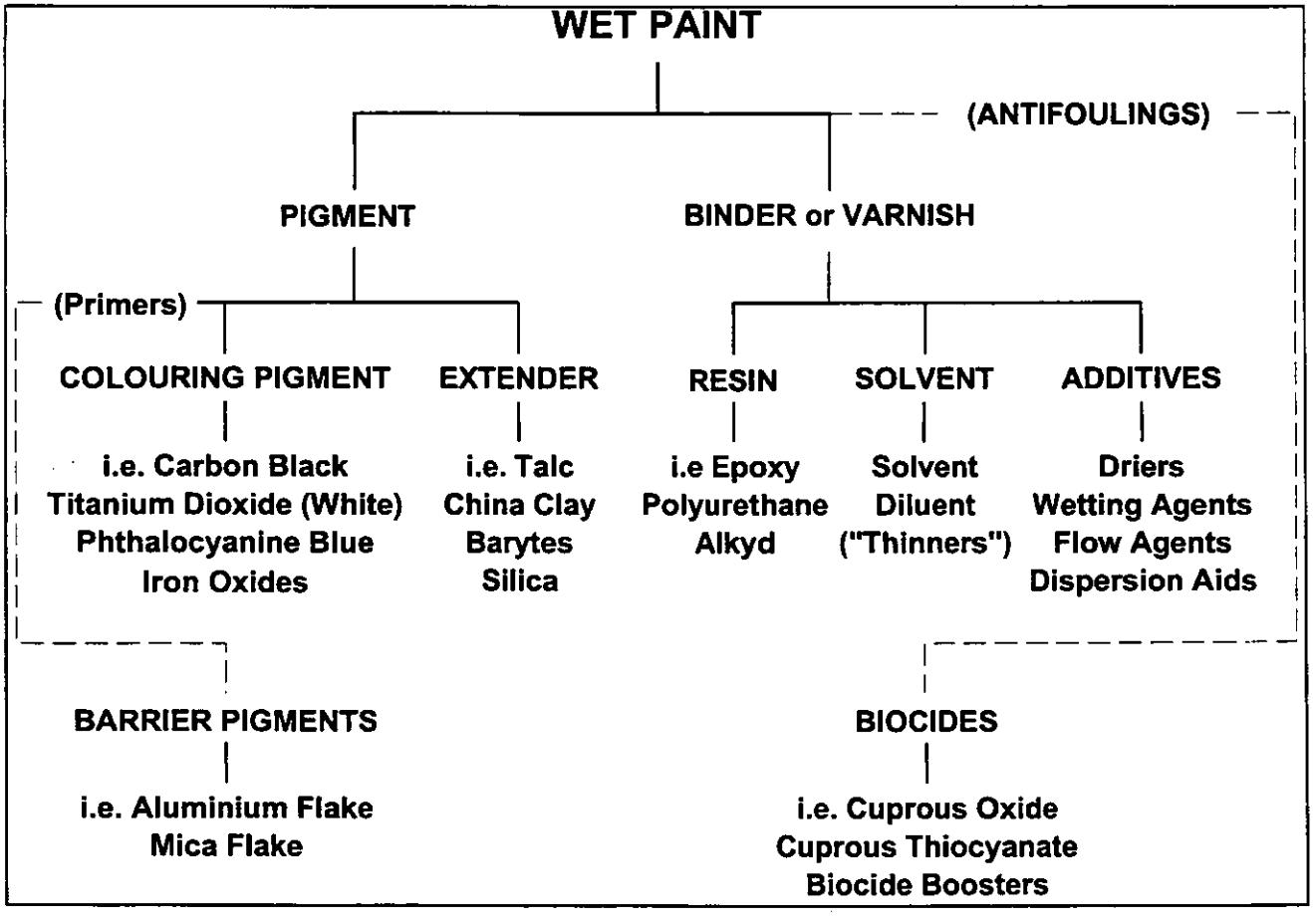


Fig 1:-Diagram Showing What a Typical Can of Paint is Likely To Contain

So what are these constituents, and how are they used?

Resins

Known technically as the 'vehicle' or 'binder', resins are the backbone of all paints and varnishes, and so usually lend their name to the paint as a generic type, (i.e. alkyd, epoxy or polyurethane). As would be expected, resins have a profound effect on the properties of coatings, determining factors such as gloss and gloss retention, abrasion and chemical resistance, adhesion, moisture permeability, and to some extent, compatibility with other paint types.

The first function of a resin is to provide a 'vehicle' for dispersed pigments and extenders, carrying them to the surface being painted; once applied, the resin must change from a liquid into a solid, binding the pigments and extenders into a cohesive film, and bonding them to the substrate. To achieve this change, the resin undergoes a series of complex chemical reactions, where comparatively small, mobile molecules are joined together into long polymer chains by a process known as 'curing', 'cross linking' or 'polymerisation'.

'Curing' is principally a chemical reaction, so the degree of cure is very much dependent on temperature (and in some cases, relative humidity), therefore likely application conditions must always be borne in mind whenever a paint is being formulated, or purchased.

While an in depth discussion about film forming reactions is beyond the scope of this book, an understanding of the behaviour and limitations of different resin types is extremely helpful when choosing a paint or varnish for any particular project.

Conventional Resins

The very first paints and varnishes were made from natural drying oils such as linseed (pressed from the seeds of the flax plant), and occasionally from fish oils. Resins made from natural drying oils are known as 'Oleoresins'.

Drying oils cure by absorbing large quantities of oxygen from the atmosphere to produce simple polymers, although this is a fairly slow process with many practical limitations.

However, these oils are also very 'fatty' in nature, and are characterised by the high concentrations of Linolenic, Linoleic, Oleic and other fatty acids that they contain. (Do you remember Linoleum)? Chemists searching to overcome the limitations of drying oils found that these acids could be reacted with high molecular weight alcohols like pentaerythritol and glycerol to produce a type of (poly)***ester***, which had far better mechanical and chemical properties than their oleoresinous predecessors.

These new resins became known as 'Alkyds', (i.e. derived from an ***acid*** and an ***alcohol***), and have provided the basis for the majority of varnishes and decorative paints from the early 1950's until the present day. They are still known as 'oil based' resins by many older painters, though this is not strictly correct.

The most immediate advantage of alkyd resins was their speed of drying and almost clear colour, but they also provided far superior gloss and durability. Alkyds can also be made from cheaper and more readily available vegetable oils such as sunflower, safflower, and rape seed oils, although most good yacht coatings are still manufactured with soya, linseed and tung oils in the interests of quality and performance.

Like oleoresins, alkyds dry firstly by solvent evaporation, followed by reaction with atmospheric oxygen to form loosely linked polymers. This 'oxidative' drying mechanism is

ideal for marine coatings, allowing prolonged storage in sealed containers and avoiding the need for separate curing agents.

This great simplicity has led to alkyds becoming very much the mainstay of yacht and other marine coatings, being easy to apply in most conditions, and combining good cosmetic appearance, protection and durability at reasonable cost.

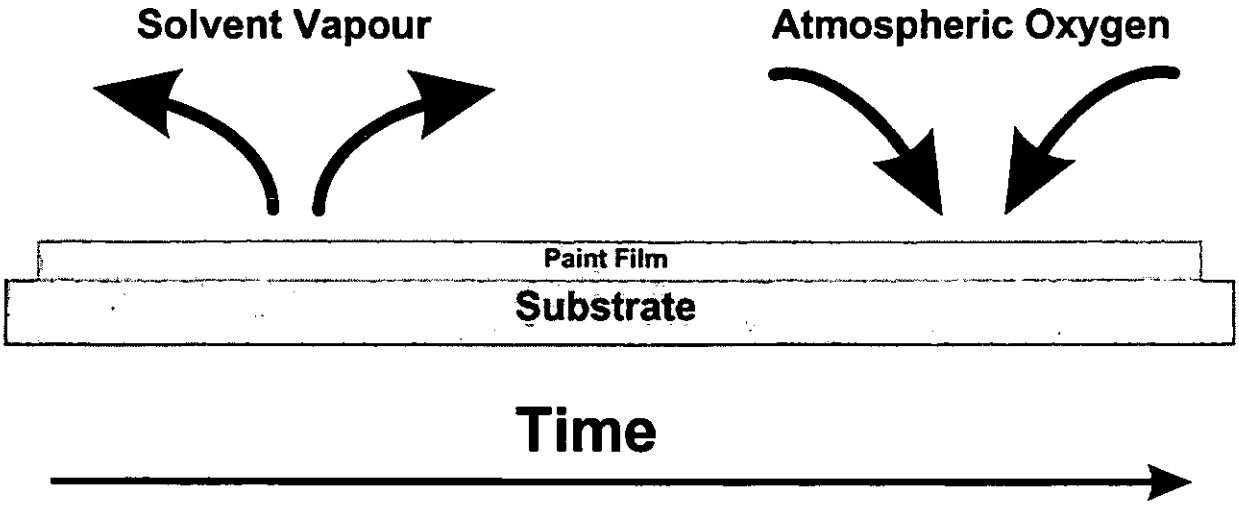


Fig 2: The Conventional Drying Process

For added convenience, drying can be accelerated by adding small quantities of metallic compounds, (known as 'dryers') which increase the rate of oxidation. Traditionally, tiny quantities of lead compounds were used for this purpose, but recent health concerns have led to alternatives like zinc, zirconium and cobalt being substituted. The presence of Cobalt is often noticeable by the purple tint that it gives to some paints and varnishes, although this is not visible in the dried film.

Standard alkyd or 'conventional' coatings provide more than adequate performance for most painting and varnishing jobs on board, and are also quite flexible for traditionally built boats where some movement can be expected. Their initial gloss is also very good at around 75 ~ 80%, which is high enough to look superb on well prepared substrates, while avoiding the rather 'plastic' appearance associated with two pack polyurethanes.

Conventional finishes can be expected to retain their gloss and appearance for around two or three sailing seasons in temperate climates, or perhaps a single season in tropical or sub tropical conditions, although precise predictions are always difficult. Ultra Violet light is one of the worst enemies of paint coatings and plastics, as it gradually destroys the chemical bonds in both resin and pigment, with the result that the coating surface breaks up into small fragments. Known technically as 'Ultra Violet Degradation' this effect is initially seen as dullness or a loss of gloss, but with time, surfaces become 'chalky' and completely drab. Climatic conditions inevitably have a major influence on the longevity of paint coatings, although industrial pollution and other local factors can also help to accelerate weathering effects.

White paints usually have the best gloss retention as their pigments reflect much of the ultra violet energy to which they are exposed, although darker colours do not have this advantage.

Moreover, darker colours tend to become hot when exposed to direct sunlight, which helps to accelerate the breakdown process.

Gloss retention can be improved significantly by the use of UV inhibitors, which absorb ultra violet light before it does too much damage to the coating, although basic formulation is always the most important factor.

Modified Resins

The alkyd resins used in conventional marine coatings are usually manufactured from soya bean and linseed oils for a good balance of durability and performance at reasonable cost. Nevertheless, these properties can often be improved by incorporating other resins or oils, and by reaction with other monomers in a process known as 'modifying'.

One of the most useful variants is the urethane modified alkyd, in which an alkyd resin is partially reacted with isocyanate monomers similar to those used in polyurethane curing agents. In effect, the resin in a urethane alkyd is already partially cured, so drying times are shortened considerably, which can sometimes cause application difficulties in warm weather.

Urethane alkyds have better hardness and abrasion resistance than conventional alkyds, with greater resistance to chemicals and water, and higher initial gloss, although their long term gloss retention is sometimes not quite as good.

'Urethane Oils' provide a slightly different approach, where a vegetable oil (rather than an alkyd resin) is reacted with isocyanates. Urethane oil resins are very tough, with good resistance to chemicals and water immersion, and so are widely used in primers for timber and metalwork above the waterline. These resins are also used in DIY paints like Japlac, although their gloss retention is poor when used outdoors, and they tend to be rather too fast drying for painting large areas like yacht topsides.

Where cost is not an obstacle, a proportion of the soya and linseed oils can be replaced with more expensive tung oil, as in many of the more expensive yacht varnishes. This technique combines the benefits of improved gloss, durability and water resistance, with a very pleasant 'old fashioned feel', although the addition of tung oil usually slows drying quite noticeably.

Another useful variant is the silicone modified alkyd, which has recently seen major improvements. Some early silicone alkyds gained a bad reputation for adhesion and overcoating problems, but recent formulations like Internationals Toplac[2] and Epifanes Nautiforte have overcome these difficulties to provide a lasting high gloss finish with excellent brush application properties. The finish and gloss retention of silicone alkyds can rival that of many two component polyurethanes, albeit with lower abrasion resistance. Unfortunately, this technology can only be used in paints, as silicone alkyd resins do not produce clear films.

We have seen some of the ways in which the performance of conventional resins can be enhanced, although this usually adds considerably to the cost of raw materials. There are also many ways in which resins can be' value engineered' to meet the pricing targets demanded by large supermarket and DIY chains. These can include substituting the more expensive oils

[2] Brightsides in the USA

with cheaper alternatives such as rape seed oil, or by reducing the actual quantity of oil used in the resin to produce what is known as a short or medium oil alkyd. While these materials appear to offer good value for money, they are not as pleasing to apply as traditional marine coatings, and will be unlikely to provide the same degree of protection.

Performance Limitations

Whatever changes are made, alkyds resins are subject to a number of shortcomings which pose severe restrictions on their use. These limitations are chiefly due to the loosely bonded nature of alkyd polymers, which are vulnerable to being broken apart by alkali. This clearly limits their chemical resistance, but less obviously, it also makes them unsuitable for underwater use on metal boats, as corrosion produces alkaline metal soaps which quickly destroy conventional coating schemes. This effect is known as 'Saponification'. These limitations apply to all conventional coatings, ***including*** yacht and marine enamels and many of the red oxide primers sold for priming bare steel .

More generally though, alkyds have poor resistance to long periods in water, and will start to soften and break down after only two or three days immersion. This obviously makes them a poor choice for underwater protection, but any form of long term exposure to water or moisture is likely to cause failure. Problems are commonly caused by wet ropes on deck, wet leaves, canvas covers, and even moisture trapped beneath flower pots! Exposure to motor fuels, strong spirits and cosmetic products (like after shaves) can also cause damage, with the latter products often leaving tell-tale rings where they have been trapped beneath bottles and spray cans, etc.

The conventional drying mechanism itself also has its weaknesses, especially when coatings are applied too thickly, or overcoated too quickly. Under these circumstances, only the outer surface of the resin is able to release solvent or absorb oxygen, so it tends to dry with a layer of semi liquid material trapped underneath it. This effect is most often seen on horizontal areas like decks and cabin soles, where it is easy (and very tempting) to apply far too much material, but it can also occur where the coating runs to create small pools. In mild cases, the coating may appear inexplicably soft and easily damaged, but in severe cases wrinkling may occur as shown in the diagram. Fig. 3

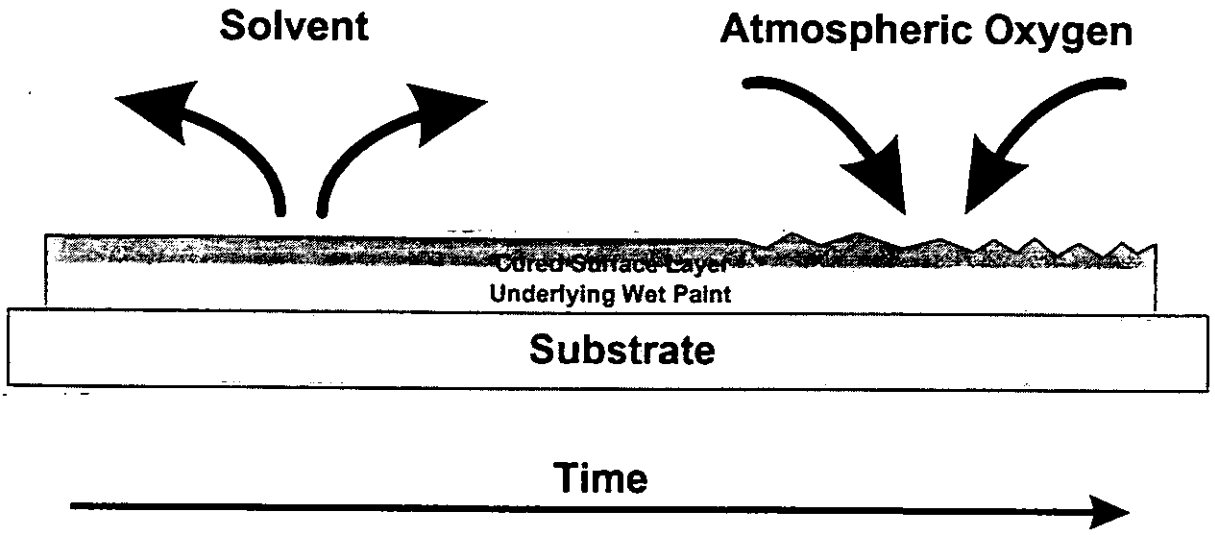


Fig 3: Diagram showing how Excessive Film Thickness can cause Drying Problems

(If conventional coatings are applied too thickly, only the outer surface will dry, trapping a layer of semi-liquid paint or varnish beneath it. As a rule of thumb, conventional paints and varnishes should be applied at no more than 100μM wet film thickness if this effect is to be avoided.)

Failure of conventional coatings to 'through dry' has become a common problem in recent years, owing to the removal of lead dryers from paints and varnishes. Although only used in tiny quantities, lead dryers were unsurpassed for promoting 'through drying', and have proved difficult to replace. Alternative dryers have been found, but it is worth noting that excessive application or premature overcoating are likely to cause difficulties, and should be avoided.

However, unlike most other drying mechanisms, the conventional drying process does not end when the coating has dried, but continues slowly throughout the life of the coating scheme. This results in gradual hardening of paint films, accompanied by gradual improvements in abrasion and chemical resistance which usually reach a peak after about four or five years. At this stage, many conventional paints are well enough cured to be overcoated with two component polyurethanes, and can be quite difficult to remove with chemical paint strippers.

Unfortunately, this drying process produces by-products which are thought to contribute to the eventual embrittlement and breakdown of the coating. One interesting consequence is that many conventional coatings tend to yellow more if they ***are not*** exposed to sunlight, eventually becoming quite dull and brown in dark areas like cabins and galleys. This is because ultra violet light breaks down the compounds responsible for yellowing, effectively 'bleaching' the coating, but as we have already seen, it does a lot of damage too. The dryers used to stimulate the drying process also tend to hasten this breakdown, so care is always taken to use only minimal amounts.

Conventional coatings will always play an important role in protecting marine structures, but the need for better durability has led to the development of many new resin systems which use entirely different technology to provide practical benefits and greatly extended service life. Coatings manufactured from these resins are invariably more difficult to apply than conventional materials, and are usually more expensive, but their outstanding performance is finding an ever increasing market within the marine industry.

Epoxies

Epoxy resins are applied to a substrate while in liquid form, where they are converted into a solid, densely cross linked polymer by chemical reaction. This reaction is entirely self contained, which allows epoxies to be applied at much higher film thicknesses than conventional coatings.

Like polyurethanes, epoxies cure to produce a rigid three dimensional molecular structure, with excellent mechanical and chemical properties; but while these two materials may appear outwardly similar, their chemistry and properties are quite different.

Epoxy polymer chains are comprised of only carbon-carbon and ether linkages, both of which are very stable; this gives epoxies their excellent chemical resistance, moisture barrier and electrical insulation properties. This combination of chemical and mechanical benefits, allied with good adhesive and penetrative qualities has made epoxies an ideal choice for marine anticorrosive primers, yacht profiling fillers and adhesives such as Araldite®.

Where appropriate, these properties can be further improved by adding 'lamellar' pigments like aluminium or mica flake for enhanced moisture barrier and anticorrosive properties. Epoxies can also be modified with coal tar to enhance their anticorrosive performance, although use in the yacht market has always been limited by their tendency to 'bleed' when overcoated with light coloured paints.

As would be expected, epoxies work well as underwater coatings, and most can also be used to protect substrates in demanding locations such as bilges, engine rooms and inside fuel tanks. Special epoxies are manufactured for potable water tanks, and are formulated to avoid the use of harmful raw materials like phenols which could contaminate or taint drinking water.

However, the epoxy materials of greatest interest to the paint chemist are the low molecular weight variants, which are far more reactive and lower in viscosity than high molecular weight types. Low molecular weight resins have the benefit of requiring less solvent addition, and as the reactive groups are more 'mobile' they can usually be cured at lower temperatures.

Low viscosity also allows versatility in formulation, allowing the manufacture of totally solvent free profiling fillers and laminating resins, as well as the solvent free high build coatings used for osmosis treatment and specialist wood coatings. But unfortunately these highly reactive materials are severely irritating to the skin, and are known to cause dermatitis and other serious disorders by repeated skin contact. Some of the lower molecular weight epoxies are also volatile, causing irritation to the skin, eyes and respiratory tract if applied in confined spaces without adequate ventilation. Amine curing agents pose the greatest risk, although most are now reacted with some base resin during manufacture to 'cross link' the most reactive (and harmful) groups, producing what is known as an amine adduct.

Nevertheless, whatever type of epoxy materials are being used, skin contact must be avoided, and all work carried out in well ventilated conditions.

Performance Limitations

Despite their outstanding chemical and physical properties, epoxies still suffer from a number of practical limitations.

The first is that epoxies have poor resistance to ultra violet light, becoming very drab and 'chalky' within just a few months of outdoor exposure. This is not a problem for underwater use or hidden areas, but where topsides and superstructures are being painted, it is customary

to use polyurethane undercoats and finishes to provide a lasting high gloss finish. Conventional enamels can also be used, but these tend to have poor adhesion to epoxies unless the surface is very well prepared, and also have comparatively poor mechanical properties.

Curing conditions are also important: It is not generally appreciated that epoxies need warm, dry curing conditions if they are to reach a full state of cure, and are to provide optimum protection. While many epoxies will cure satisfactorily at temperatures down to 7 or 8 °C (45 or 47 °F), essential reactive groups within the resin become immobile at lower temperatures, bringing the curing reaction to a halt. Unfortunately, subsequent heating even to quite high temperatures will not re-start the curing process, and it may be necessary to remove the affected coatings if they are badly undercured.

A further problem involves the tendency of some epoxies to form a thin, sticky layer of amine carbomate on their outer surfaces while curing. Better known as amine sweating or amine blushing, this phenomena is caused by migration of amine curing agent to the coating surface, where it reacts with atmospheric moisture and carbon dioxide. Amine carbomate is water soluble (forming an alkaline solution), and is likely to cause blistering and detachment if not removed before overcoating.

Solvent free coatings and fillers are most at risk from this problem, which is most likely to occur in cold, damp curing conditions where rate of cure is comparatively slow, giving the hygroscopic curing agent plenty of time to migrate. Warm, dry curing conditions help to minimise this tendency, and also improve curing.

Like polyurethanes, the solvents used in epoxies are rather more aggressive than ordinary white spirit, and are prone to softening conventional coatings. As a general rule, epoxies must not be applied over any coating which is unsuitable for underwater use; nor can they be used to protect or 'convert' an otherwise unsuitable coating scheme.

Polyurethanes

Most true polyurethanes are supplied as two separate components, comprising a polyol base component and an isocyanate curing agent which must be mixed together shortly before the paint is applied.. Once mixed, the two components react together to form a densely cross linked, three dimensional molecular structure, with outstanding resistance to ultraviolet degradation, mechanical damage and chemical attack.

The polyol base component is a type of polyester, which provides reactive hydroxyl (OH) sites with which the isocyanate curing agent can react. Polyols are manufactured from a wide range of raw materials, including some of those used to produce alkyd resins. The isocyanates are a family of nitrogen compounds existing in both aromatic and aliphatic forms, all containing the Nitrogen=Carbon=Oxygen (N=C=O) isocyanate group. Most early formulations were based upon the aromatic variant 'toluene diisocyanate', but were very prone to premature yellowing and loss of gloss, although it must be said that TDI did provide a good degree of versatility in formulation. However, health concerns and the need to improve outdoor durability have meant that nearly all polyurethanes are now cured with the less reactive (and more expensive) aliphatic compound hexamethylene diisocyanate.

In practical terms, polyurethanes will retain their finish for at least twice as long as conventional materials, and are far more resistant to the wear and tear of life on board. Polyurethanes also have excellent natural adhesion to well prepared gelcoats, and are an obvious choice when choosing a scheme to rejuvenate old and faded fibreglass boats. They

also work well when applied over epoxy anticorrosive schemes, although care is needed to avoid undercure caused by reaction with any residual solvent from the epoxy coatings. Moreover, their excellent resistance to heat and chemical attack makes them an ideal choice for the galley and cabin, where they can last for twenty years or more and still look as good as new.

Polyurethanes are, however, comparatively impermeable to moisture, which can cause problems on some timber substrates. Furthermore, while comparatively flexible in a bending sense, polyurethanes are not very elastic, and are usually considered unsuitable where movement or flexing is likely to occur. They are also more difficult to repair than conventional coatings, and so are less suitable in areas prone to mechanical damage.

Polyurethanes are ***comparatively*** tolerant to poor application conditions, and will cure reasonably well at temperatures down to 7 or 8 °C (45 or 47 °F), although their curing agents have a tendency to react with moisture in preference to the polyol base. This sometimes causes 'undercure' in cold or damp environments, leading to soft films, poor gloss, and in extreme cases, gas bubbling within the paint film.

This moisture sensitivity is put to good use in single component 'moisture cured' polyurethane wood primers such as Blakes Single Pack Polyurethane Varnish and International UCP.[3] Moisture cured primers work extremely well on bare timber, penetrating deep into the grain where they can react with moisture in the wood fibres. These primers are easy to use, but should be applied thinly to prevent clouding caused by the tiny bubbles of carbon dioxide gas evolved while curing. Overcoating intervals must also be strictly observed if problems with intercoat adhesion are to be avoided.

A similar approach is used in some fibreglass 'wash primers', which contain a small amount of isocyanate 'curing agent' dissolved into a much larger volume of solvent. These are applied thinly to the gelcoat, where the isocyanate reacts with free hydroxyl groups in the polyester to provide chemical adhesion. Fibreglass primers can work well as antifouling primers, but are unreliable for more demanding applications.

Some moisture cured undercoats and finishes are also available (notably from the Dutch company Sikkens), although manufacturing difficulties mean that these are unlikely to become mass market products.

Unfortunately, the solvents used in polyurethane coatings are more aggressive than white spirit, and are prone to softening and wrinkling conventional coatings. Nevertheless, 'aged' enamels can sometimes be overcoated to gain the cosmetic benefits of polyurethanes, although the mechanical properties of the scheme will only be as good as the weakest coat.

Performance Limitations

Two component polyurethanes provide excellent cosmetic and mechanical performance in a wide variety of applications, but there are inevitably some restrictions.

The main limitations are concerned with the moisture sensitivity of polyurethanes during cure, and can usually be avoided by painting in warm and dry conditions. Care must also be taken to avoid contaminating the paint components and thinners with moisture at all stages.

[3] US Equivalent = Interprime Wood Sealer Clear 1026

Polyurethane curing agents are especially prone to moisture absorption during storage, and must not be used if they have started to gel, or have discoloured beyond a pale straw shade.

Use of correct thinners in polyurethanes is also important: white spirit as used in conventional paints will cause flocculation or gelling, while epoxy thinners will cause undercure and possibly bubbling owing to their alcohol content. Likewise, adequate overcoating intervals must be allowed when applying polyurethane finishing schemes over epoxies, as any residual alcohol may adversely affect cure.

While a well cured polyurethane has an exceptionally hard surface, it must be remembered that the total film thickness of the finish is considerably less than that of a polyester gelcoat, and any repeated abrasion will quickly wear through the coating scheme. Fender wear is the most common problem here, and can be largely avoided by replacing old and dirty fenders. New fenders should be washed occasionally with warm soapy water to remove sticky surface deposits which attract sand and grit. The use of fender socks can also be found helpful.

Unfortunately, all polyurethane curing agents contain traces of free isocyanate monomer, a highly toxic material which can cause serious respiratory disorders if inhaled while spraying. To avoid this risk, full face air fed respirators ***must*** be worn when applying polyurethanes with a spraygun, and all other personnel evacuated from the area.

Brush application is, however, quite safe provided that adequate ventilation is provided and good working practices are observed.

Other Types of Resin

The resins that we have discussed so far are known as 'convertible' resins, because they undergo a permanent and irreversible chemical change on drying, and are not re-soluble in their original solvents. Convertible coatings work well if they are applied in good drying conditions, but their performance if applied under unfavourable conditions can be very poor.

These drawbacks can often be overcome by using a 'non-convertible' resin system, which dries solely by solvent evaporation, and does not need to undergo any permanent chemical change. These are sometimes known as 'lacquer drying' coatings. Cellulose paints are probably the best known example, although these have limited uses today apart from small car repairs, aerosol paints, and nail varnishes.

In marine practice, chlorinated rubber paints and vinyl tars are the most widely used examples, and can provide excellent anticorrosive and moisture barrier properties provided that an adequate film thickness is applied. However, the abrasion resistance of these coatings is poor, and being non convertible, they are readily re-dissolved by their own solvents or by spillage of oils and fuels.

Cellulose paints have largely been replaced by acrylics which provide much better performance, and can be used in both solvent and water borne formulations. However, pure acrylic coatings have found few applications in the marine industry, as their resistance to abrasion and long term water immersion is poor. A further drawback is that spray application and high temperature stoving is usually required to achieve a good cosmetic finish.

One useful variant is the acrylic polyurethane, (technically known as a hydroxyl branched acrylic), which is cross linked with isocyanate curing agents to enhance its mechanical and chemical properties. Examples like Awlgrip's Awlcraft 2000 and International's Interspray 800 are easy to apply by spray, and provide an exceptionally high gloss finish, but are unsuitable for brush application.

Most of the resins and coatings that we have discussed so far require significant additions of organic solvents during their manufacture, which then evaporate shortly after application. Apart from the high cost of these wasted materials, organic solvent emissions are very polluting, and are associated with photochemical smog and other environmental problems which afflict our towns and cities.

Solvents can also pose severe health and fire hazards, so maximum effort is now being put into formulating solvent free and reduced solvent coatings. Indeed, in many countries legislation has been introduced to limit the percentage of these 'Volatile Organic Compounds' (or VOC's), present in paints, leading to the development of so called 'VOC compliant' and 'high solids' coatings.

However, the ultimate goal is to eliminate organic solvents altogether wherever possible. Solvent free epoxies are now widely used for both industrial and marine applications, and a few solvent free polyurethanes are also available. Water borne coatings are also becoming highly developed, where resins containing only a minimal amount of solvent are dispersed into water as an 'emulsion' of tiny droplets. As the water evaporates, these droplets fuse together to form a continuous film which behaves in much the same way as usual solvent borne coatings. Where necessary, the resin system can also be isolated (or 'blocked') from its aqueous base, so allowing the use of resin systems that would not usually tolerate moisture.

Pigments and Extenders

Pigments play an essential role in the formulation of paint coatings. Apart from the obvious benefit of providing colour and opacity, pigments significantly improve the adhesion and film strength of coatings. Pigments also play an important role in primers, where they are used to inhibit corrosion and to provide a barrier against moisture and oxygen. However, as the primary use for pigments is to provide colour, we shall look first at how they work in this role:

Visible light is comprised of electromagnetic energy having wavelengths between 0.4 to 0.7μM. Violet light has the shortest wavelength at about 0.4μM, followed by blue, green yellow orange and red light, which has a wavelength of about 0.62μM. Wavelengths above and below these figures are not directly visible to the human eye, although they sometimes affect our perception of colours.

White pigments like titanium dioxide appear white because they reflect all colours (or wavelengths) of visible light more or less equally, while coloured pigments absorb light of some wavelengths while reflecting others, so all that we see is the reflected light. Black pigments absorb almost all visible light including infra red, which is why black surfaces become very hot in direct sunlight.

Up until the late 1970's, lead and cadmium pigments were popular for their bright, strong colours and good resistance to fading, but these have now been replaced almost universally with organic pigments which are much safer in use. The opacity of these organic pigments is often poor, although they now have much better UV resistance (or lightfastness) than some early examples. Some organic pigments (notably toluidine red) are also quite soluble in organic solvents, and tend to bleed into lighter colours applied over them: this poses a particular problem when used in antifoulings. Other notable organic pigments include the phthalocyanine (or 'Monastral') blues and greens with their characteristically strong, clean colours, which are widely used for tinting, and to produce deep shades like Oxford Blue and British Racing Green.

Where more subtle colorants are required, red or black iron oxides and yellow ochres are often used, either in their naturally occurring form, or (more commonly now) synthetically manufactured. These do not have the clean colours or high tinting strengths of organic pigments, but they do provide much better opacity.

These are just a few examples, but in all there are literally hundreds of pigments available to the paint chemist, each having its own particular benefits, be it of colour, tinting strength, opacity, lightfastness, cost or availability. In practice, it is usually possible to manufacture any one colour with many different pigment combinations, but this often leads to problems when trying to match existing shades owing to an effect known as 'Metamerism'. Where this occurs, paints may appear to match perfectly under one light source (i.e. daylight), but will appear markedly different under other lighting conditions. This creates a particular problem when trying to colour match one manufacturers shade with another, or when trying to replicate the shade of polyester gelcoats.

Fluorescent pigments are also worthy of mention because they convert ultra violet light that we cannot see into visible light, which is why they appear to 'fluoresce' or 'light up'. Unfortunately, the chemical structure of many pigments (especially organics) is prone to being broken-down by ultra violet light, bringing about a permanent change in colour. This effect is better known as fading, and can be minimised by binding the pigment with a suitable

resin, and by adding ultra violet inhibitors to absorb the harmful rays before they do too much damage.

The ratio of pigment to binder in the dried paint (known as the 'Pigment Volume Concentration') is also significant, and plays an important part in determining qualities like gloss, opacity and weather resistance. Paints with high PVC's are popular in the domestic market for their good opacity and ease of application, although their gloss levels and weather resistance may be comparatively poor. Undercoats usually have the highest PVC's for optimum obliteration and sanding properties, and could almost be regarded as 'underbound'.

Yacht finishes tend to have quite low PVC's, with more than adequate resin to completely surround each pigment particle. This sometimes means that several coats are required to achieve complete obliteration of the underlying colour, although gloss and weather resistance is much improved as a consequence.

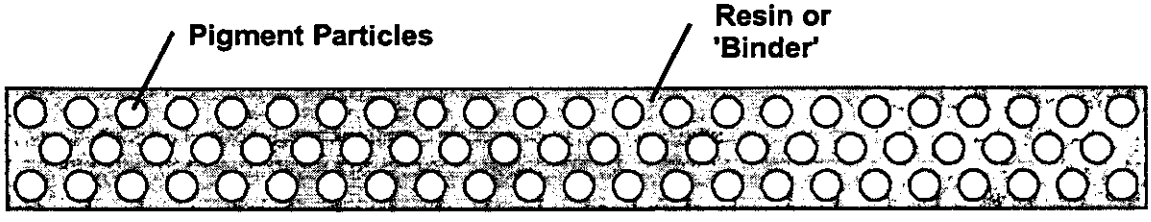


Fig 4. Cross Section of a Well Bound Paint Coating, showing how pigment particles are completely surrounded by resin.

The use of pigments in primers is particularly interesting: Many primers formulated for metal substrates contain metallic pigments such as powdered zinc or aluminium flake, which provide some sacrificial protection in the event of mechanical damage. Others contain pigments such as red iron oxide or zinc chromate, which provide good anticorrosive properties even when they are applied in thin films (as in holding primers).

Pigments with leaf or flake like structures are particularly useful in primers, where they overlap like roof tiles to form an effective barrier against both moisture and oxygen. These 'leafing' or 'lamellar' pigments are also used in 'barrier coats' to reduce the absorption of aggressive solvents, and to reduce unsightly bleeding from coal tar coatings. Less obviously, the rather rough or granular surface finish produced by leafing pigments also helps to improve intercoat adhesion, a property which is put to good use in some antifouling 'tie coats'. In marine coatings, aluminium and mica flake are the most popular lamellar pigments, but some heavy duty epoxy tank coatings use glass flake pigments to protect against exceptionally aggressive cargoes.

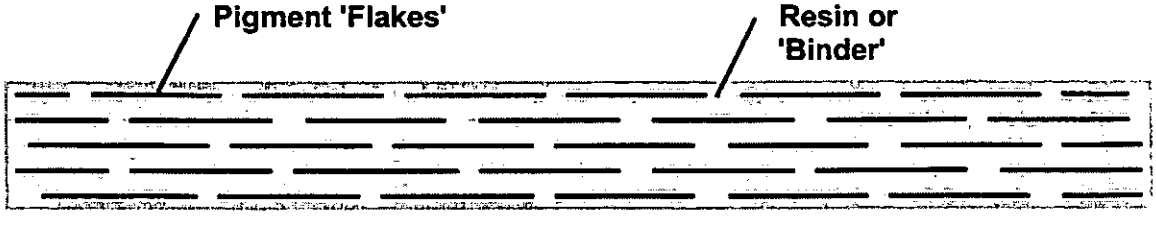


Fig 5: Diagram showing how Leafing or Lamellar Pigments improve the Barrier Properties of coatings

So far we have discussed pigments which are used to provide colour, inhibit corrosion or provide barrier like properties. However, there is another group of pigments known as 'extenders' which do not fit into any of these categories, but which nevertheless play an important role in coating formulation.

Many pigments would provide limited opacity (or hiding power) if used by themselves, and would be expensive if used in sufficient quantities to achieve complete obliteration. By using an extender like barytes (barium sulphate) or china clay, much smaller quantities of colouring pigment are needed, while opacity is improved. The largest quantities of extenders are used in undercoats, where long term colour retention is not too important, but good opacity and ease of sanding is essential.

Another useful group of extenders are the thixotropes like silica powders and bentone clays, which are used to modify the 'body' and 'feel' of coatings. Small quantities of thixotropes are commonly used to improve application qualities and film build, and to help prevent settlement of pigments during storage. Larger quantities are used in the manufacture of non drip paints, and in high build epoxy primers where wet film thicknesses of 300μ (0.012") or more can be achieved without the risk of sagging.

Silica powders can also be used as 'matting agents' to reduce the gloss levels of varnishes and paint finishes.

A rather different type of extender is used in the low density profiling fillers used for filling and fairing yachts: the density of these fillers is all important, so a large amount of their volume is taken up by glass or polypropylene 'micro balloons' which being hollow are very light in weight. Apart from minimising the total mass of the filled yacht, the very low density of these fillers allows application thicknesses of 2 cm (¾ inch) or more with little risk of the filler slumping under its own weight.

Solvents, Diluents and Thinners

In terms of paint formulation, solvents could be described as something of a necessary evil: they are expensive, they pose fire and health hazards, and are associated with photochemical smog and other environmental problems. Nevertheless, without solvents, the manufacture and application of many paints could never take place.

Most of the resins used to make paints and varnishes are supplied either as very viscous, syrupy fluids, or as solids. These must be dissolved in solvents to reduce their viscosity so that pigments and extenders can be incorporated, and so that paint can be processed and filled into tins.

Once the paint has been manufactured, further solvent is often added by the end user in the form of a thinner or reducer, to adjust viscosity to suit the application method and conditions. By this stage, 75 or 80% of the applied paint may be solvent, with only 20 or 25% actual paint solids remaining.

As with pigments, there is a wide range of solvents available to the paint chemist, most of which are either extracted from crude oil, or less commonly now, from coal and wood processes. Solvents are classified by their chemical type (i.e. aromatic hydrocarbons, esters, ketones and alcohols), and also by their evaporation rates.

There would be little point in examining the significance of the different chemical types here, except to say that solvents are chosen for their ability to dissolve certain types of resin, and

are therefore specific to certain types of coating. These are known as 'true solvents' because a specified resin is infinitely soluble in them.

If a solvent of the wrong chemical type is used, the paint may gel, and could even fail to cure properly. Interestingly though, many resins will tolerate limited amounts of an incompatible solvent, provided that a sufficient quantity of true solvent is also present. Solvents that can be used for thinning, but which are not 'true solvents' are known as 'diluents', and often provide better application characteristics than true solvents used alone.

Diluents are widely used in spray thinners for two pack polyurethanes where a large degree of viscosity reduction is required, although care is needed in formulation to ensure that the diluent always evaporates before the true solvent. Likewise, some epoxies require separate thinners and equipment cleaners, because the thinner contains a large amount of diluent, and can only be tolerated in limited quantities.

The rate of solvent evaporation has a significant effect on application properties, and is an important factor in coating formulation. Spray thinners typically contain a mixture of five or six different solvents, the most volatile of which are used to help spray atomisation, although these usually evaporate before they reach the surface being painted. The slower evaporating solvents are used to promote flow, levelling and wet edge, and may take several hours (or even days) to completely evaporate. Unfortunately, volatile solvents absorb a great deal of heat as they evaporate, effectively refrigerating the applied paint. This tends to encourage moisture condensation when spraying in humid conditions, and may result in dulling or loss of gloss.

Much slower evaporating solvents are used in brushing thinners, and in high temperature or 'tropical' spray thinners where flow and wet edge properties are important: indeed, it is often possible to use a compatible brush thinner to 'slow down' a spray product in hot weather, although it is always best to check with the manufacturer first.

Additives

While additives account for only 3 or 4% of a paint or varnish, they play a vital role in making it work.

Some of the most important additives are the 'dryers' used in conventional coatings to promote absorption of oxygen from the atmosphere. The actual quantity of dryers used varies from batch to batch, and is usually determined from drying tests carried out in the Quality Assurance laboratory using a Drying Track Recorder. Excessive additions of dryers must be avoided, as they accelerate film ageing and promote solvent entrapment.

Similar additives are used to adjust the rate of cure and pot lives of two component polyurethanes, while the rate of cure of epoxies is usually inherent in their formulation, and can only be slightly altered by additives.

Ultra Violet absorbers are used in some coatings to absorb harmful UV rays before they can damage chemical bonds in resin system to cause loss of gloss and chalking. Other additives can include silica matting agents to provide a satin finish, anti skinning agents, flow and wetting agents, and special additives to help overcome manufacturing problems.

A limited number of these additives are made available to end users, usually to accelerate drying, or to overcome application problems such as 'cissing'. While some of these can prove useful in overcoming specific problems, it must be stressed that paint formulation is a very complex subject, and that no single additive can ever cure all ills. The use of silicone anti

cissing agents in particular demands extreme caution, for while small amounts can help to prevent cissing, excessive use will actually promote it. Moreover, any subsequent coats are even more likely to ciss, and their adhesion will be reduced.

Paint Manufacture

When the work of formulation and testing has been completed, our paint is finally ready to be manufactured. The first stage in this process is to dissolve the resin into solvent to make what is basically a simple varnish, which may take several hours. The pigments and extenders are then stirred into a portion of the resin solution to make a slurry called a 'mill base' or 'grind charge' ready for the dispersion or 'grinding' stage.

The dispersion process itself is one of the most important stages in the whole manufacturing process, and plays a significant part in the quality and appearance of the applied paint. Paints made with well dispersed pigments provide far better colour and obliteration than poorly dispersed examples, and also have better gloss. The traditional ways of doing this was to put the slurry into a 'ball mill', which is simply a very large steel drum lined with porcelain (or steatite), and part filled with porcelain balls. As the drum is rotated, the balls rise up one side of the drum, and then cascade down the other side (rather like a large washing machine), dividing the pigment into smaller and smaller particles. The dispersion process continues for sixteen hours or so, until the pigment particles have been reduced to a size of (typically) less than five microns when measured with a 'Grind Gauge'.

Ball Milling has now largely been superseded by faster methods such as horizontal bead milling and high speed dispersion, although the principles are much the same.

With the pigments dispersed, the slurry is 'let down' with the remainder of resin and solvent, and transferred to a large mixing tank. The batch is then tinted to the specified shade using concentrated pigment dispersions before samples are taken to the Quality Assurance Laboratory for batch testing.

Using these samples, test additions of solvent and additives like dryers are made to determine how much of each should be added to the batch to achieve correct viscosity and drying times. The sample is also tested for specific gravity to confirm that all ingredients have been added, and is applied to a piece of tinplate, glass, or special black and white test cards to check for correct colour, gloss, opacity and freedom from flocculation. Depending on the product, there may be other special tests, but it will be seen that nothing is left to chance.

When these tests have been completed, the batch is finally approved for filling off into tins, using special filters to remove any foreign matter. Final samples are also taken, and will be retained until there is little likelihood of the product remaining on chandlers shelves.

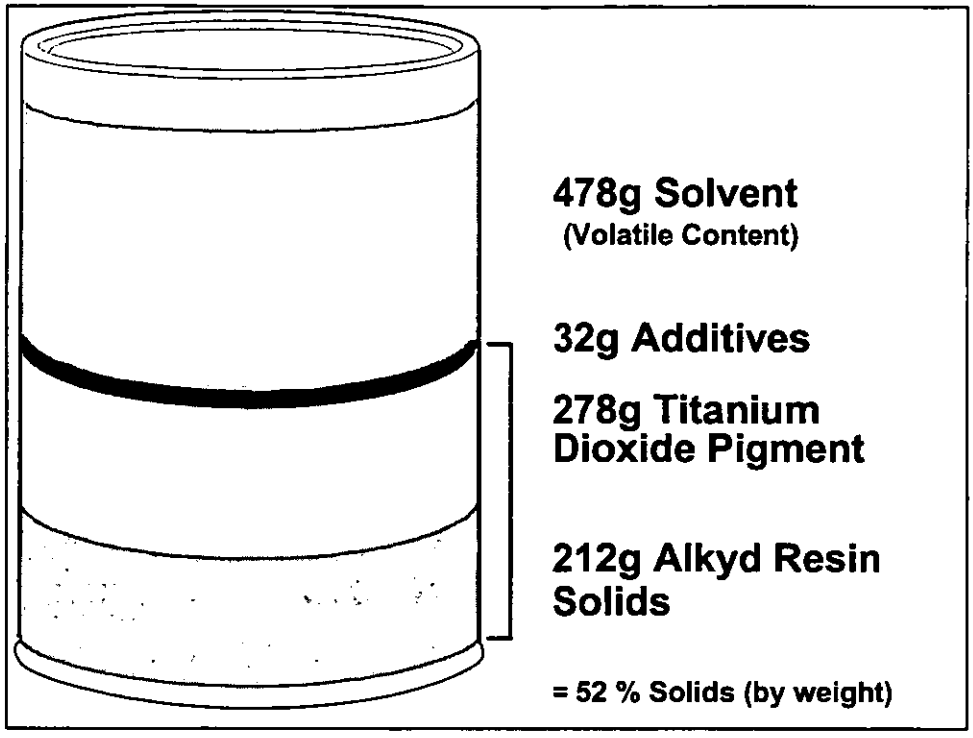


Fig 6. Constituents of a Typical 750 Ml Can of White Enamel

Chapter 7

Past, Present and Prospects of Antifouling

Dr Volker Bertram

Past, Present and Prospects of Antifouling

Volker Bertram, HSVA, Bramfelder Str 164, D 22305 Hamburg, bertram@hsva.de

Abstract

A survey of antifouling approaches in history is given. Sheathing and various paints have been widely used in the past, but also electricity, steam, and even radioactivity have been proposed. Self polishing past.TBT paints were thought to be the final answer to the antifouling problem, but then found to contaminate the environment, poisoning marine life including fish. With the coming ban on TBT paints, some historical concepts are revived in research. Copper-based paints may also face bans in the future. Other alternatives include low surface energy paints, possibly in combination with cleaning robots, and biological paints or electro-conductive paints.

Fouling

Fouling is the undesirable growth of organisms on artificial structures immersed in seawater, Figs.1 and 2. The most visible form of such fouling are barnacles and seaweed which degrade the performance of ships considerably. Like all other transport trades, shipping lines also try to minimise fuel consumption. World-wide, 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 130 μm. However, is drastically increased by fouling. The process of fouling can be divided into four stages, Davis and Williamson (1995), Fig.3:

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 uni-cellular organisms then sense the surface and settle on it, forming a microbial biofilm. 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, Conn et al. (1953).
   - 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 biofilm to a more complex community that typically includesmulticellular 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 decreases the ship's performance sometimes drastically. Collatz (1984) reports 20% increase in frictional resistance (i.e. about 15% in total resistance) for a 150m long 15kn ship. Gitlitz (1980) illustrates the economical impact of these numbers: "To give you some idea of the economic cost of fouling let us take the example of a VLCC operating at 15 knots. It consumes fuel at the rate of 170 tons per day. For a 300 day operational year the fuel cost (at $ 80/ton) amounts to over 4 million U.S. dollar. Moderate fouling can easily increase the fuel required to maintain speed by 30% or over 1 million dollar!"

Fouling is not just an economical factor for ship operators, it is also an unacceptable waste of natural resources. Antifouling, the prevention of marine growth on ships, is thus both an economical and ecological necessity.



Fig.1: Fouling (green algae), source: Dr ME Callow

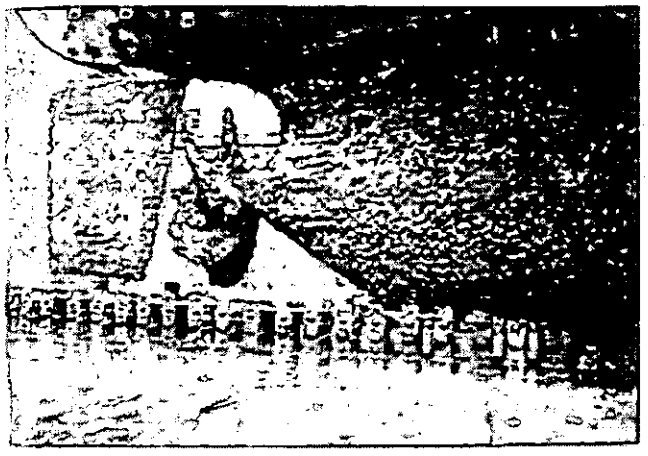


Fig.2: Massive shell fouling, Clare (1995)

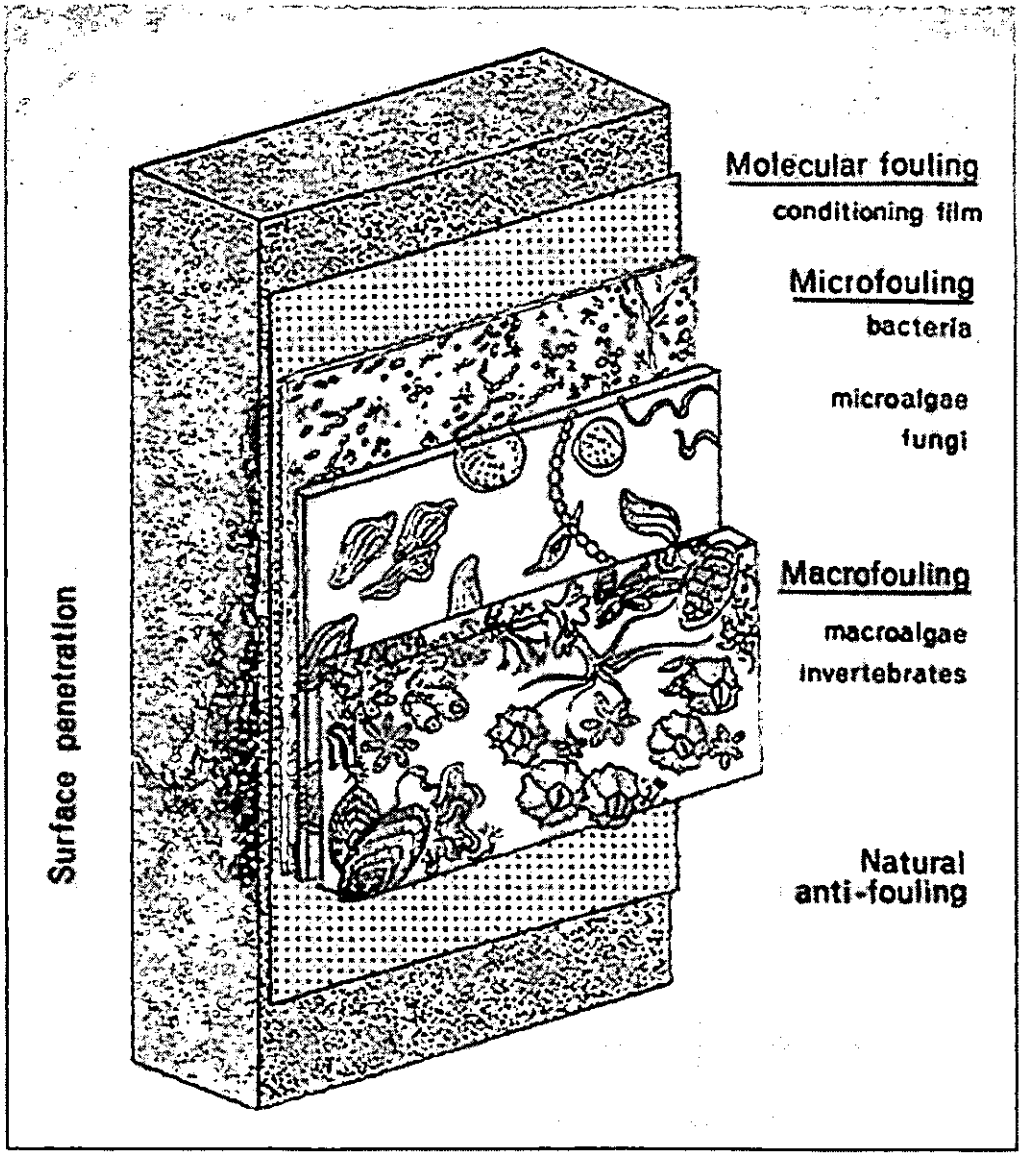


Fig.3: The four main stages of marine fouling, Davis and Williamson (1995)

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 1960's 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" in the early 80's 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.

However, 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 waters 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, e.g. Isensee et al. (1994). These concerns prompted world-wide regulations restricting the use of organotin antifoulants. Today researchers look for alternatives: new paints with better safety performance or altogether different approaches to antifouling.

Fig.4 surveys the historical development of antifouling methods to be discussed in more detail in the following chapters.

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 copolymer antifoulant)
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 - ???

Fig.4: Historical change of fouling control

2.1. Sheathing

The history of (metallic) sheathing for fouling protections dates back to ancient times. In the third century BC, Greeks nailed lead plates on ships with copper nails. This lead sheathing was used in England, France, and Spain up to the 18th century. Charles II of England (1660-1685) is reported to have the royal barge protected by this technique. But the antifouling effect was not so good. With the advent of iron rudders, corrosion became a problem and in 1652 the British navy stopped using lead sheathing. From the 15th to 18th century, wooden sheathing was widely used. This technique paints wooden panels with tar, grease, oil, sulphur, or mixtures of these products and then nails the panels on the ship hull. But the most successful technique remained copper sheathing. The first documented formal validation of the antifouling effectiveness of copper sheathing was a test on the English frigate ALARM in 1758. But problems with corrosion persisted. In 1824, the British chemist H. Davy proved that zinc, tin, and iron corroded in the presence of copper sheathing. He tried anodic protection on the British navy vessel SAMRANG to overcome this problem. These experiments were probably the first applications of anodic protection against corrosion.

With the advent of steel ships, both fouling and corrosion problems had to be overcome. In the middle of the 19th century, the British navy researched extensively for antifouling alternatives. Anodic protection techniques in combination with copper sheathing were pursued but remained in an experimental stage. In a frantic search for a solution of the antifouling problem, such obscure materials as felt, canvas, rubber, ebonite, cork, cement, and paper (!) were tried, but found to be ineffective. The rapidly increasing demand for steel ships in the second half of the 19th century ended the era of metallic sheathing and the era of antifouling paints started.

The 1980's saw a renaissance of research for the sheathing approach. Japanese researchers investigated covering the hull with a copper alloy with a target durability of over five years. Copper was unsuited with respect to corrosion, 90/10 Cu-Ni alloys with respect to antifouling effectiveness. Eventually, a Cu-Mn alloy was developed and tested on a large ship navigating the Pacific Ocean and a 40gt ferry in Nagasaki Port. The ocean liner confirmed satisfactory antifouling performance, but the ferry boat showed barnacle growth after six months. The US Maritime Administration, Arco Marine Inc. and the Copper Development Association Inc. tested copper alloy coating on the "Arco Texas" (VLCC) and reported similar effectiveness, Anon. (1982b). More recently Nakao (1995) reports of Japanese tests with copper-beryllium alloys showing improved results over Cu-Ni alloys. This approach seems to be promising in terms of effectiveness, but high installation costs make it unattractive at present. Further research into production technology is required before a practical alternative to paint can emerge from this approach.

2.2. Antifouling paints

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 McInness used copper sulphate as antifoulant in a metallic soap composition. This 'hot plastic paint' was very similar to the 'ItalianMoravian' paint (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 the paint was expensive and its 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 mid-1950's, Van der Kerk and co-workers discovered the broad biocidal properties of tributyl compounds. In 1958 Juan Montermoso and co-workers were given the first US patent for organotin acrylic polymers. In the early 1960's the antifouling properties of tributyltin (TBT) started to be commercialised. 1/10th to 1/20th the amount of organotin as compared to copper was required for full algae and barnacle control. 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' in the early 1980's because these systems could provide up to 5 years fouling-free performance. However, concerns about their effect on marine life grew as marine biologists proved in research alarming damage in areas with dense ship traffic. This resulted in the 1990's in regulations restricting the use of TBT paints. By 2008, TBT paints shall be banned altogether.

Antifouling paint releases in contact with seawater biocides which form a toxic boundary layer preventing marine growth. A certain concentration of these antifoulants has to be maintained for effective protection. As toxicants are washed away by convection, the paint has to re-supply the protective boundary layer with new toxicants. According to this leaching mechanism, paint may be classified into soluble (self-polishing) and insoluble matrix (contact) paints. Further classification according to the leaching mechanism of self-polishing paints is possible (depletion type, hydration type, hydrolysis type).

The older contact-type paints consisted of a main matrix of vinyl or rosin with mainly copper oxide as antifoulant. Seawater penetrates the paint film as antifoulant dissolves leaving a honeycomb structure. This increases surface roughness and thus resistance. It also yields an exponentially decaying leaching rate, releasing far more toxicant than necessary in the beginning and dropping below the minimum effective level long before all toxicants in the paint have been released. After about one year, ship performance usually dropped drastically making a dry-dock interval necessary for re-painting.

Self-polishing paints consisted of rosin, oleo-rosin, and today mainly acrylic polymers with copper or organotin compounds as main antifoulants. These paints dissolve slowly in seawater exposing particles of antifoulant. As the whole film dissolves, the surface remains smooth (= self-polishing) and an almost constant leaching rate is obtained. Various self-polishing paints have been developed tailored to ship types, speed, and operation area. Self-polishing paints allowed up to 4-5 years between dry-dock times. Tin-free paints are usually copper-based. The performance of tin-free paints is not yet the same as of TBT paints. Tin-free paints require much higher leaching rates of copper than TBT or tin-copper based paints. Therefore, usually more paint is required, and even then the paints are not 100% effective, Nakao (1995). But paint makers are active to improve this situation.

2.3. Other antifouling methods

Many alternatives to antifouling paints were proposed and patented between the middle of last century and this century. But all were found unpractical. In 1863 a "poison leaching patent" was awarded to a system that distributed a toxic mixture of sulphur, resin, and fish-oil through pipes from the ship. In the 20th century,

some patents proposed (chlorous or other) gas insertion at the keel. Also the use of steam from steam engines was proposed as antifouling measure.

In 1862 mechanical patents proposed scrubbing of the hull by rotating knives. This proposal can be seen as a forefather to present ideas using robot technology for mechanical cleaning of hulls.

In 1891 T. Edison patented his ideas for a DC (direct current) antifouling system. (Edison was heavily opposed to using AC (alternating current) as he deemed it irresponsibly dangerous for humans. To prove his point, he developed the electric chair. However, the efficiency of AC eventually decided the sometimes very emotional AC/DC dispute.) In 1911 the first AC system was patented. But to prevent barnacle growth, very strong currents were needed making the system uneconomical. In 1907 J. Schoenberger obtained a US patent for electric protection of the ship hull (or sheathing for wooden ships) by forming a boundary layer of antifoulant gases through electrolysis "to protect the hull making paint obsolete". In the 1960's, these ideas were revived, Yoshii et al. (1967), Kimura et al. (1971). Seawater was electrolysed directly to generate biocidal Cl_2 and ClO^-. A direct approach installed electrodes longitudinally on the ship's bottom plates. The active components generated at these electrodes were supposed to diffuse over the hull. An indirect approach installed an electrolytic tank in the ship. Then active components were ejected and diffused on the hull. In both approaches, however, efficient and uniform dispersion of the active components proved to be difficult preventing eventually practical use.

In the 1960's, ultrasonic antifouling methods were investigated in Norway, England, and Japan. Mori et al. (1969) attached a nickel oscillator to the hull and showed good antifouling effects by oscillating at 27Hz and 28Hz for a vibration acceleration level of more than 200G. However, to create oscillations over 200G on the entire hull surface required too many oscillators and too much energy and the project was finally abandoned. In the mid-1980's a Hydrosonic Hull Tender was tested by the US Coast Guard, Anon. (1982a). Again, it was reported effective but unpractical and not further pursued.

In the early 1970's, Japanese shipyards tried lining the ship hull with neoprene rubber sheet of several millimetre thickness containing a small percentage of organotin compounds, but the difficult lining and renewal job made this method unpractical. Other proposals included heating of the ship hull, radio-activity (technetium-99 coating), and 'biological warfare' (barnacle cement enzyme). Some of these approaches are discussed again today as TBT paints did not live up to the expectations of the early 1970's to be the final answer for the antifouling problem.

3. Future antifouling systems

Today, almost exclusively antifouling paints are used that prevent fouling by killing (microbial) sea life. The short-term solution to the TBT paint restrictions is using copper-based paints. Some of the currently favoured copper-based paints have added herbicides such as triazine. However, like TBT, copper-based antifouling agents work by poisoning the unwanted organisms, so biologists fear that they too could cause environmental problems. The use of copper-based coatings is still allowed, but the US Environmental Protection Agency and the European Union have begun to review their effects.

If we want to develop low or non-toxic antifouling systems, we have to understand biochemistry of marine micro-organisms and mechanics of initial adhesion better. Basic research topics for possible future antifouling applications include:

1. Bio-chemistry
   a) Inhibition of biosynthesis of protein and polysaccharides
   b) Application of hormone, antibiotics
   c) Change of pH and temperature of sea water
2. Surface chemistry and physics
   a) Low surface-energy materials
   b) Surfactant
   c) Surface electrical charge and potential
   d) Electric conductivity

3.1. Biological paints

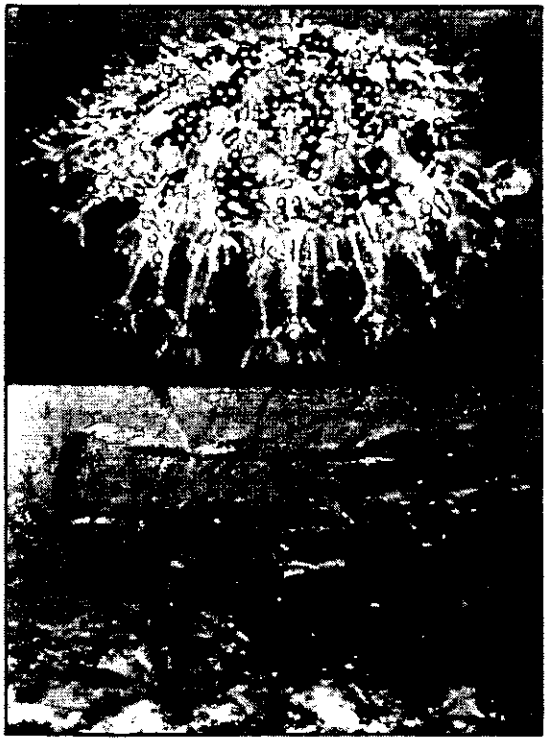
In gardening, ecological methods to repel parasites enjoy a renaissance. Certain plants are known to repel certain parasites and a proper mixture of plants in a garden may reduce if not eliminate the use of pesticides. Marine biologists discovered that also barnacles and other marine organisms contributing to fouling are also repelled by certain plants and natural products. Some of the proposed antifoulants remind of the concoctions of last century's 'miracle patent paints'. For example, Japanese researchers found that a mixture of horseradish, eucalyptus oil, and green tea repels sea life. One is tempted to add: 'not only sea life'. The American answer is a paint involving hot pepper and tabasco which was found to deter certain marine organisms. On a more scientific basis, research on the actual mechanisms of repulsion and chemical agents used by the repelling plants and animals is active, but at an early stage. Antifouling paints using similar mechanisms as the human body (mouth and blood system have natural antifouling protection) have been proposed, but not realised, Goupil et al.

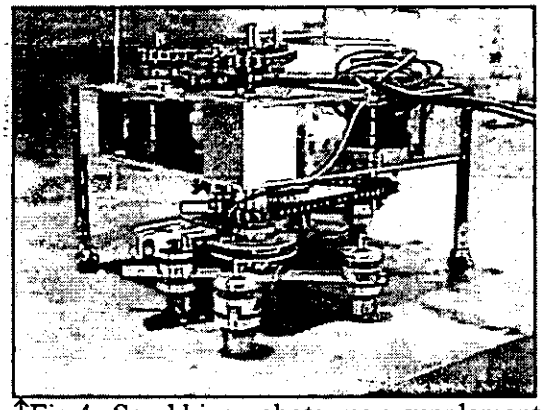
Clare (1995) gives a good overview of research into biological antifoulants for ships summarised in the following. An array of sea creatures point the way to natural antifouling agents, repelling marine organisms without causing widespread harm. Many aquatic animals, especially those that attach themselves to the bottom of the sea, run the risk of being swamped by the same organisms that foul ships, so they have evolved strategies to beat off these enemies. In laboratories around the world, these creatures are analysed. Their cells and tissues contain a multitude of compounds which could function as antifouling agents. Extraction techniques are straightforward. Step one is to grind up the tissue and apply a series of solvents to soak up and separate fractions containing different chemical ingredients. Next, these chemicals are separated with standard techniques that separate molecules according to their size and chemical structure. At each stage, the fractions are tested to see whether they prevent fouling organisms like barnacle larvae, algal spores and bacteria from settling on the surface of a laboratory dish.

A wealth of potential antifoulants has already been obtained from sea creatures such as corals. In the early 1980s, researchers at Duke University Marine Laboratory in North Carolina isolated several substances with antifouling properties from corals and a species of sea pansy. All these natural products prevented barnacle larvae settling on laboratory dishes at concentrations which were four to five orders of magnitude lower than the dose needed to kill them. The sea grasses have also thrown up some potential antifouling compounds. In the early 1990s, researchers at the Hopkins Marine Station found in laboratory tests that a crude extract of a certain eelgrass prevented settlement of some marine bacteria, algae, barnacles and tube worms. All the evidence suggested that the vital ingredient was an aromatic compound known as zosteric acid. This compound does not fend off all biofouling organisms, but it has shown some promise in short-term field tests against hard fouling organisms such as barnacles and tube worms. The bryozoans that encrust rocks and seaweeds have also yielded antifouling compounds which are only one-tenth as toxic as TBT, but is six to eight times as potent when it comes to inhibiting the settlement of larvae. Even bacteria and algae, usually thought of as fouling organisms themselves, are yielding antifouling compounds. Bacteria have been studied since 1993 by researchers at the University of New South Wales in Sydney. Bacteria isolated from the surface of a sea squirt have proved especially promising, having yielded three active components. Two of these, a protein and a low molecular weight compound, are stable. These substances could eventually prove highly profitable. Bacteria are generally easy to culture, and extracting the active compounds has been straightforward. Genetically engineering the bacteria to yield more of the active compound, or a more active variant, could also be an option in the future. The small molecule is toxic, but the protein seems to inhibit the settlement of barnacles, sea squirts and spores of a seaweed by some non-toxic means. The mechanisms how some compounds repel without being toxic are not yet understood.

Patents have been filed for some of the compounds and work on formulating coatings for field tests has started. However, the natural compounds are still some way away from being a practical alternative. It may take another decade before copper-based coatings can be replaced. Isolating promising compounds is just the first step. Before a compound can replace the toxic concoctions in use today, it will have to be shown to be effective for a wide range of fouling organisms. World-wide, over 400 marine organisms are important in

causing fouling problems. The compounds found so far deter only a fraction of these. It will also have to be safe. Some of the natural products may turn out to be too toxic, requiring official registration. In the US,any product that prevents biofouling is classed as a pesticide by the Environmental Protection Agency and the same goes for its counterparts in most other Western countries. For the US alone, registration is likely to take three years or more and cost over $1 million. Once a suitable compound has been identified and approved, it will have to be engineered to make a coating that stays active for several years. Then it will be up to the chemists or microbiologists to find ways of producing it in commercial quantities. The world fleet requires large quantities of antifouling paint. Industrial methods to produce and apply biological repellents have yet to be developed. No one would seriously contemplate the alternative, which would be to dredge up tonnes of exotic sea creatures and extract the active agent from them.





↑Fig.4: Scrubbing robots may supplement LSE coatings, Univ. of Hiroshima robot

← Fig.5: Sea pansies and eelgrass contain natural antifoulants, Clare (1995)

3.2. Low-surface energy paints and robots

Fouling may be prevented basically by making adhesion of slime mechanically difficult. Such "non-stick" coatings are called low surface energy (LSE) coatings. Fouling is simply swept away if the relative velocity between surface and water is sufficient. Even if fouling is not completely prevented, LSE coatings make the surfaces easier to clean, e.g. by wiping or low-pressure rinsing. The LSE coatings developed so far are mostly based on fluorinated silicone elastomeric polymers. LSE coatings contain no biocides and remain active as long as the coating remains undamaged.

They have been widely used for inlet pipes of power plants. There are also prototype applications on submarines and sport boats. On fast-moving boats, they can be self-cleaning, but on slower ships cleaning is necessary. LSE coatings may then be combined with scrubbing robots or remote operating scrubbing vehicles. Such scrubbing robots are under development at the University of Newcastle, the Technical University of Hamburg-Harburg, and the University of Hiroshima. A remote operating vehicle for scrubbing is under development in the USA, Zoccola (1998).

The coatings are so far relatively soft, but research is active to develop tougher surfaces. E.g. the US Office of Naval Research is spending 4 million dollar per year on its antifouling programme, which is focused on the search for a tougher non-stick coating, Clare (1995). So far cost is also a problem, as LSE paints are typically five to ten times more expensive than other antifouling coatings.

3.3. Electro-conductive paints

Since the early 1990's, Mitsubishi Heavy Industries has developed a practical electrical antifouling system named MAGPET, Nishi et al. (1992), Usami (1995), Bertram (1996). The system is briefly described in the following. Sea water contains various salts, but predominantly NaCl. In a hydrolysis water is decomposed into hydrogen and OH^- ions. The OH^- ions react with the Cl^- ions forming ClO^- ions which are well known as antifouling agents. The actual process in sea water is somewhat more complicated, but can be approximated by:

Anodic reaction

$2\ Cl^- \rightarrow Cl_2 + 2e$

$OH^- \rightarrow O_2 + 2\ H_2O + 4e$

$Cl^- + 2\ OH^- \rightarrow ClO^- + H_2O + 2e$

Cathodic reaction

$2\ H_2O + 2e \rightarrow 2\ OH^- + H_2$

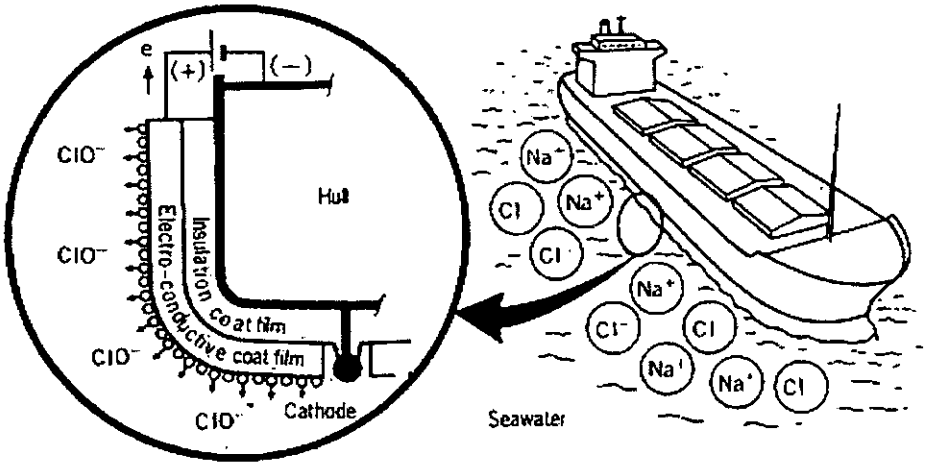


Fig.6: Principle of electro-conductive paint system MAGPET

The water contact surface of the hull shell plating is coated with an electro-conductive paint film. A small current is passed through the paint film attracting hyperchlorous ions. This prevents adhesion of marine growth such as micro-organisms, algae, and seashells. The hyperchlorous ions form only a thin layer (50 to 100 µm). 0.05 ClO^- ppm suffice. The ions disappear as they depart from the hull reacting with other components in the seawater. Thus, there is no contamination of the seawater. The required current is very weak and in a similar order of magnitude as current for anodic corrosion protection. Thus it does not affect humans or ship electronics. The current is approximately 0.1...0.2 A/m^2. The paint serves as anode. Port and starboard side are used alternatingly as anode and cathode. Field tests showed that marine fouling commencing after 3 hours without protection. Thus a typical frequency for alternating sides is 2 hours. The coating needs to be highly conductive, yet highly resistant to oxidation. The MAGPET system uses a three-layer coating to achieve this:

1. The first coating is an insulating coating based on some epoxy compound. It prevents energy losses into the steel structure of the ship.
2. A highly conductive coating based on carbon-acrylic resin paint. Between this coating and the first coating titanium foils (10 cm wide, 50-100 µm thick) increase further the conductivity.
3. Outer protective coating based on a carbon-vinylchloride resin paint. This coating is somewhat electrically conductive, but resistant to the aggressive ClO^- ions and prevents thus oxidation.

As in this technology no (poisonous) particles are leached into the seawater, the coating remains smooth and saves thus more fuel than conventional TBT coatings. Since 1994, several medium-size and large ships have been equipped with this system and have been operating successfully, Usami (1995). The system has also been applied to the inlets of a power plant in Japan, Usami and Kitamura (1998). It remains to be seen if the technology will live up to the claims of its developers.

4. Concluding remarks

Antifouling methods for ships date back to ancient times, but still we are striving for a solution that satisfies all aspects of easy application, durability, effectiveness, and minimum ecological impact. Creativity, interdisciplinary co-operation, and a lot more research will be required before we might be able to find this 'final answer' to the ship antifouling dilemma. It is encouraging to see both a growing awareness of the problem and first steps which could lead eventually towards the desired goal.

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Chapter 8

Anti Fouling Technology

Dr David Arnold

(Chapter not submitted)

Chapter 9

Fouling Resistant Coatings prepared from Low Surface Energy Polymers

John Tsibouklis
Thomas G N Nevell
Paul Graham
Maureen Stone

Fouling Resistant Coatings prepared from Low Surface Energy Polymers: a non-toxic approach to marine antifouling

John Tsibouklis, Thomas G. Nevell, Paul Graham and Maureen Stone

School of Pharmacy and Biomedical Sciences, University of Portsmouth,
Portsmouth P01 2DT, United Kingdom.
e-mail: john.tsibouklis@port.ac.uk

Abstract

An alternative to chemical attack on established colonies (bleaches, detergents) and to toxic surfaces (antibiotics, copper, organotm additives to paints) is to utilise surfaces of environmentally-friendly, non-toxic polymeric materials onto which marine colonisers will not adhere; essentially to inhibit settlement by removing the ability of the surface to form a permanent bond with the microorganism. In this chapter, the molecular design considerations for the fabrication of smooth film structures of such materials will be described, together with some observations of their ability to resist marine fouling organisms.

Keywords

Low-energy-surfaces, polymeric coatings, non-toxic, antifouling

1. Introduction

1.1 Marine biofouling

The accumulation and growth of marine organisms on almost any surface immersed in seawater has always given rise to potential operational difficulties, with major economic, strategic and practical implications, for commercial and naval ships. Relatively recent concerns are, additionally, for underwater electronic equipment, for marine structures *e.g.* oil rigs and for other immersed equipment *eg* cages for salmon farms, cooling-water pipes from power stations, Fig 1.

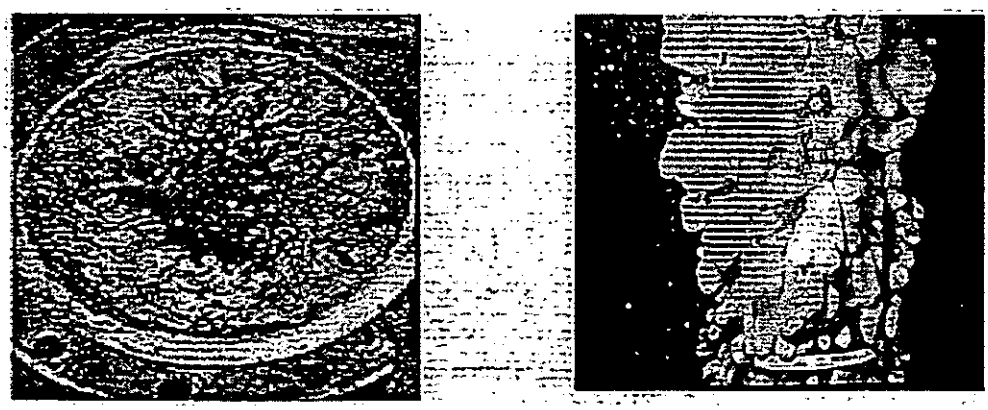


Figure 1. Biofouling: heat exchanger (left); growth of fouling on"~supporting leg of an oil rig (right).

Marine fouling may involve some thousands of marine organisms, depending on conditions (Fig 2). It is recognised that microfouling ('bioslime': microalgae, diatoms) and macrofouling

(weed *eg Enteromorpha, Ectocarpus* and marine animals *eg* barnacles, mussels, tubeworms) usually become established on a predominantly bacterial biofilm which has been formed by the settlement and growth of sessile bacteria (Little, 1984; Mitchell, 1984).



Figure 2. Development of marine fouling on a poly(methylmethacrylate), Perspex, sheet: bimonthly intervals (May to September) in Poole Harbour.

Protection of ships against fouling has involved toxic coatings: copper plating for wooden hulls (eg Cutty Sark, Greenwich), copper-containing resins and paints, elastomers and paints containing organotin compounds and self-polishing organotin copolymers (SPCs). Organotin coatings have proved to be very effective, particularly SPCs for large, fast-moving ships, but their extensive (perhaps indiscriminate/profligate) use has caused serious harm to many marine animal species; in response to this, widespread legal restrictions are intended to prevent their use for small boats. Nevertheless, organotin residues (with extremely low aqueous solubility) are rather persistent in seawater and surface contamination has been detected in to oceanic shipping lanes as well as being mapped in surveys of enclosed seas (Varney, 1999). The development of an adequate non-toxic protective system is both urgent and difficult.

1.2 The biofilm

As in most environments, marine bacteria adhere readily to surfaces for survival and propagation. Whether or not it is a necessary precursor, biofilm formation usually precedes bioslime growth or macrofouling. Most surfaces immersed in seawater are first covered by a "conditioning layer" of adsorbed organic material. Polysaccharides and proteins, for example, tend to be adsorbed strongly from aqueous solution by most surfaces (Schrader *et al.*, 1988). Bacteria readily become attached, leading to development of the biofilm; a sequence of four stages is involved:

- *phase 1* is associated with the transport of bacteria to the biological surface,
- *phase 2* involves reversible adhesion to that surface and reflects the point at which the van der Waals' interactions overcome the repulsive electrostatic forces,
- *phase 3* is the stage at which specific interactions involving chemical (covalent, ionic, hydrogen) bonding develop between the substrate and the bacterium, and
- *phase 4* is the colonisation of the surface and the formation of a bacterial biofilm.

Organisms addressing a substrate may become adhered if their polysaccharide exudates are compatible with the surface such that strong and/or extensive binding can occur. Adhesion

(phases 2 and 3) is therefore promoted by the conditioning layer. Once colonisation has been achieved, formation and subsequent growth of the bacterial biofilm is largely independent of the substrate. Within the biofilm, the bacteria tend to be protected from external antimicrobial agents (and, in/on living organisms, from the host defences). The general outcome of bacterial colonisation of surfaces is the formation of an adherent layer (biofilm) composed of bacteria embedded in an organic matrix, Fig 3. This calyx is usually a polysaccharide exopolymer that is generated by the bacteria. As the biofilm builds up, oxygen and nutrients become depleted close to the substrate but growth continues towards the seawater interface.



Figure 3. Typical biofilm

2. Inhibiting the bacterial colonisation of surfaces

Algae and macrofouling organisms are the main targets of antifouling paints and coatings. However, the biofilm modifies the surface properties of substrates and, once established, attracts bioslime and macrofouling independently of the underlying substrate. Whether the conditioning layer and the biofilm are essential precursors for fouling by algae and higher fouling organisms remains uncertain. However, in developing less environmentally damaging systems to protect against biofouling, it is a reasonable strategy to target the biofilm and its establishment. In the marine context only two approaches have been tried to any extent.

- *incorporation of antimicrobial agents into the substrate* (*e.g.* loading of the surface with bacteriocides)
- *surface modification to prevent biofouling* (*e.g.* hydrophilic modification; low surface energy coatings)

It is axiomatic to the latter approach that surface properties which minimise the initial adsorption process would also make the substrate unattractive for the direct attachment of marine organisms. The approach has the advantage that, if material integrity is maintained (and this also would be one of the requirements for viable application) then environmental pollution by toxic substances could be avoided. Low-surface-energy coatings, the subject of this chapter, are believed to function by presenting a "non-stick" surface to bacteria and other colonising microorganisms (Tsibouklis *et al.*, 1999b; Evans and Clarkson, 1993). Interest in this approach dates from the early 1980s when silicone elastomers were first tried as coating materials; more recently, it has been observed that gorgonian corals, which have low energy surfaces, are not susceptible to colonisation by marine microbes (Clare *et al.*, 1992; Vrolijk *et al.*, 1990).

3. Surface Energy

Surface Energy is the energy required to create a unit area of surface (*eg* by dividing a bulk solid or by spreading a liquid film); it provides a measure of the strengths of forces of attraction between molecules, within bulk phases or across interfaces.

The surface energy (γ) of a material is expressed (Wu, 1992) by: $\gamma = \gamma^{\circ}\rho^{\beta}$ (γ° and β are temperature-independent constants, and ρ is the specific gravity of the material). For polymeric materials, the value of γ° is determined mainly by the chemical structure at the surface: it has long been established that, consistently with the high electronegativity of the F atom and its correspondingly weak van der Waals' interactions, the surface energy of constituent groups decreases in the order $CH_2 > CH_3 > CF_2 > CF_3$ (Lau and Burns, 1974; Bernett and Zisman, 1960; Dettre and Johnson, 1966; Dettre and Johnson, 1969). The value of β (the Macleod exponent), which is normally in the range 3.0 - 4.5, is determined by the overall structure of the macromolecule. Finally, the entropy of the surface is of some significance: amorphous materials exhibit lower surface energy values than crystalline counterparts (Glennon, 1998).

3.1 Surface energy determinations

The surface free energies of polymer samples may be determined by contact-angle goniometry; that is, the measurement of the angle which a drop of liquid forms with the surface (Fig 4).

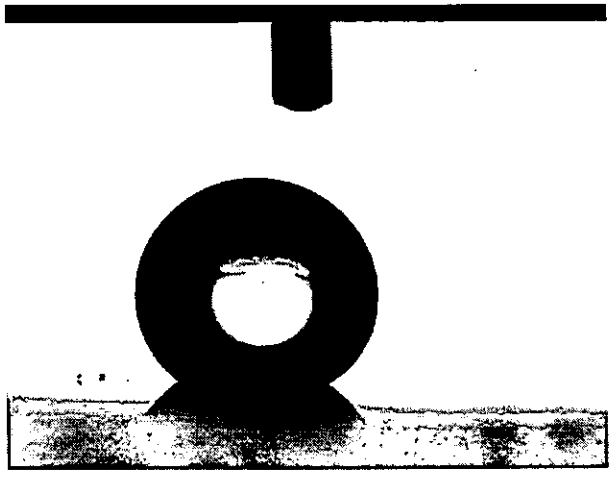


Figure 4. Droplet of water (5 μl) deposited on the surface coated with a low-surface-energy polymer

Measurements of liquid droplets (2-5 μl, *i.e.* sufficiently small for gravitational effects to be negligible) are performed at a constant temperature, typically 25 °C, and under saturated vapour. A complementary method involves observations of small air bubbles at an immersed surface. Another method is based on the Wilhelmy plate experiment, in which a partially-immersed plane face of the sample is tilted until the liquid surface at the boundary is flat. The methods have their own advantages and applications.

The determination requires a uniform plane surface. Any form of roughness gives rise to 'hysteresis', with the angle for a liquid boundary advancing across a surface exceeding that for a receding boundary. This effect gives rise to the extremely high water repellence of the finely-corrugated waxy surfaces of some plant leaves (Holloway, 1994). Heterogeneous surfaces also give rise to hysteresis. Independent observations of surface topography (using *e.g.* atomic force microscopy) contribute to the interpretation of contact angle measurements.

One of several, reasonably consistent, methods by which surface energies for organic polymers and other non-metallic / ionic solids ($_S$) may be evaluated is the surface-tension-component theory (Good and Van Oss, 1991). According to this approach, the surface energy of a solid, γ_S, combines three contributions, *eq. 1*:

$$\gamma_S = \gamma_S^{LW} + (\gamma_S^+ \gamma_S^-)^{1/2} \qquad \textit{(eq. 1)}$$

An analogous equation may be written for a covalent liquid ($_L$).

γ^{LW} Liftshitz/van der Waals component;
γ^+ Lewis-acid component;
γ^- Lewis-base component.

For a drop of a liquid at equilibrium with a solid surface, γ_S^{LW}, γ_S^+ and γ_S^- can be calculated (*eq. 2*) by performing liquid-solid contact angle measurements (θ).

$$\gamma_L (1 + \cos\theta) = 2[(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + (\gamma_S^+ \gamma_L^-)^{1/2} + (\gamma_S^- \gamma_L^+)^{1/2}] \qquad \textit{(eq. 2)}$$

γ_L surface tension (surface energy) of the liquid;
subscripts: S = solid, L = liquid

By measuring contact angles for three well-characterised liquids (in terms of γ_L^{LW}, γ_L^+ and γ_L^-; Kaye and Laby, 1992), three equations with three unknowns are generated. Doubly distilled water, diiodomethane and 1,1-ethanediol are typically employed.

The surface energies of some materials are shown in Table 1; the closeness of the values for PTFE and paraffin wax is, perhaps, unexpected. Quite apart from the difficulty of creating adequate adhesion between PTFE and other materials, this fluoropolymer shows a disappointingly poor resistance to marine fouling, particularly by algae; this has been attributed to surface microcrystallinity (Brady, 1994; Griffith and Bultman, 1980). Silicone elastomers may generally be prepared with smooth surfaces, as shown by small hysteresis effects. Due to the flexibility of the –Si-O-Si- backbone, they absorb many solvents, including water. Contact angles decrease over time, reflecting effects such as solvent absorption and molecular conformational changes close to the interface. However, the long-term resistance to fouling shown by just a few of these materials is not reflected by strikingly characteristic liquid contact angles, surface energies or time-dependent behaviour (Edwards *et al.*, 1995; Nevell *et al.*, 1996).

Table 1. Surface energies of some common materials

Material	Common name	Surface Energy / mJm^{-2}
poly(methylmethacrylate)	Perspex, PMMA	40
poly(ethylene)	polythene	34
poly(dimethylsiloxane)	silicone	22
poly(tetrafluoroethylene)	Teflon, PTFE	20
paraffin wax		22

4. Performance demands

If a polymeric film with low surface energy characteristics is to be usefully employed as a fouling-resistant coating it should fulfil a number of performance requirements, including:

(i) good film-forming characteristics
(ii) good mechanical properties *i.e. scratch resistance, tensile strength, flexural strength*
(iii) chemical/biological inertness *i.e. resistance to attack by solvents, acids, bases, enzymes, ultraviolet light etc.*

In addition, the coating must be non-toxic, if it is to represent a significant advance on the current antifouling technology. Silicone elastomers (non-toxic) are good with respect to (i) and (iii) but not (ii). Some improvements in mechanical properties may be obtained by incorporating solid fillers; in one commercial product, General Electric RTV11, the calcium carbonate filler is believed also to contribute to the maintenance of a fouling-resistant surface, by dissolving very slowly to leave a smooth film of polymer (Bullock *et al.*, 1999).

5. Molecular design requirements for low-surface-energy polymers

It is established that amorphous, comb-like polymers possessing a flexible linear backbone onto which are attached side-chains with low intermolecular interactions, Figure 5, will exhibit low γ values (Owen, 1988). The fluorosilicone structure would appear to show promise, by combining backbone flexibility with surface fluorine atoms. However, surface energy measurements and X-ray photoelectron spectroscopy have shown that, for some of these structures at least, the fluorine-containing groups are buried and methyl groups are exposed at the surface (Tsibouklis, *et al.*, 1999a; Thorpe *et al.*, 2000).

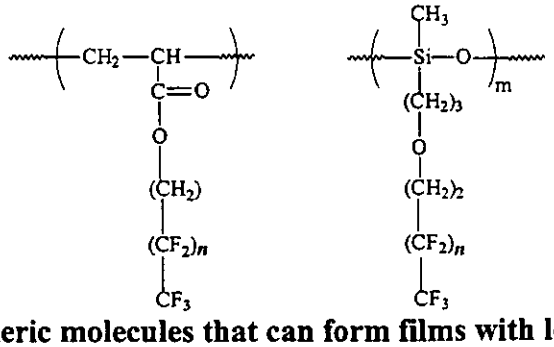


Figure 5. Typical polymeric molecules that can form films with low energy surfaces.

6. Materials investigated

Recent work at the University of Portsmouth has been focussing on a range of well-defined acrylate-type materials. The preparation and characterisation of poly(fluoroalkylacrylate)s **I** and poly(fluoroalkylmethacrylate)s **II**, involving Schotten-Baumann synthesis of monomers and polymerisation with azo*bis*isobutyronitrile (AIBN), has been described (Stone *et al.*, 1998; Graham *et al.*, 2000b; Tsibouklis *et al.*, 2000).

$-(CH_2\text{-}CH(CO_2(CH_2)_2(CF_2)_{x-3}CF_3))_n-$ **I** x = 6,8,10,12

$-(CH_2\text{-}C(CH_3)(CO_2(CH_2)_2(CF_2)_{x-3}CF_3))_n-$ **II** x = 6,8,10,12

7. Film formation

Films of these materials could be coated, from solution or from the melt (*ca.* 100 °C), onto supporting substrates (10 x 10 x 1 mm) of glass, Teflon® (ptfe), poly(methylmethacrylate) (PMMA) and polyester/glass-fibre composite (grp). The films were generally of good quality but with the poly(fluoroalkylacrylate)s there were some cracks in the films used, particularly those deposited on glass.

For the melt-processed fluoroalkylpolymers, surface roughness was greater with longer fluorinated side-chains. The films were generally clear and hard, although the dodecylfluoropolymers (x = 12) tended to give translucent films. Surface studies using X-ray photoelectron spectroscopy showed that in films the perfluorocarbon side-chains segregated preferentially towards the surface (Tsibouklis *et al.*, 1999a). The surface energies of most of the fluoropolymers were low, Table 2.

Table 2. Surface roughness (R_a) and advancing contact angles for water, diiodomethane (*DIM*) and ethylene glycol (*EG*) on: poly(perfluoroalkylacrylate) (I), and poly(perfluoro alkylmethacrylate) (II) film structures; the corresponding surface energy components are also presented.

Sample	R_a/nm	Contact angle, θ°			Surface energy (mJ m^{-2})			
		H_2O	*DIM*	*EG*	γ_s^{LW}	γ_s^+	γ_s^-	γ_s
poly(perfluoroalkylacrylate)s								
x = 12	11.0	125	112	120	5.0	0.1	1.6	5.6
x = 10	9.6	117	112	108	6.2	0.1	2.2	6.9
x = 8	5.1	114	108	108	6.9	0.0	3.7	7.0
x = 6	3.1	113	105	110	10.2	0.4	4.3	12.9
poly(perfluoroalkylmethacrylate)s								
x = 12	7.13	125	109	107	5.8	0.3	0.1	6.1
x = 10	1.17	124	104	105	7.3	0.2	0.1	7.5
x = 8	0.41	121	104	106	7.3	0.1	0.5	7.7
x = 6	0.29	123	103	102	7.6	0.3	0.0	7.8

8. Toxicity/Biocompatibility

One of the most significant features of the low-surface-energy approach to marine antifouling is its non-toxic nature. Strong evidence that the fouling-resistant nature of the low-surface-energy films was in no way related to toxicity has been provided by animal experiments, performed principally with reference to potential medical applications of the materials, Fig 6. The rat model was employed throughout and standard regulatory procedures were followed, with close monitoring. No infection effects could be detected and there was no bacterial attachment to the sample discs (Tsibouklis *et al.*, 1999b).

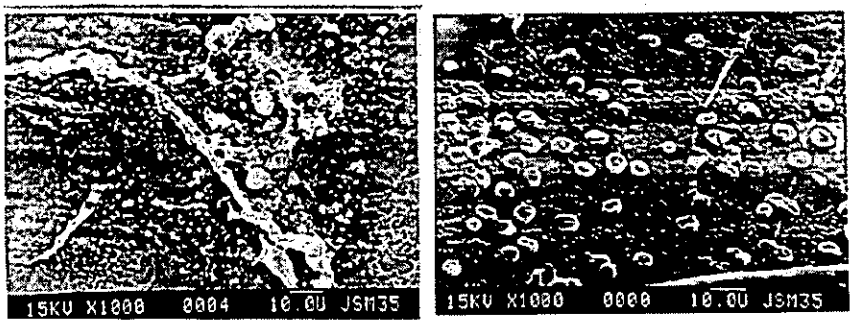


Figure 6. SEM micrograph of polymer discs after seven days implantation in the rat: (a) Teflon control (collagen fibres and platelets are clearly visible); and, (b) Teflon coated with poly(perfluoroalkyl acrylate) (showing the presence of blood platelets on the surface).

9. Antifouling performance

9.1 Bacteria

Tests were conducted with a selection of marine bacteria. Sub-cultures of mixed *Pseudomonas spp. (P. cepacia, P. paucimobilis and P. fluorescens),* recovered from the inter-tidal zone of corroded steel piling in Portsmouth Harbour UK, and sulphate-reducing bacteria (SRB) strain A1-1 *Desulfovibrio alaskensis* NCIMB 13491, were grown to the stationary phase respectively in artificial seawater / Marine Postgate Medium C 4/1 v/v (Tsibouklis *et al.*, 1999b) or degassed Marine Postgate Medium C. *Pseudomonas sp.*NCIMB 1534 (North Sea) and *Alteromonas sp.* NCIMB 2141 (Ria de Pontevedra, Spain) were cultivated in marine broth 2216 (Bacto™, DIFCO Laboratories, Detroit USA).

Closed batch-culture tests of long-term settlement were conducted on poly(fluoroalkylacrylate)s and some poly(acrylate)s, and initial settlement on poly(fluoroalkylmethacrylate)s. The procedures for long-term tests (using *Pseudomonas spp* and SRB) and short-term tests (using *Pseudomonas sp.*NCIMB 1534 and *Alteromonas sp.* NCIMB 2141) may be summarised (Graham, 2000a) as follows. In the former, one sample of a test material and one control sample were held vertically in a universal bottle; sufficient samples were set up to allow for analysis (AFM/SEM) in triplicate after appropriate incubation (28 °C, periods up to 5 months). In the latter (5 hours), petri dishes were used, each containing one sample of each test material and control settled bacteria were stained and

counted by epifluorescence microscopy. On all of the controls, bacterial settlement was rapid and the cells became strongly attached. For example with *Pseudomonas* NCIMB 1534 and *Alteromonas* NCIMB 2141, coverages reached 5.5-8.3 x 10^3 cell mm^{-2} after 5 hours; with SRB and *Pseudomonas spp.* coverages reached 8.9 x 10^4 and 9.5 x 10^4 cell mm^{-2} respectively after 2 weeks and mature biofilms were observed after 3 - 5 months (Fig 7).

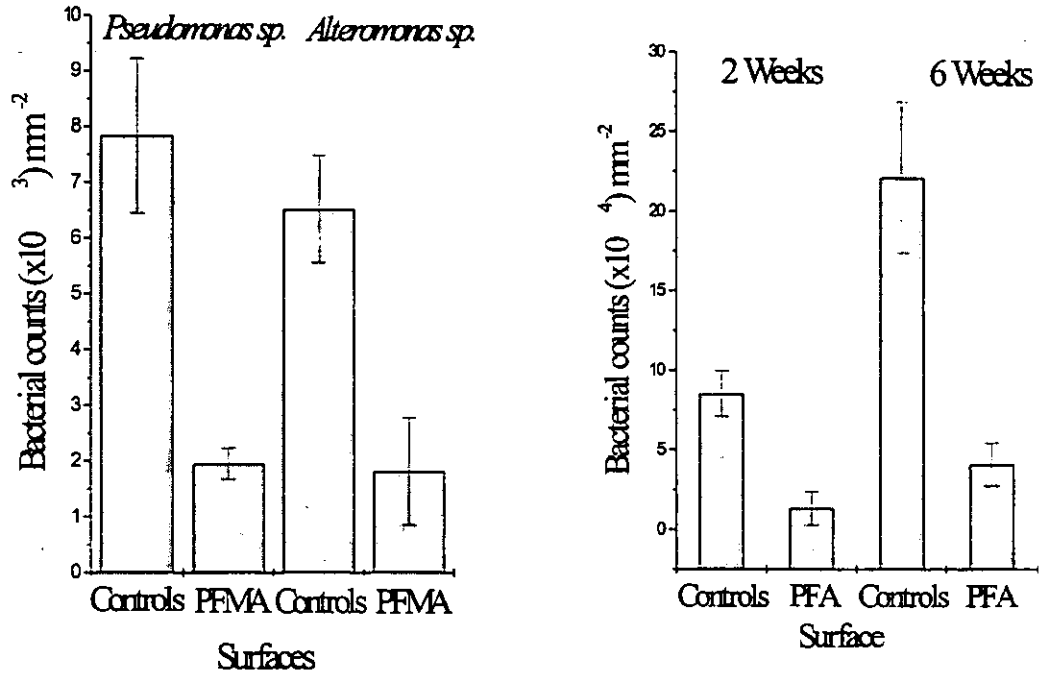


Fig. 7. Settlement of bacteria on melt-coated fluoroalkyl polymer films and controls: a, *Pseudomonas* NCIMB 1534 and *Alteromonas* NCIMB 2141 (after 5 hours, 20 °C) on poly(fluoroalkylmethacrylate)s; b, mixed *Pseudomonas spp.* (after 2 & 6 weeks, 28 °C) on poly(fluoroalkylacrylate)s.

With films of both poly(fluoroalkylacrylates) (I) and poly(fluoroalkylmethacrylate) films (II), early settlement of *Pseudomonas* NCIMB 1534 and *Alteromonas* NCIMB 2141 was *ca.* 25 % of that on the controls. At this stage there were no significant differences between the fluoropolymers. After 2 weeks' exposure of poly(fluoroalkylacrylates) (I), the corresponding proportions were 5-20 % with *Pseudomonas spp.* and 10-15 % with SRB. The non-fluorinated alkylacrylates with long side-chains also showed early resistance to settlement by SRB but this was not maintained and mature biofilms were formed. By contrast, the relative resistance to settlement of the poly(fluoroalkylacrylates) (I) was maintained over 5 months. With these surfaces, settled bacterial colonies were weakly attached and very easily displaced, such that only single bacteria or small groups were not removed by gentle rinsing. This is demonstrated in Figure 8, which is an atomic force micrograph (AFM) of a fluoroalkylacrylate film after exposure to SRB; the exopolymeric matrix is seen to spread rather poorly over the sample surface.

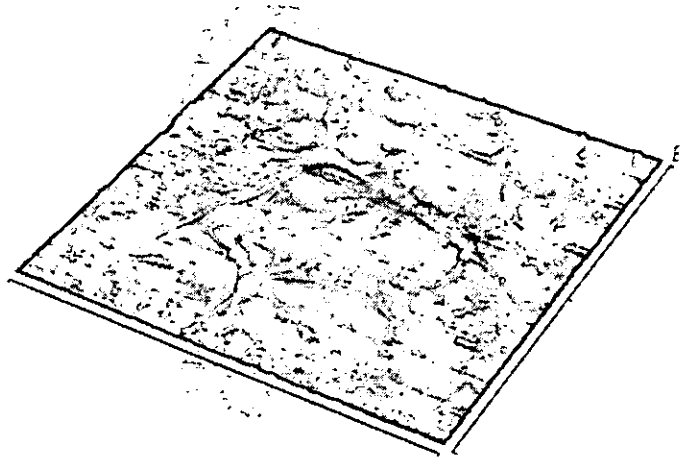


Figure 8. AFM image (30 μm^2) of exopolymer matrix from a, sulphate-reducing bacteria strain A1-1 *Desulfovibrio alaskensis* NCIMB 13491 on melt-cast films of poly(fluoroalkylacrylate)s.

9.2 Enteromorpha zoospores

Enteromorpha thalli were collected from Wembury, Devon and zoospores were released as described by Callow *et al.*, 1997.

Independent experiments were carried out respectively for poly(fluoroalkylacrylate) and poly(fluoroalkylmethacrylate) films, using Petri dishes (9 cm) each containing one sample of all films and controls (Graham, 2000a). Settlement of *Enteromorpha* zoospores was much less on the films of poly(fluoroalkylacrylate)s than on the uncoated controls. However, the majority of zoospores settled on the films were over cracks or surface imperfections; it was not possible to discriminate between locations with our counting procedure. Unbroken films of poly(fluoroalkylmethacrylate)s showed rather less settlement and there was also some discrimination between the controls: settlement on glass was 4 x greater than on ptfe and >12x greater than on the fluoropolymers, Fig 9.

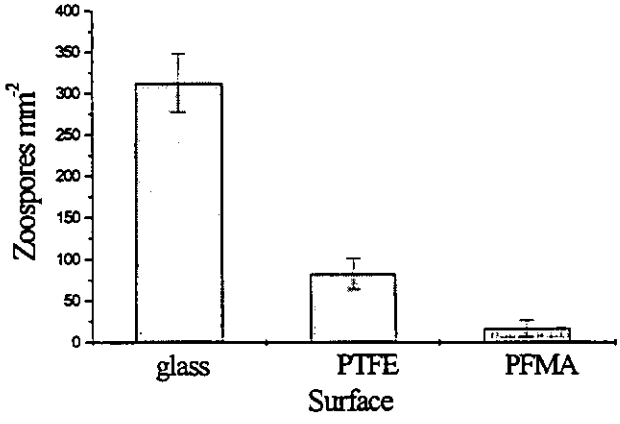


Figure 9. *Enteromorpha* settlement (20 °C, dark, 1 hour) on controls and melt-coated films of poly(fluoroalkylmethacrylate)s.

9.3 Barnacle Cyprids

The settlement over 14 days of cyprid larvae of *Balanus amphritite* Darwin (Clare, 1996) on films of poly(fluoroalkylmethacrylate)s is summarised in Fig 10. In all experiments 30-40 % of cyprids eventually (*ca.* 14 days) settled on the samples or controls.

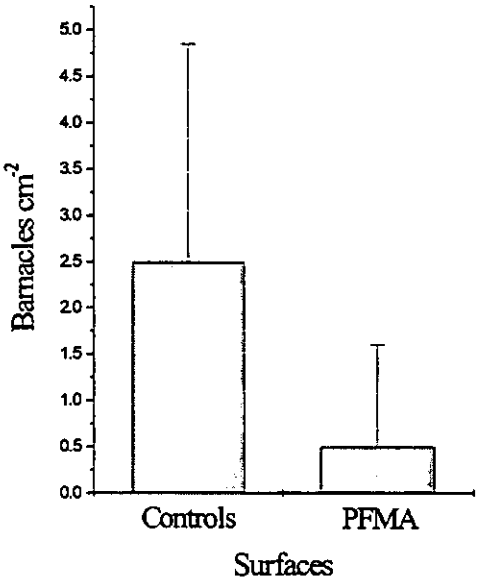


Figure 10. Settlement of barnacle cyprids of *Balanus amphritite* Darwin (1-14 days, dark, 28 °C) on films of poly(fluoroalkylmethacrylate)s.

Glass was much more attractive than pmma but, interestingly, no cyprids settled on any of the ptfe controls. Settlement on other non-fluorinated polymers was also considerable. Most of the poly(fluoroalkylmethacrylate) films attracted only one or two cyprids, which developed normally.

10. The future

The principal aim of this work has been to compare the ability of some marine bacteria, algae and higher fouling organisms to settle and develop on low-surface-energy fluorinated materials. Similar materials have shown promising resistance to marine fouling (*e.g.* Lindner 1992) but their long-term performance is not yet established. A potential problem for antifouling protection is that of producing large well-adhered areas of smooth fault-free protective film. The value of making the effort to achieve this may be assessed from observations made with small areas. Although some of the films used here were imperfect, the observations do enable some assessment of the importance of surface faults, as well as of the fundamental resistance of the materials to the organisms employed.

Although only a small selection of marine bacteria was used, their settlement rates on the controls were reasonably similar. Settlement was considerably less on the fluoropolymers (10

- 25 % of controls) and bacterial attachment was generally much weaker. However there was no correlation between attachment and film quality; indeed the better-quality poly(fluoroalkylmethacrylate) films on glass or PTFE showed somewhat higher settlement (relative to controls) than the cracked films of poly(fluoroalkylacrylate)s. Except at surface cracks, individual settled bacteria were hard to find by AFM but residual exopolymer showed that there had been considerable attachment prior to washing. The present observations showed no effect of small variations in surface roughness but ptfe controls were much more extensively covered than any of the fluoropolymer films. The implication is that bacteria can settle on these fluoropolymer films but cannot become strongly attached unless there are major and/or extensive surface defects. Observations would have been affected by, for example, washing conditions that may have differed slightly between experiments. The much more extensive settlement on PTFE is consistent with previous observation (*e.g.* Brady *et al.*, 1987) and with their more difficult displacement from the microporous surface.

The experiments with *Enteromorpha* zoospores were of relatively short duration. Hence, although some bacterial settlement cannot be ruled out, biofilm development will have been limited. The observations therefore are likely to reflect the ability of the zoospores to settle on the surface directly rather than on top of attached bacteria, although the formation of a conditioning layer cannot be ruled out. The poly(fluoroalkylacrylate) films showed good resistance to settlement except at surface cracks. For the poly(fluoroalkylmethacrylate) films, which were not cracked, resistance to settlement was greater for polymers with longer fluorinated side-chains and hence for surfaces with greater proportions of fluorine atoms. Small variations in surface roughness appeared to have little influence. The apparently contradictory result for uncoated PTFE shows, however, that extensive surface porosity does enable the zoospores to settle even on completely fluorinated surfaces.

In the experiments on the settlement of barnacle larvae, the non-fluorinated analogues of the fluoromethacrylate films under consideration were included for comparison. Their slight tackiness prevented the larvae from manoeuvring on the surfaces but this did not prevent the development of those that settled initially in the correct orientation. The poly(decylmethacrylate) films were more attractive than others tested, which were similar to the PMMA controls. With the poly(fluoroalkylmethacrylate) films very few larvae settled. There was no discrimination between the polymers. Surface roughness at the magnitudes involved was not a factor, since the surface microporosity of PTFE did not enable any settlement to occur. It is possible that the few larvae settling on these fluoroalkylpolymer films were attached at film faults.

It is notable that the bacteria, algal spores and barnacle larvae showed different responses to the fluoropolymer films. Although significantly lower than on the controls, bacterial settlement on the films was still appreciable; however, almost all bacteria were weakly attached and easily displaced. Settlement of the *Enteromorpha* zoospores showed some sensitivity to the fluorine content of the polymer, but the surface porosity of the PTFE control appeared to promote settlement on this material. Cyprids, by contrast, did not settle on PTFE, indicating that in this case the scale of the surface roughness was too fine to influence attachment.

The overall indication is that smooth films of fluoropolymers show considerable promise as materials for fouling-resistant coatings, but that further work is required to achieve adequate

smoothness over large areas of film, freedom from cracks and surface blemishes and strong attachment to underlying substrates.

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Chapter 10

Workshop – Calculating the Cost of Marine Surface Roughness on Ship Performance

Dr R L Townsin

Workshop - Calculating the Cost of Marine Surface Roughness on Ship Performance.

Dr. RL Townsin - Consultant

Abstract

This chapter provides the information, means and opportunity to calculate the speed and power penalties resulting from the roughness of an anti-fouled hull surface. The information concerns the sources and causes of anti-fouled hull surface roughness, the definition and measurement of hull roughness, and the relation between roughness and added drag. The means are formulae for the calculation of added resistance, power and fuel consumption. Data are provided for worked examples in the workshop.

Marine roughness, Added resistance, Ship performance penalties.

1. Sources and causes of anti-fouled hull surface roughness.

The new ship at outdocking.

The roughness of the final coat of anti-fouling on a new ship results from the rheological characteristics of the paint itself and, more importantly, from the circumstances of its application. In laboratory conditions, a paint might finish with a peak-to-trough measure of 40 μm MHR (q.v. later). The best ever recorded figure for a new ship roughness was 78 μm AHR (q.v.) and a typical 'good' finish today will be, say, 125 μm AHR. ref. (1).

The principal 'applied' roughnesses are as follows:

- Orange peel - this texture arises from the limitations of the flow of the paint.
- Runs and sagging - due to an over thick application.
- Waviness - spray fan blowing waves in the wet deposited paint.
- Overspray - solidified droplets of paint arriving at the wet painted surface giving a 'sandy' texture, due to spray gun too far from surface.
- Grit inclusions - due to wind blown dust, blasting grit etc.
- Crazing - cracks and crazes due to paint and environmental circumstances.

A 'bad', new finish might be 450 μm AHR, from any of the above causes.

In-service roughness.

The hull roughness of a ship in-service increases between re-coatings. This is due to failures of preparation, application and of the paint itself, and, usually more importantly, due to surface damage in-service.

The principal in-service roughnesses are caused as follows:

- Welds and surface defects at new building, which are not properly cleaned, will give rise to corrosion and blistering.
- Old corrosion pitting, when overcoated, gives rise to a 'negative' roughness.
- Paint detachment may be of the new coating or of the overcoated previous coating and there may be a substrate compatability problem.

- Recoating over inadequately cleaned off fouling residues.
- Surface damage in-service arises from many causes eg. anchors and cables, fendering, tug nosing, groundings, drydock block damage.
- Underwater cleaning in the hands of non-specialist divers using inappropriate equipment can also cause damage. Later in this School there will be an account of how underwater cleaning can be carried out correctly. This raises the important issue of paint hardness, which arises, eg., when considering slime cleaning from the new, low surface energy antifoulants.

2. The definition and measurement of hull roughness.

Following the Froude's work on roughened planes, one of the earliest attempts at hull roughness definition was by sand grain comparison. The Prandtl/Schlichting/Nikuradse work on flow through sand grained pipes (1934) ref.(2) was invoked to attempt both a definition of ship hull roughness and its penalty. During the 1940's there was an interest in the possibility of laminar (low drag) wing sections for aircraft. An aerofoil roughness gauge was developed at the National Physical Laboratory, consisting in a flexible steel foil with a longitudinal slot, which could be bent around a wing section. A trolley could be run over the foil with a stylus passing through the slot. The perpendicular, mechanically amplified movement of the stylus over the rough wing surface was then recorded against the distance travelled by the trolley. This idea was developed to measure ship hull roughness, specifically for the well known 'Lucy Ashton' trials of the 1950's ref.(3). The method for defining hull roughness then, is still in use today, although the instrument has been improved to become the BMT Hull Roughness Analyser (HRA). It is singular that no other hull roughness definition has been developed and no other instrument has been sucessfully put on the market.
The universally adopted parameter is Rt(50), which is the distance in μm, perpendicular to the surface, from the highest roughness peak to the lowest trough, in a distance of 50mm. The 50mm determines the long wavelength cut-off, whilst the diameter of the ball at the tip of the stylus determines the short wavelength cut-off. It was argued, in the 'Lucy Ashton' work, that the longer wavelengths, like plate waviness, would not affect resistance and could not be called roughness. Similarly, short wavelengths, say less than 1mm, would also have no effect on drag.

Since Rt(50) varies all over a hull, some averaging system is required, which must link up with a procedure for surveying a hull.

At a measuring station on a hull, one arm's length pass of an HRA trolley yields about m = 12 values of Rt(50). A complete hull survey should cover over 100 equally spread measuring stations on both sides and the bottom.

$$AHR = k = \text{Average Hull Roughness}$$

$$= 1/n \sum MHR \quad \ldots\ldots n \text{ about } 100$$

$$MHR = \text{Mean Hull Roughness (of one pass)}$$

$$= 1/m \sum Rt(50) \quad \ldots. m \text{ about } 12.$$

The histogrammatic representation of survey results, both as grouped (MHR) and ungrouped Rt(50) data will indicate the influence of surface damage , and this is explored at length in ref. (4). An outcome of such studies, for example, shows that whilst an ablative antifouling paint (eg. SPC), does indeed 'polish', or become smoother in service, the ship becomes rougher due to surface damage. Ref. (4) also includes a standard procedure for a hull roughness survey and its analysis.

3. Roughness and added drag.

It should be noted that there is an arbitrariness about Rt(50) as an appropriate roughness measure, both as to its cut off values and the whole question of whether peak-to-trough height is the correct or adequate measure to correlate with added drag. Perhaps, as well as a roughness height measure, there ought to be a 'texture' parameter to describe the shape of the roughness peaks and to define their distribution. These questions have been extensively researched and discussed, eg. Ref.(5).

The foundation for research is the measured added drag of various rough surfaces, the topographies of which have been carefully measured, usually yielding a set of 'roughness' and 'texture' parameters in addition to Rt(50). Among those parameters proposed, have been kurtosis, skewness and the even moments of the power spectrum of the roughness profile.

The drag measurements that have been undertaken have usually been on rough flat plates, internally roughened pipes or on rotating cylinders. The correlation of the various parameters, or combination of parameters, are not usually with the added drag values directly, but with the roughness function.

If the boundary layer flow velocity u, at a distance y from a smooth surface, is plotted against log y, the curve is linear between about 0.5 δ and 10 - 15% δ, (the 'inner law'), where δ is the boundary layer thickness.

It is usual to non-dimensionalise the plotting as u/u_o against $\log_e yu_o/\nu$, where u_o is the flow velocity at the edge of the boundary layer and ν is the kinematic viscosity.

It has been found that these flow parameters for a surface which is rough, behave in the same linear manner. The smooth and rough linear sections are found to be parallel, with the rough line $\Delta u/u_o$ below the smooth. $\Delta u/u_o$ is called the roughness function, and it is this that research has attempted to correlate with various statistical roughness measures.

When the roughness function is plotted against $\log_e hu_o/\nu$, where h is a particular statistical roughness measure, all the available experiment data is often scattered and no correlation can be found. However, when h = Rt(50) a correlation can be detected provided that:

- the surface is an undamaged, conventional, anti-fouling paint and
- the surface is not excessively rough, viz. Rt(50) < 225 μm say.

It was on this basis that the 19th ITTC (Madrid 1990) recommended the adoption of a new roughness penalty formula and a revised power prediction correlation allowance, ref (6).

4. Formulae for the calculation of added resistance.

The following formulae are based upon the work described above. A more complete account may be found in the references at the end of this chapter.

The work described in ref.(7) involved the use of an integral momentum method for the calculation of the frictional drag of five ship types - ULCC, products carrier, containership, small tanker, frigate - both smooth and with homogeneous roughness over a range of severity. Those familiar with these procedures will know that a skin friction equation is required and, for this purpose, Coles law of the wall / wake, was used, which has the roughness function as one term. Any deficiencies in the accuracy of the integral method were largely offset since only the difference, ΔC_F, between C_{Frough} and $C_{Fsmooth}$, was required. The correlation between the roughness function and any roughness measure, however, has to be as reliable as possible.

The results from the calculations showed:

- a linear relationship between ΔC_F and $(AHR / L)^{1/3}$ at a fixed speed for each ship, where L is length between perpendiculars.
- for a given ship and hull roughness, ΔC_F was found to be speed dependent.

Whilst there is no theoretical justification for the 1/3rd power as a lineariser, the idea came from the work of Telfer, esp.ref.(8), who reanalysed Froude's sand roughened planes data to give a relationship of the form:

$$C_{FR} = A\,(h/L)^{1/3} + B$$

Telfer also advocated a smooth ship extrapolater:

$$C_{FS} = C + D(R_n)^{-1/3}$$

Subtracting the smooth from the rough yields:

$$\Delta C_F = A\,(h/L)^{1/3} - D(R_n)^{-1/3} + \text{constant}$$

which is speed dependent.

This form was applied to the detailed calculations for the five ship types referred to above and a satisfactory fit to the results was given by:

$$10^3 \Delta C_F = 44[(AHR/L)^{1/3} - 10(R_n)^{-1/3}] + 0.125 \qquad \text{--------equation 1.}$$

This is the formula adopted by the 19th ITTC, ref (6).

Consider a change in roughness from AHR = k_1 to k_2, $k_2 > k_1$. If the ship maintains the same speed, the increase in the resistance coefficient as the ship roughens from k_1 to k_2 is:

$$10^3 \Delta C_F = 44[(k_2/L)^{1/3} - (k_1/L)^{1/3}] \qquad \text{----------equation 2.}$$

k and L must be in the same units!

Let the total resistance coefficient be C_T = (total resistance) / $0.5\rho SV^2$ and C_F is the frictional resistance coefficient, then the fractional added resistance is:

$$\Delta R/R = \Delta C_F/C_T = 0.044[(k_2/L)^{1/3} - (k_1/L)^{1/3}] / C_T \quad \text{----------equation 3.}$$

5. Formulae for the calculation of added power and fuel consumption.

The resistance increases due to hull surface deterioration and we may consider two possibilities:

- Speed is maintained and therefore power and fuel consumption increase.

This is appropriate to the maintenance of schedules on a liner service e.g. a containership.

- Power is maintained and therefore the speed drops.

If power is constant the fuel consumption is constant except for the effect of reduced r.p.m. This is like a tanker operation.

6. Power increase $\Delta P/P$ at constant speed.

Let η= the open water propeller efficiency.
Let T= propeller thrust.
Let P= shaft power.

$$P = TV / \eta \quad \text{.....smooth hull}$$

$$P + \Delta P = (T + \Delta T)\, V / (\eta+\Delta\eta) \quad \text{.....with added roughness resistance}$$

$$= (TV/\eta)(1+ \Delta T/T)(1+\Delta\eta/\eta)^{-1}$$

$$\therefore 1+\Delta P/P = (1+\Delta R/R)(1+\Delta\eta/\eta)^{-1} \quad \text{----------equation 4.}$$

The added resistance at constant speed may be calculated as shown above: it remains to establish a relationship between $(1+\Delta R/R)$ and $(1+\Delta\eta/\eta)^{-1}$. Noting that $\Delta R/R$ is almost the same as $\Delta T/T$, the relationship can be calculated from the propeller design data. For most propellers, the relationship is closely linear in the relevant range and, of course, the curves intersect at (1.0, 1.0). As a handy guide, the following approximate relationships hold, in the relevant range, for a ro-ro ship and a tanker, which typify the liner and the bulker:

$$(1+\Delta\eta/\eta)^{-1} = 0.17(1+\Delta R/R) + 0.83 \quad \text{.....for ro-ro ship}$$

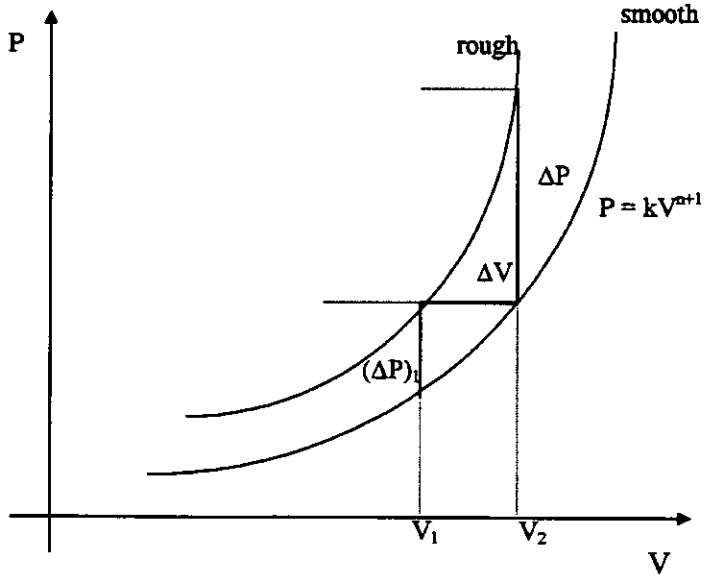
$$= 0.30(1+\Delta R/R) + 0.70 \quad \text{.....for tanker.} \quad \text{--------equations 5.}$$

7. Speed loss at constant power.

Let $R \propto V^n$ where n may be regarded as constant over a small speed range V_2 to V_1
then $P = kV^{n+1}$
Suppose resistance is increased at any speed due to deteriorating hull condition and suppose that the resulting fractional increase in power $\Delta P/P$ is constant over a small speed range, then the equation of the rough power curve will be (see figure below) :

$$P = kV^{n+1} + \Delta P$$

Rough and smooth power curves.



At V_2 power for smooth ship $= kV_2^{n+1}$
V_1 power for rough ship $= kV_1^{n+1} + (\Delta P)_1$

Thus, for the same power $kV_2^{n+1} = kV_1^{n+1} + (\Delta P)_1$

$$k(V_1 + \Delta V)^{n+1} = kV_1^{n+1} + (\Delta P)_1$$

$$[(V_1 + \Delta V)/V_1]^{n+1} = 1 + (\Delta P)_1/P_1$$

$$(1 + \Delta V/V_1)^{n+1} = (\Delta P)_1/P_1 + 1$$

Using the Binomial Theorum, since $\Delta V/V$ is small,

$$1 + (n+1)\Delta V/V_1 \cong (\Delta P)_1/P_1 + 1$$

$$\Delta V/V \cong \Delta P/P\,(n+1)^{-1} \qquad \text{----------equation 6.}$$

and $\Delta P/P$ is the fractional change in power at constant speed due to added resistance, which can be found from the preceding analysis.

8. Determination of the speed index n.

The simple relationship $P = kV^{n+1}$ can only hold with adequate accuracy over a small speed range around the speed of interest. It follows that n will not only vary from one ship to another but also vary at different speed positions along a given speed to power curve. Typical values are given in Table I below, which are taken from ref. (9).

For a given speed to power curve we note that :

$$P_2/P_1 = (V_2/V_1)^{n+1}$$

and hence $n+1 = \log P_2/P_1\,(\log V_2/V_1)^{-1}$

from which it is simple to estimate n from a given speed to power curve around a particular speed.

Table I. Values of the speed index n for 4 ships at each of 2 speeds.

ship type	*length*	*speed (knots)*	*speed index n*
low speed cargo ship	122 m	10.5	2.19
		8.9	2.11
intermediate cargo liner	140 m	16.0	2.29
		13.6	2.36
large passenger ship	230 m	24.0	3.00
		20.4	2.29
cross channel ferry	100 m	24.5	4.55
		20.8	3.62

Whilst the ship types are somewhat dated, Table I illustrates the likely variations in n.

9. Examples.

A containership of length 274.32 m has $C_T = 2.52 \times 10^{-3}$ at service speed and the hull roughness deteriorates from 150μm to 500μm AHR over an interdock cycle. Use equation 3.

$$\Delta R/R = 44/2.52\ [\{500/(274.32x10^6)\}^{1/3} - \{150/(274.32x10^6)^{1/3}\ ]$$
$$= 44/(2.52x649.7)\ [\ 7.937 - 5.313\ ]$$
$$= \underline{0.071 \text{ or } 7\%}$$

Where it is impossible to estimate a value for C_T a very approximate estimate may be made from $C_T = 0.018\ L^{-1/3}$ which, in the above case, gives $C_T = 2.77x\ 10^{-3}$ changing $\Delta R/R\%$ to 6.4%.

Using the ro-ro formula in equations 5, as representative of a containership propeller, and inserting $1+\Delta R/R = 1.071$, we find:

$$(1+\Delta\eta/\eta)^{-1} = 0.17 \times 1.071 + 0.83 = 1.012$$

Hence: $\Delta P/P = 1.071 \times 1.012 - 1 = \underline{0.084 \text{ or } 8.4\%}$

To calculate the speed loss at constant power, we have $\Delta P/P$, above, the power increase at constant speed: it remains to find a value for n. For a containership $n \cong 2.1$ (from the speed to power curves in ref.10.), then :

$$\Delta V/V = [1/(1+2.1)] \times 0.084 = \underline{0.0271 \text{ or } 2.7\% \text{ speed loss.}}$$

In this case, of constant power, the fuel consumption rate is constant but there is increased consumption due to extra time at sea, and there will be other financial penalties.

10. Economics issues.

Usually, the ship operator is principally interested in the financial outturn from alternative outer bottom maintenance strategies. The drydock, maintenance and out of service costs may be predicted for a given strategy for a period of say 10 years. The increase of fuel costs due to predicted hull surface deterioration may be calculated as above. An analysis may then be made using discounted cash flow calculations. It is not appropriate to develop these issues further in this workshop, but a clear development may be found in ref.(11).

All of the foregoing assumes a continuously effective antifouling and this seemed possible at the introduction of organo-tin biocides in an ablative matrix. Today, as TBT coatings are being phased out, a lower standard of antifouling provision has to be accepted, at least for the next few years.Some fouling in service must be expected, and, in the case of the 'non-stick' coatings, the presence of slime is likely. Maintenance strategies must therefore include costed items for underwater inspection and cleaning. At present there is no method for assessing the added drag of a fouled surface, principally because there is no measure of fouling which can be correlated with its fluid resistance. It is generally understood, however, that fouling penalties are usually severe and so it is prudent to ensure that they do not occur.

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Chapter 11

Characterisation of Degradation of Organic Coatings

Dr Emmanuel Aragon

Characterisation of Degradation of Organic Coatings

E. Aragon
ISITV Institute, University of Toulon and Var
Toulon, France
e-mail : aragon@isitv.univ-tln.fr

Abstract

This paper deals with an important industrial problem that is also a very difficult scientific topic. How could it be possible to estimate the durability of an anticorrosion organic coating?
For answering, the first and fundamental problem, which is considered here, is to validate the experimental techniques that are available for characterising the degradation of the organic coating after natural or artificial ageing. This validation is the first step of a largest work that deals with the correlation problem between natural and artificial ageing. The final goal will be to determinate durability of an anticorrosion coating in its environment in order to improve maintenance planning.

Keywords

Organic coating, paint, degradation, ageing, characterisation.

1. Introduction

There are different well-known techniques and methods described by following standards:

Designations		Standards	Characterisation
Evaluation of degradation	Blistering Rusting Cracking Flaking Chalking	ISO 4628/2 - ASTM D 714 ISO 4628/3 – ASTM D 610 ISO 4628/4 - ASTM D 661 ISO 4628/5 - ASTM D 772 ISO 4628/6 - ASTM D 4214	Surface of paint or metal/coating interface
Adhesion tests	Pull-off test	ISO 4624, ASTM D 4541	Cohesive and adhesive properties within the paint system and at the metal/coating interface
	Cross cut test	ISO 2409	Adhesive properties at the metal/coating interface
Gloss measurements	Brilliance	ISO 2813, ASTM D 523, BS 3900	Surface of paint
Colour measurements	spectrophotometry	ISO 7724	Surface of paint

Table 1: Standardised characterisation methods of degradation of paint coatings

The difficulties with these standardised methods are to make a good interpretation of the observation or measurement. The evaluation of the exposure results is often performed manually by visual comparison.

The best method for testing coatings is outdoor exposure of coated specimen in the required environment. However, it takes a very long time to get information about the quality of the protection. Another common method is accelerated weathering in salt spray cabinets, humidity chambers or QUV test chambers. These methods (natural or artificial ageing) do not give any information about the protective mechanism or the observed degradation mechanism. The only information that is obtained consists of the conclusion that one system is more damaged or degraded after a certain time than another. Moreover, natural and artificial methods cannot be well compared: correlations are very difficult and still qualitative. The major problem is that these methods do not give quantitative data for fundamental properties of the coating.

It is always dangerous to conclude by measuring only effects without considering the reasons of the observed phenomena. That it means that the characterisation of degradation must be carried out knowing and in relation with the environmental factors that are caused degradation. For instance, UV and salt spray degradations will not have similar consequences. Moreover, the characterisation of degradation must be carried out in relation with the mechanisms of degradation. Then, good interpretation means comprehension of phenomena! Different mechanisms can be consider:

	Mechanism	Environmental factors
Chemical	Photo degradation	UV
	Hydrolyse	Immersion or condensation water
Physical	Erosion	Wind or rain
	Water uptake	Immersion or condensation water
	Osmotic blistering	Condensation water or immersion in unsalted water
Electrochemical	Anodic undermining	Anodic polarization or galvanic association
	Cathodic delamination	Cathodic protection

Table 2: Main mechanisms of degradation of paint coatings

Table 2 presents a classification of mechanisms that distinguish chemical, physical and electrochemical mechanisms. If weathering factors independently of application problems (osmotic blistering due to surface contamination) and external electrochemical influences (anodic or cathodic polarizations) are only considered it appears that even physical mechanisms are influenced by the chemical properties of paint. Then, the chemical behaviour of the binder is the main parameter to consider for understanding degradation.

Of course, a natural degradation is very complex because it is a combination of different mechanisms. On the other hand, an artificial degradation appears simpler if only one environmental factor is considered but it cannot then be representative of the reality and any correlation will be not possible. Then, artificial ageing cycles must be developed and the more

complex they are, the more correlations might be possible. Complex cycles means to combine different ageing factors, which correspond to different mechanisms.

The knowledge of the chemical mechanisms of the binder degradation is the fundamental step for studying ageing of paint. For understanding these mechanisms different experimental techniques, destructives or not, can be used.

	Non destructive	Depth of analyse	Origins of degradation
Spectrophotometry	X	Surface	Chemical degradation
Brilliance	X	Surface	Chemical degradation and/or erosion
Micro hardness	X	≈ 10µm	Chemical degradation
IR/ATR	X	≈ 10µm	Chemical degradation
EIS		Coating and metal/coating interface	Water uptake Delamination
Thermal Analysis		Depends on sampling	Chemical degradation

Table 3: Presented characterisation techniques of ageing

The aim of this paper is to present these different experimental techniques and their sensitivity.

2. Non-destructive tests

2.1 Spectrophotometry and brilliance

These measurements are well known and widely used for characterising ageing of paint mainly for following colorimetric evolution with time under natural or artificial UV conditions. These characterisations concern strictly the surface of the top coat.

2.1.1 Colorimetric measurements

Spectrophotometric measurements allow detecting very low modification of colour surfaces exposed to UV with a greater sensibility and reproducibility than human eyes.
The characterisation might be reversible. For instance, after UV artificial ageing, we have observed a colorimetric evolution on alkyd paint. But, after removing the degradation products by washing with alcohol, the colorimetric variation compared to the non-aged reference becomes near zero.

2.1.2 Gloss measurements

This characterisation is very simple: light is directed onto the surface of the test specimen at a defined angle (20°, 60° or 85°) and the reflected light is measured photo electrically. The more the intensity of the reflected light received by the detector decreases due to surface modification the more the gloss decrease. As a consequence, the gloss measurement characterised a roughness evolution of the paint surface.
The characterisation might also be reversible. If the gloss measurement is carried out on the degradation products before washing, the result is mainly influence by these products. On the

other hand, after washing the obtained gloss measurement depends on surface degradation morphology after ageing. A very low gloss evolution would be observed due to a uniform degradation. Therefore, even for the simplest method, it's necessary to well understand the signification of each measurement.
Then, the gloss measurement characterised the surface morphology. This characterisation is very qualitative. Atomic Force Microscopy (AFM) would provide very interesting and higher quality, but much more expensive observations.

2.2 Vickers micro hardness

The micro hardness technique, being an elegant, non-destructive, sensitive and relatively simple method, enjoys wide application. The micro hardness technique is more often used on metallic materials but some applications have also been in the characterisation of polymers (Baltà Calleja and Fakirov, 1997). This methodology has been used for characterizing polymer material ageing (Shah et al., 1994)(Startsev et al., 1998).
We have studied the application of the technique for following the degradation evolution of paint coating with time of UV exposure.
One of the most important features of the hardness test is that the hardness value depends on the applied load. The well-known relation:

$$HV = K.\ P/d^2$$

give the Vickers hardness HV as a function of the applied load (P), the indentation diagonal (d) and K that depends on the geometrical of micro hardness indentation. The penetration depth is a function of the geometrical of micro hardness indentation and of the measured value of d. The very small indenter size allows considering micro hardness as a non-destructive test.

The characterisation concerns the first 10 μm depth of the top coat surface.

Table 4 shows micro hardness results obtained on different top coat. The presented values are the average of 10 measurements.

	Acryl urethane	Alkyd	Chlorinated rubber
Reference	17.9 (0.6)	3.4 (0.1)	5.2 (0.2)
Salt spray	19 (1.1)	9.1 (1.4)	6.2 (0.7)
Condensation water	18.4 (1)	8.6 (0.6)	9.8 (2.3)
Cyclic test 1	21.5 (1.5)	**24.7** (2.1)	21.8 (3.1)
Cyclic test 2	**27.2 (1.6)**	11.5 (0.6)	15.9 (2.4)
Cyclic test 3	26.8 (1.9)	22.3 (3.08)	**24.6 (2.7)**

Table 4: Micro hardness results as a function of different artificial ageing tests and different top coats (standard deviation into brackets)

Table 4 shows that cyclic test 2 and cyclic test 3 (the definition of the cyclic tests 1 to 3 and the total duration of the artificial tests are given on Table 5) are the most aggressive for the acryl urethane but cyclic test 1 and cyclic test 3 are more aggressive for the alkyd and chlorinated rubber top coats.

The first conclusion is the specific answer of each top coat in relation with the chemical characteristics of the binder. Moreover, the technique appears to be not very sensitive for separating the ageing effect due to the different artificial tests: cyclic tests 2 and 3 are equivalent for the acryl urethane top coat; cyclic tests 1 and 3 are equivalent for the alkyd and chlorinates rubber top coats.

	Exposition (total duration)	Total UV exposure	Standard
Salt spray	(1440 h)	0	ISO 9227
Condensation water	(810 h)	0	ISO 6270
Cyclic test 1	Rain/humidity/UV (1344 h)	181 h 49 MJ/m^2	NF T 30-049
Cyclic test 2	Immersion/water vapour/ UV (1440 h)	240 h 97 MJ/m^2	NF P 84-402
Cyclic test 3	Humidity/cold/UV (1440 h)	576 h 135 MJ/m^2	NF T 30-550

Table 5: Artificial ageing tests corresponding to results of Table 4

Comparison between Table 4 and 5 shows the great influence of the UV exposure on the hardness evolution. It is obvious that salt spray and condensation water have very low influence on hardness whereas concerning cyclic tests, hardness values might be correlate to UV exposure excepted for the alkyd top coat for which cyclic test 1 is the most aggressive. This cyclic test is characterised by UV/rain rotation i.e. synergic effect of a chemical degradation (UV) combined with physical erosion by rain, which has a significant influence on the alkyd top coat. The specific answer of each top coat in relation with the chemical characteristics of the binder and the weathering factors is confirmed.

Another study on a silicone modified alkyd top coat illustrates the interest of hardness measurements. A continuous exposure to artificial UVA has been applied in a UV chamber (irradiance: 0.77 W.m^{-2}.nm^{-1} – temperature: 60°C). Figure 1 shows the hardness evolution as a function of UV exposure.
A logarithmic evolution is observed. It might indicate a classic kinetic law, which characterises the degradation mechanism.
The hardness measurements carried out on a reference, which has not been submit to UV and temperature (conservation at room temperature) confirm that the measured hardness are not due to drying under ageing conditions.

As a conclusion, the hardness measurements allow to characterise ageing of anticorrosion paint coatings on steel substrate but the technique is not very sensitive for separating the ageing effect due to different artificial tests. Moreover, hardness is only a characterisation of degradation consequences and does not allow reaching mechanisms. On the other hand, hardness measurements would be used for characterising degradation evolutions on industrial site after some complementary validation by more sensitive techniques.

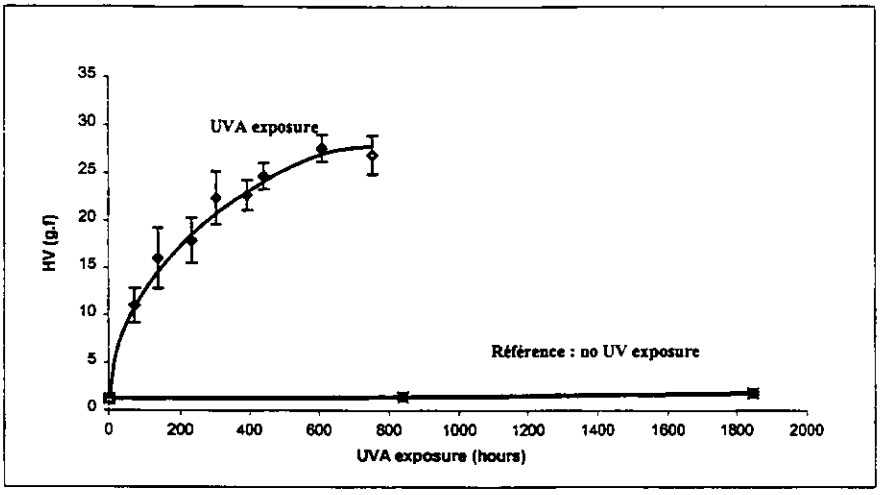


Figure 1: Micro hardness evolution as a function of UVA exposure

2.3 Micro spectroscopy ATR

IR spectrophometry has been extensively used to analyse the chemical changes in weathered specimens such as polymer coatings, paper, paint...Among the different reflection techniques (mostly specular reflection, diffuse reflection and Attenuated Total Reflection (ATR)), the top surface ATR technique is suitable in the present case even if difficulties in establishing an exact contact between the internal reflection element and the rough aged specimen are encountered. A hard silicon crystal (1150 Knoop) is suitable for analysing hard materials such as paint-coated metals. The incidence radiation's depth of penetration d_p can be calculated knowing the wavelength of the incidence radiation, the refractive index of the crystal (Si=4) and the refractive index of the analysed sample. In practice, it is generally accepted that the real analysed depth is about 3 d_p. Thus, in the spectral range 650-4000 cm-1, the depth of penetration of the infrared beam for a sample with a refractive index of 1,5 is between 0.6 and 4.8 μm. This very small size allows considering ATR as a non-destructive test.
FTIR spectra can also be recorded in the transmission mode (KBr disks) using mechanical scraping but owing to the lack of control in the scraped thickness the results are worse.

For instance, comparison between IR spectra obtained with the acryl urethane top coat under ageing conditions of cyclic tests 1, 2 and 3 (see Table 5) shows a degradation of the binder. Figure 2 shows evolution of band intensity between 1500 and 1900 cm^{-1}. At 1527 cm^{-1} (amide II band of low intensity) disappears whereas the band at 1607 cm^{-1}, which is more intense and thus gives more reliable comparative results, appears when ageing. This band can be ascribed to the amide II band of a primary urethane that corresponds to a degradation product. By this way a chemical mechanism process of degradation has been proposed for the acryl urethane top coat.

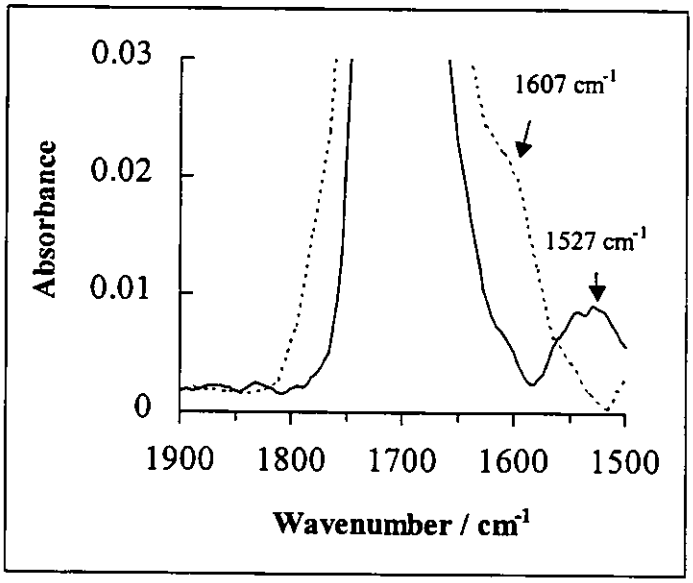


Figure 2: Average micro-ATR spectrum of acrylic urethane paint unexposed and exposed (dotted curve) to cyclic test 3 (see Table5)

A quantification of the binder degradation can be obtained by measuring the band area at 1607 cm^{-1}. The result is normalized to the CH_2 stretching vibration at 1460 cm^{-1} that can be considered constant in the present conditions of degradation. Figure 3 shows the ratio A(1607)/A(1460) as a function of UV radiation.

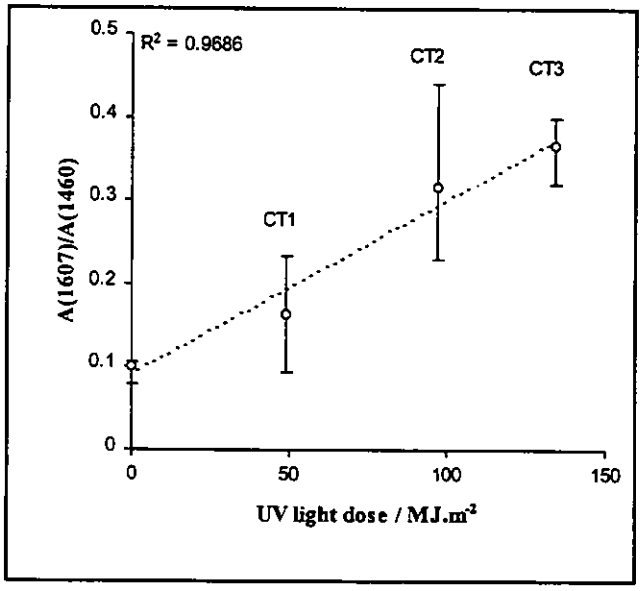


Figure 3: Fractional gain of the 1607 cm-1 amide II signal as a function of UV light dose received by acrylic urethane top coat (cyclic tests indicated into brackets)

Figure 3 shows that the advance in chemical degradation can be directly related to the UV light dose received by the samples.

3. Destructive tests

3.1 Thermal analysis

Thermal analysis allows obtaining the value of the glass transition temperature T_α that is modified with ageing.

3.1.1 Glass transition temperature

Two major types of transition temperatures characterize polymeric materials: the crystalline melting temperature T_m and the glass transition temperature T_α. The glass transition temperature is the temperature at which the amorphous domains of polymer take on the characteristic properties of the glassy state: brittleness, stiffness and rigidity. T_α is a second-order transition involving only a change in the temperature coefficient of the specific volume (a plot of the temperature coefficient of the specific volume versus temperature shows a discontinuity).

Glass transition temperature is now commonly used to characterise material ageing. For instance, insulating cable under radiation conditions has been studied by means of T_α measurements (Chailan et al., 1995). In the same way, it has been shown that T_α increases during thermal oxidation of epoxy resins (Huy et al., 1992-1993).

The physical state of a polymer, glassy or rubbery, is a major importance for the permeability of the organic coating. Above the glass transition temperature the mobility of the polymer segment increases. This results in an increase of the permeability, i.e. a decrease of the barrier properties, of the polymer due to the increase in the diffusion coefficient for permeating molecules. The addition of plasticisers also increases the mobility of the polymer segments, yielding the same result as exceeding T_α. Highly polar polymers can be strongly affected by the permeation of water: the entrance of water results in dramatic decrease of T_α (Bosch and Funke, 1990), which will be accompanied by an increase of the permeability when the temperature exceeds T_α.

During drying, T_α value increases with solvent evaporation but as soon as T_α exceeds room temperature the material become glassy and solvent evaporation becomes more difficult. This solvent retention induces incomplete drying and therefore lower T_α value of the coating. Commonly, T_α value increases also with pigment concentration even if some pigments like micaceous iron oxides have no effect on glass transition temperature.

For an organic coating material, the value of T_α is mainly influenced by three parameters: the solvent retention, the water absorption and the pigment concentration.

3.1.2 Differential Scanning Calorimetry (DSC)

A variety of methods have been used to determine T_α, including dilatometry, thermal analysis, dynamic mechanical behaviour (DMA) or dielectric loss. The most commonly used method for bulk polymer is Differential Scanning Calorimetry (DSC). DSC reflects the change in heat capacity of a sample as a function of temperature by measuring the heat flow required to maintain a zero temperature differential between an inert reference material and the polymer sample.

It is very difficult to determinate the T_α value of paint coating by DSC. After ageing, the coating or one of the coats of the paint system must be selectively removed from the substrate: these sampling problems do not allow a sensitive determination. Moreover, the very small mass of products collected causes too low thermal effects for materials like paints that contain a very high level of charges. As a consequence DMA is more suitable.

3.1.3 Dynamic Mechanical Analysis (DMA)

By measuring the response of a material to an externally applied deformation as a function of the rate of deformation, temperature, or time, it is possible to separate and quantify the viscous (non-reversible and non-recoverable energy part) and elastic (reversible and recoverable energy par) properties of the material. These rheological properties of solids are obtained by applying a mechanical oscillatory strain to the material under test, and detecting the force transmitted through it. The test may be conducted over a wide range of temperatures and oscillatory frequencies. The elastic contribution is characterized by the real part of the complex Young modulus E' and the viscous contribution by tan δ, which corresponds to the evolution of the mechanical loss i.e. energy loss due to internal rubbing into the material. E' and tan δ are two parameters depending on temperature and their evolution allow to identify the glass transition temperature as shown on figure 4.

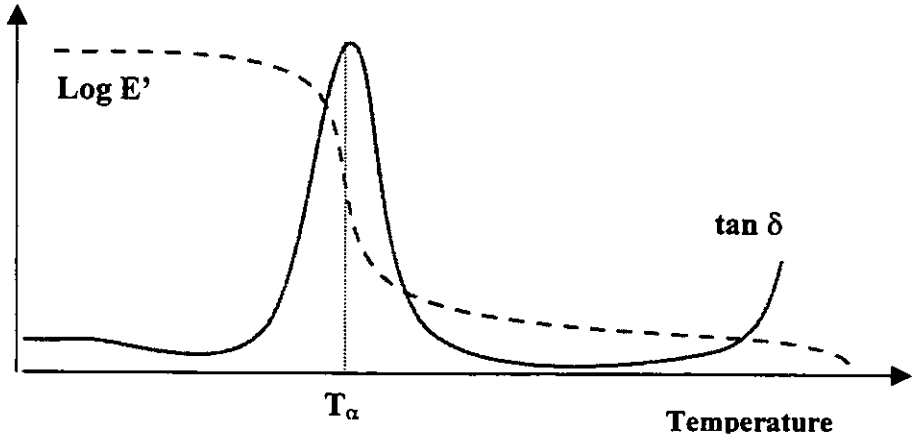


Figure 4: Glass transition temperature determination by DMA

First, we will focus on the effects of experimental parameters that influence measurements. Principle of this approach consists in making a sandwich of the coating material between two steel plates. Coating film is first unstuck from the metal substrate using a razor. For that, he whole system (coating on its substrate) is heated just above its glass transition temperature

during few second. By this way, the coating is in its rubbery state and will not brake during the unstuck treatment. The obtained film is cut for getting rectangular shape of about 4×10 mm^2 and placed between two steel plate of 5×40 mm^2. The sandwich sample is placed in the solid viscoanalyser using a single cantilever tool. The main experimental parameters are the temperature range and temperature rate of heating, the applied strain and the excitation frequency. Previous study (Cuillery et al., 1997 and 1998) has investigated a steel/polymer/steel sandwich and has shown that the polymer relaxation process was little affected by polymer interface quality. That it means that temperature of the alpha relaxation of the polymer material does not depend strongly on the sandwich manufacturing.

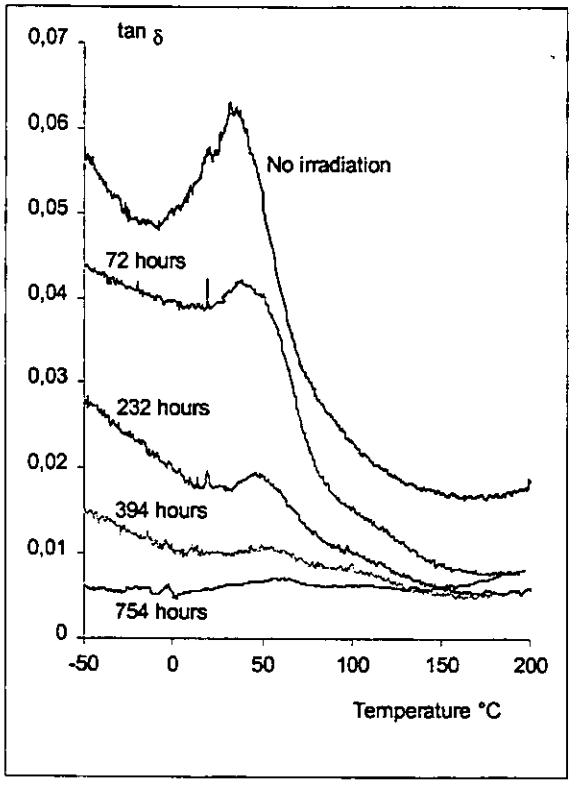


Figure 5: Spectrum of tan δ of a coating material (1 Hz, 5 K/min, 0.5% strain, temperature range between –50°C to 180 °C)

Figure 5 shows tan δ evolution as a function of temperature and UV exposure time. Three main observations must be made:

- Glass transition temperature T_α, measured at the maximum of tan δ curve, increases with UV exposure,
- The height of tan δ peak decreases as UV exposure increases,
- A second tan δ peak appears at higher temperature and seems independent of UV exposure.

For surely concluding that the observed T_α evolution is due to UV ageing, an un-irradiated sample has been tested after the same time of natural ageing at room temperature. No significant evolution is observed. As a consequence, the T_α evolution cannot be attributed to a post-curing of the paint coating.

3.2 Electrochemical Impedance Spectroscopy

As corrosion of coated metals is an electrochemical process it is useful to evaluate the merits of electrochemical techniques in coatings research. DC-technique does not have a broad applicability as the large perturbation applied by the technique makes it destructive and moreover with coatings exhibiting a high DC-resistance the technique gives a poor response. However dynamical techniques such as AC-impedance measurements provide the possibility of investigation systems with a high resistance due to their dielectrical properties. In this way it is also possible to investigate rapid processes and moreover to separate processes characterised by various kinetics: mainly diffusion through the coating and corrosion at the coating/metal interface. This enables the study of the water uptake of the coating (absorption and diffusion mechanisms) and therefore the knowledge about the interaction between the water molecules and the polymer (binder) of the coating. On the other hand, the technique provides the possibility of early corrosion detection, revealing the protective mechanism and monitoring the ageing of the coating due to ageing (Westing, 1992).
Impedance measurements are fundamental because they provide information about the two main properties of anticorrosion paint: barrier properties i.e. water uptake and swelling of the coating polymer and adhesion of the coating to the metal substrate.
It must be noticed that the paint specimen is immerged in an electrolyte and therefore the characterisation technique is associated with an ageing factor. Measurements are carried out after longer and longer immersion times.

3.2.1 Determination of water uptake by impedance measurements

Figure 6 shows evolution of impedance diagram as a function of immersion times in a NaCl 0.1 mol/l electrolyte. The Nyquist curve represents imaginary part Z'' of the complex impedance as a function of the real part Z'.

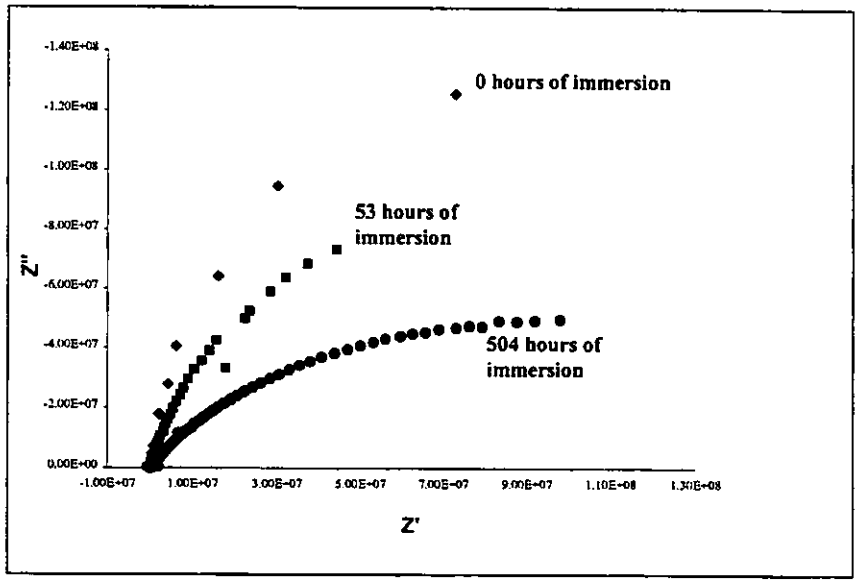


Figure 6: Nyquist impedance plots as a function of immersion times of a two coats epoxy paint system

On each diagram, the high frequency semi-circle is only observed. It characterises the transport processes through the coating. The low-frequency semi-circle is not observed: this indicates that the specimen presents good barriers properties.

The evolution as a function of immersion time can be characterised by following the resistance value R_P (pore resistance) that is given by the diameter of each semi-circle measured on the abscissa axes (axes of the real part Z' of complex impedance). The dielectric properties of the coating are given by the value of the capacitance C_C (coating capacitance) measured for a well-chose frequency. Some models allow to determinate the water uptake Q from the capacitance determination. Figure 7 shows the evolution of Q value as a function of immersion time. This curve is typical of a fickian process i.e. a physical mechanism of diffusion. During the first hours of immersion, a rapid water uptake occurs due to water diffusion in the initials and natural pores of coating. It is a transitory evolution after what the coating reach an equilibrium state. Figure 7 doesn't show the last stage of evolution which occurs after longer immersion time and that corresponds to a rapid degradation of coating and therefore rapid lost of anticorrosion properties.

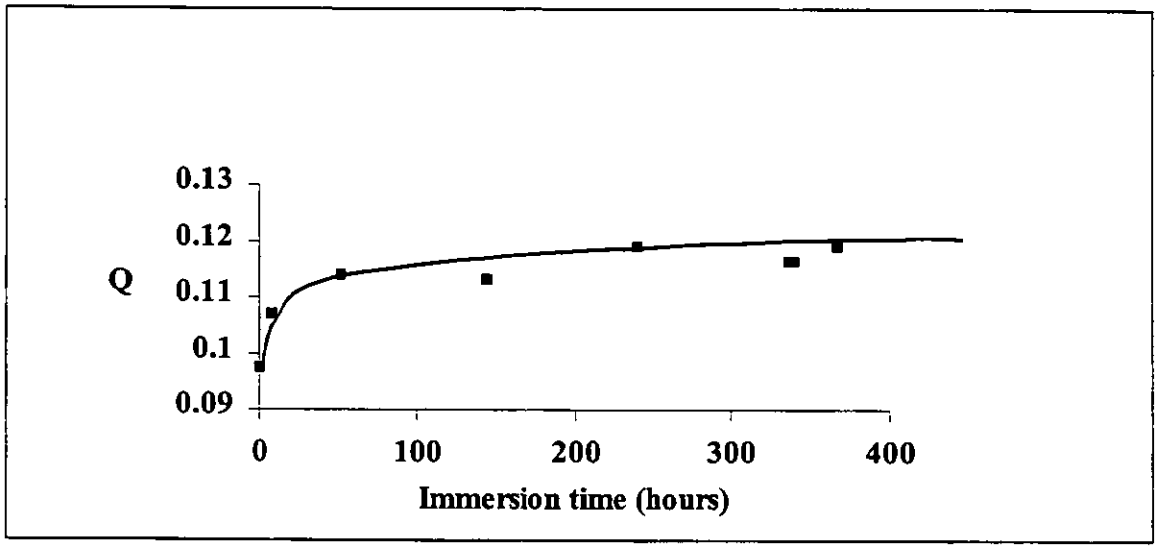


Figure 7: Water absorption as a function of immersion time for a two coats epoxy paint system

3.2.2 Determination of the reactive area of organic coated metals using the Breakpoint Method (BPM)

Evaluation of the electrochemically active area of a coated metal is an important indicator of the anticorrosion properties of a coating. EIS can be used for this purpose with good results. The breakpoint method has been developed to measure the delaminated area, or area where the organic coating is detached from the metal and not protected. The complete mathematical development of the breakpoint method has been reported elsewhere (Haruyama et al., 1987), but the final result has been expressed by the equation:

$$f_{45} = K.\ A_d/A$$

in which the ratio of the delaminated area (A_d) and the total area of the sample (A) is proportional to the breakpoint frequency (f_{45}), the frequency at which the phase angle θ of the impedance is 45°. The constant K is dependant on the studied system and is equal to:

$$K= 1/(2.\pi.\varepsilon.\varepsilon_o\ \rho_o)$$

where ε_o is the vacuum permittivity, ε is the dielectric constant of the organic coating, and ρ_o is the specific ionic resistance of the hydrated coating.
In the Haruyama theory, only the high-frequency breakpoint (f_{45}) is indicated as proportional to the delaminated area. It is not possible to find a breakpoint value for all impedance measurements. In the initial step of degradation in some cases, the phase never decreases below 45°, and therefore, the breakpoint method requires extrapolations. Some authors (Hack et Scully, 1991)(Mansfeld and Tsai, 1991) have found good experimental agreement between the values obtained by the BPM and by observation following ASTM D 610.

Before running measurement, an artificial defect (about 100μm) is drilled into the coating to provide a known value of the area of the defects. By this way, ρ_o is considered to be equal to the specific resistivity of the electrolyte because of the very large size of the artificial defect.

Figure 8 shows a typical example of A_d evolution as a function of immersion time. The delamination process starts after about 20 hours of immersion and later a decrease of A_d is observed due to passivity on steel surface.

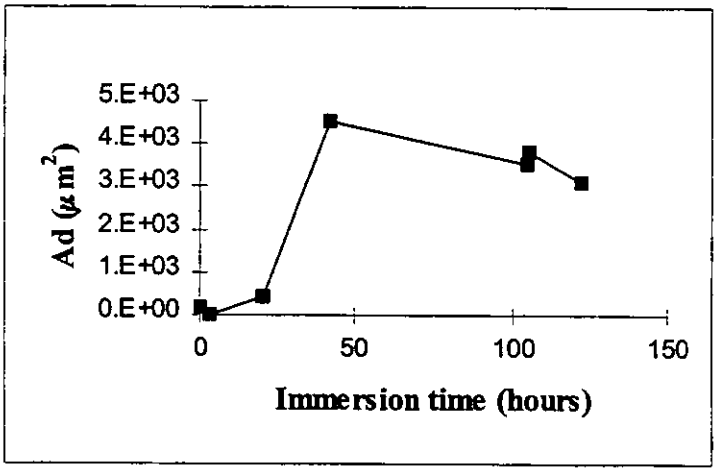


Figure 8: Active area A_d evolution as a function of immersion time of an organic coated metal

4. Conclusion

Evaluation of ageing of anticorrosion organic coatings is a very difficult problem for which a fundamental work of validation of experimental methods is first necessary. For that, it is absolutely necessary to well understand the signification of the obtained measurement. Two types of methods are useable: those, which only provide characterisation of ageing effects and those, which allow reaching information about degradation mechanisms. The first one, which could be more easily used on industrial sites, have to be first validated by using the second one that are more complex and laboratory methods. As a consequence, comparison between methods that present different sensitivities is very interesting.
Table 6 shows the correlation between 3 different experimental techniques applied on top coats after ageing cyclic tests presented on Table 5. Some important observation must be made:

- The correlation between the 3 methods is good for each top coat,
- The sensitivities of each experimental technique are different. The more sensitive results are obtained by ATR spectroscopy that allows getting precise data on chemical mechanism of degradation,
- The sensitivity is also variable with the top coat: better for the chlorinated rubber than for the acryl urethane,
- The answer of each top coat is specific of the ageing parameters

From the most aggressive to the less aggressive ↓	Acryl urethane top coat	Alkyd top coat	Chlorinated rubber top coat
Spectrophotometry	CT 3/ CT 2 SS/CW	CT 1 CT 2 SS/CW	CT3 CT 2 CT 1 SS/CW
Microhardness	CT 2/ CT 3 SS/CW	CT 1/ CT 3 SS/CW	CT3 CT 2 CT 1 SS/CW
IR/ATR	CT3 CT 2 CT 1 SS/CW	CT1 CT 2 CT 3 SS/CW	CT3 CT 2 CT 1 SS/CW
Main ageing parameter	UV duration	UV/rain rotation	UV duration

Table 6: Comparisons between different experimental techniques of characterisation used on different top coats

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Chapter 12

Environmental Testing of Coatings

Dr C Nigel Tuck

Environmental Testing of Coatings

Dr C. N. Tuck
Paint Consultant,
e-mail n_tuck@email.msn.com

Abstract

The environmental testing of coatings, their durability and their lifetime predictions. Coatings for the marine environment focusing on topcoats and antifoulings. The major polymer technologies used in topcoats, their strengths and weaknesses in terms of exterior durability and how their predicted qualities compare with the observed durability from the exposure testing. The effects of the pigmentation on the exterior durability. The impact that VOC legislation is having on topcoat technology and the development of high solids and waterborne systems. The validity of the conventional methodologies employed by the paint industry for environmental testing of these new coatings will be examined. New antifouling technologies are examined in a similar way.

Keywords

Topcoat, Antifouling, Exterior Exposure, Lifetime prediction.

Introduction

This paper will cover the environmental testing of coatings, their durability and their lifetime predictions. It will concentrate, naturally, on coatings for the marine environment and will focus on topcoats and antifoulings. Primers will not be covered in any detail as several of the talks in the current program are focussing on them. This is also the case for antifoulings, but with the visit to International Paints testing site for antifoulings coming up shortly after this paper, it will add understanding to what will be seen there.

The paper will look at the major polymer technologies used in topcoats, their strengths and weaknesses in terms of exterior durability and how their predicted qualities compare with the observed durability from the exposure testing. The effects of the pigmentation on the exterior durability will be covered.

Alkyds, Vinyls, Chlor Rubbers, Epoxies and Polyurethane technologies will be covered and treatment will include their basic chemistry and normal fields of use.

The techniques used to evaluate the environmental performance of topcoats will be discussed; including natural exposure at Florida and Arizona test sites and accelerated testing in QUV.

Consideration will then be given to the impact that VOC legislation is having on topcoat technology and the development of high solids and waterborne systems. The validity of the conventional methodologies employed by the paint industry for environmental testing of these new coatings will be examined.

The emphasis will then switch to antifoulings and a similar treatment will be followed. A run through the technology used in antifouling will be given; bearing in mind that this subject was dealt with in a previous session. The test methodologies used by International Paint at their site in Newton Ferrers will be discussed.

A view on the next generation of antifoulings will be given in terms of their performance and longevity, and of the suitability of current test methods in predicting the behaviour of these products in service.

Topcoat Exterior Performance

1) Alkyds

Alkyd resins form one of the biggest, if not the biggest, genre of surface coatings resins. They date from the late twenties as commercial products for paints and their use has encompassed all the surface coatings market segments, from automotive to decorative, from marine to aerospace.

The name alkyd was proposed by Kienle in 1927 and is the euphonic contraction of 'al' from alcohol and 'cid' from acid, (rewritten as 'kyd' to aid pronunciation). Alkyds are polyesters containing a fatty acid chain and are the product of the reaction of polyhydric alcohols, polybasic acids and fatty monobasic acids.

Alkyds have been classified by 'oil length' and it is a convenient method of dividing them into three broad groups.

Classification	% Fatty Acid (as triglyceride)	Phthalic Anhydride %
Short Oil	30-42	38-46
Medium Oil	43-54	30-37
Long Oil	55-68	20-30
Very Long Oil	>68	<20

Raw Materials Used for Alkyd Preparation.

Oils are used as raw materials in alkyds to impart flexibility, to allow ambient temperature cross-linking through oxidation of the fatty acid double bonds and to allow/promote flow, wetting and levelling during film formation. The most common polyol used in alkyds is glycerol, a triol. Glycerol is used in alkyd resins of all oil lengths.

Pentaerythritol is also a common polyol for alkyd preparation. It contains four primary hydroxy groups and forms more complex resins with phthalic anhydride than does glycerol. Long oil alkyd paints made with pentaerythritol have superior adhesion, weather-resistance, colour, lustre, water resistance and chemical resistance properties in comparison with trihydric alcohols, such as glycerol, and they dry faster than trihydric alcohols.

Phthalic anhydride is the most employed diacid in the alkyd resins industry. Phthalic anhydride gives alkyd resins with hardness and chemical resistance, due to the phenyl structures resistance to rotation. This structure also causes alkyds made from phthalic anhydride to be susceptible to hydrolysis. Isophthalic acid, IPA, is principally used in polyester resins and has less application for alkyd resins due mostly to cost constraints. Its correct use in alkyd formulation enables improvements in resistance to corrosion, hydrolysis and yellowing. It improves the drying rate, as well as hardness.

In many ways, the choice of phthalic anhydride and a fatty acid defines all that is both good and bad about alkyds. Phthalic is the acid of choice because of cost, fatty acids are used to enable ambient cure, ease of surface wetting and cheapness. This sums up alkyds, cheap, effective, easy to use. Down sides are poor exterior durability and yellowing - both of these attributes can be avoided by not using phthalic acid and not using fatty acids, but that puts both the economics and the ease of use out of the window. I.e. it throws the baby out with the bath water!

The weakness of an alkyd has always been their resistance to alkaline hydrolysis and the susceptibility of the unsaturated fatty acid chain to degradation by continuing oxidation, post crosslinking.

Alkyds prepared from oils or fatty acids that are unsaturated, undergo crosslinking or drying by oxidation. The amount and speed of oxidative crosslinking has been shown to be dependent on the degree and type of unsaturation in the fatty acid chain.

The network of crosslinked chains is resistant to solvent and is hard and tough. Unfortunately, the very double bonds that allow this ambient temperature crosslinking are also the downfall of the alkyd. Oxidation of the double bonds continues after initial crosslinking, resulting

eventually in chain scission and film degradation. The fatty acid double bonds are also the cause of yellowing of alkyds. Yellowing is due to β scission as a side reaction during the oxidative crosslinking process. The unsaturated aldehyde produced by the leaving of pentane and a hydroxy radical is an intense yellow colour. The yellowing is much more intense in the absence of light because the aldehyde is 'bleached' by daylight.

Alkyds, like all esters, are susceptible to hydrolysis, i.e. the reverse reaction back to acid and alcohol. The alkyd made from phthalic anhydride is particularly susceptible because of the so-called neighbouring group effect. The result is chain scission by water and breakdown of the alkyd paint. The effect can be minimised by using IPA and pentaerythritol, as mentioned and also by modification of the alkyd by silicones, usually in the form of poly dimethyl siloxanes.

Silicone alkyds are some of the most durable finishes used in the marine industry and their performance is second only to polyurethanes.

Isocyanates may be used to modify alkyds resulting in urethane alkyds. The improvements in hardness and chemical resistance are significant, but the weakness to hydrolysis is still present.

Vinyl Resins

Vinyl resins are copolymers of vinyl chloride or vinyl acetate with various other monomers. They can be formulated to have good chemical resistance and good water resistance. Unfortunately, they are very susceptible to UV degradation and so are not used in exterior situations in marine applications.

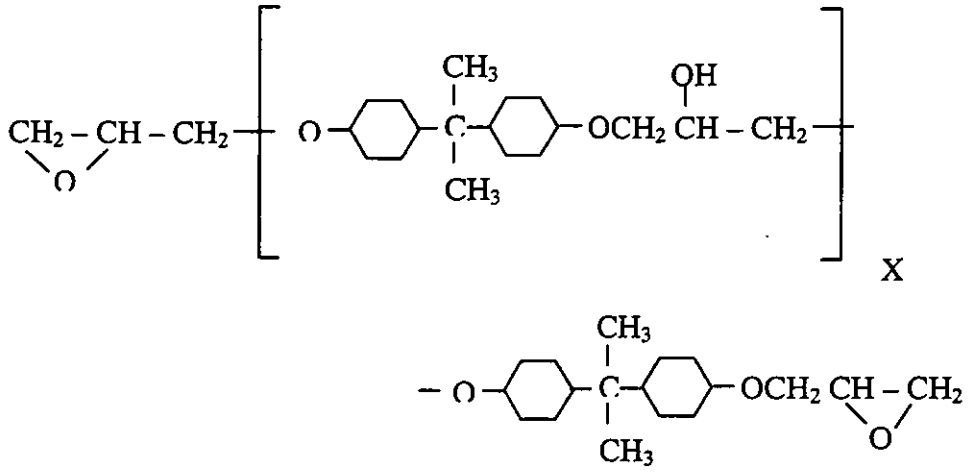
Chlorinated Rubbers

Chlorinated rubber paints have excellent resistance to water and consequently find many uses in underwater marine applications. The are also chemically inert and are not attacked by acids or alkalis and can therefore be used in conditions where cathodic protection is in use.

They are, however, strongly affected by UV light. They can and are stabilised against UV attack by the use of plasticisers with high extinction coefficients over the wavelengths 3100 – 2900 Å. UV attacks chlorinated rubber and causes severe discoloration, so the stabilisers should be non-migratory. Pigmentation helps resist UV and a degree of chalking in a chlorinated rubber paint is desirable, if gloss reduction can be tolerated.

Epoxies

Epoxy resins are the products of condensation of epichlorhydrin and diphenylolpropane derivatives. The best known of the latter is Bisphenol A. The product has the following structure:



Where X indicates the repeat unit.

Epoxy resins have outstanding toughness, rigidity and temperature resistance, imparted by the Bisphenol A moiety. They have excellent chemical resistance from the ether linkages and the hydroxyl groups impart excellent substrate adhesion properties.

However, as seems inevitable in organic coatings, a strength is also a weakness. The Bisphenol A moiety also confers a severe susceptibility to UV attack, such that cured epoxy resins will undergo unzipping in the presence of sunlight and are therefore not suitable as gloss topcoats, unless a rapid loss of gloss, which leads to 'chalking' is tolerable. Chalking is the presence of unbound pigment particles on the surface of a film that can be brushed off, hence the term chalking.

The unbound pigment particles arise because the surface of the paint film has degraded by the resin breaking down, releasing previously coated pigment particles. These pigment particles can have a positive effect in preventing further resin breakdown by acting as a UV screen. Hence, if initial chalking can be tolerated, epoxy coatings can be used as exterior topcoats and the other advantages of epoxies enjoyed.

Epoxy resins are used with polyamides and polyamines as cure agents in 2 pack epoxy coatings. The polyamines or amides react with the epoxy groups, under ambient temperatures, to form the crosslinked network of polymer chains that are so chemical and solvent resistant. Epoxy coatings may be used in temperatures as low as 5° C, but cure is slow and unreliable at less than 7°C. Very low temperature cure agents are available, but performance of the coatings produced is less spectacular.

Polyamine cured epoxies are the most chemically resistant and polyamide cured epoxies are the most water resistant and flexible.

Polyurethane Resins

The basis for these coatings is the reaction of an isocyanate group, - NCO, with a hydroxy group, OH, on a polyester or acrylic polymer. Hence they are 2 pack coatings, the pigmented component is the acrylic or polyester resin and the clear cure agent is the isocyanate prepolymer.

The reaction of an isocyanate group with a hydroxy group leads to the formation of a urethane group, hence the term polyurethane when polyfunctional isocyanates are cured with polyhydroxy resins.

Urethane groups are highly water-resistant and have a resilient toughness not seen in other coatings. Isocyanates that do not contain aromatic groups can be used to formulate coatings that are resistant to UV light and hence very durable as exterior topcoats.

Two pack polyurethanes represent the top of the class in exterior durable coatings and they may be used at temperatures as low as 0° C, as they will crosslink at these temperatures, albeit rather slowly.

Influence of Pigmentation on Exterior Weathering of Topcoats

With certain pigments, UV radiation is absorbed and converted into heat. These pigments act as efficient screens in protecting the resin from UV radiation and so confer good durability on the paint film. Carbon black, red iron oxide and phthalocyanine blue are the best known examples. Iron oxide, even in the transparent from and at low concentrations will act as an efficient screen.

Black paints are usually pigmented with carbon black, which is a strong UV absorber. Consequently, black gloss finishes retain their gloss and film integrity longer than most other colours, in the same resin system.

For other dark colours, the resistance to UV degradation depends on the individual pigment, but if even small amounts of carbon black or iron oxide can be included, the resistance is increased.

White paints and pale shades are based on rutile titanium dioxide and will show chalking over a period of time. Rutile TiO_2 absorbs UV radiation strongly and although much is dissipated as heat, some of the crystals are excited and catalytic degradation of the resin at the surface results.

The surface activity of the TiO_2 is reduced by coating the pigment particles with oxides of aluminium, silicone and zirconium, either singly or in combinations. Hence, the grade of TiO_2 chosen for an exterior topcoat is a special treated exterior grade.

Pale shades are produced by the addition of coloured pigment dispersions to white paint and the pigments used in these dispersions can vary considerably in lightfastness. Some pigments which have a good lightfastness when used as sole pigment, or masstone, can be rather transient when reduced with TiO_2. Among the most lightfast of the organic pigments are the

phthalocyanine blue and green, the quinacridones, dioxazines, anthraquinones and the new Ciba pigment, DPP.

In addition to pigments, another class of materials has a large effect on the performance of a coating on exposure to UV light, and that is the UV absorbers.

Tinuvin 1130 is a UV absorber and is 50% / 38% mixture of two hydroxyphenyl-benzotriazoles, the remainder of the material being polyethylene glycol. Tinuvin 292 is a hindered amine light stabiliser composed of a mixture of bis (1,2,2,6,6-pentamethyl – 4-piperidinyl) sebacate and methyl (1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. The combination of these two light stabilisers is synergistic and with a silicone alkyd, for example, can produce a paint formulation of outstanding exterior durability.

It can therefore be seen that the weathering of a topcoat depends on a combination of parameters, the nature of the resin system, the pigmentation and the presence of additives. For a chosen resin system, be it alkyd, epoxy or polyurethane, there are a number of parameters within the individual resin that will determine the performance of the coating, as has been described. Therefore, when a coating is to be tested for exterior durability, a good idea of the probable durability is already to hand before the test commences. This is an important consideration when designing tests or deciding upon which tests will be used. Equally, when a new coating is being designed for an exterior application, an appreciation of the strengths and weaknesses of the polymer system, the pigmentation and the additives will, of course, be taken into account. In the majority of cases, environmental testing is conducted on a coating with an expected outcome and environmental tests are designed to look for specific issues within a predicted envelope of results. This has potential for problems.

Weathering Test Procedures

When designing test methods for looking at the exterior durability of a topcoat the key issues are water, in the form of rain and humidity and UV radiation. Testing for resistance to specific chemicals is a lesser issue with topcoats, although resistance to acid rain is an important consideration.

Real Time Exposure Testing

The most obvious way, (and arguably the only way), to test the performance of a coating for weathering resistance is to place the coating on the appropriate substrate in the environment where it is intended to be used. However, two things mitigate against this simple approach. The first is that the weather is a variable! It is of course seasonal, can vary from year to year and over relatively short geographical distances. It also varies enormously around the globe! The second is the timescale of the test. If a coating is being designed to last for 15 years, is it necessary to test it for that length of time?

Therefore a natural weathering test and test site should be relatively severe to enable differentiation between coatings and to enable relatively short test durations. It should possess as consistent as possible weather conditions through the seasons.

The Paint Industry has settled on two standard test sites and test methods to enable comparisons between topcoats performances to be made. The first test site is in Florida, USA, and the weathering test consists of exposing the test coating on a panel inclined at 45° and facing due south. The coatings are exposed for periods as short as 6 months and as long as 5 years, depending on the expected lifetime of the coating.

The coated panels are examined at suitable intervals and assessed for gloss, chalking, colour change, cracking, blistering and adhesion. The validity of the test is that a coating of known performance in terms of lifetime in the environment where the coating is to be used, is exposed alongside the test coating.

The Florida test station has high solar radiation and high humidity and it is estimated that one year's exposure in Florida is equivalent to about three years in northern Europe.

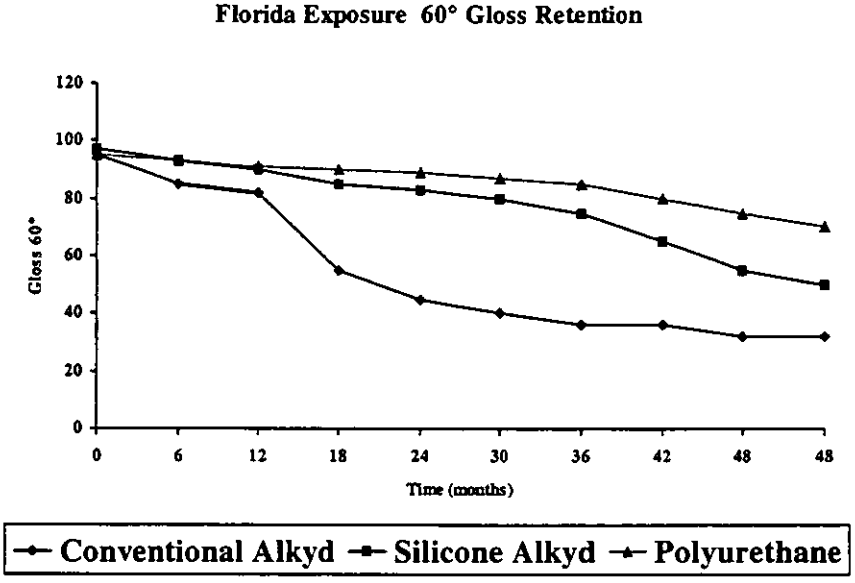
The Florida test has become industry standard for exterior coatings, but the time scale of the test is too long as a screening test for coatings development and so some form of accelerated test was required that was still essentially a natural exposure. To this end a test site in Arizona's Death Valley was developed. The test site is located in an area of very low humidity and very high solar radiation and the test method uses a machine called Emmaqua, Equatorial Mount with Mirrors and water spray.

A number of polished aluminium mirrors reflect the sun's rays onto the test panels, which are sprayed automatically with water for a short period every hour. The machine is mounted on an axis, which is geared to follow the suns path, so that sunlight strikes the panels at a consistent angle during the hours of sunshine. It is estimated that 5 weeks exposure in Emmaqua is consistent with 6 months exposure in Florida.

Florida exposure testing is relatively expensive; Emmaqua testing is outrageously expensive! To minimise costs at Emmaqua, only very small panels are used, and this is a restriction in assessing results. A typical Florida test panel is 30 cm by 10cm and a coating would be exposed in triplicate, whereas an Emmaqua panel would be in the region of 8cm by 3cm.

The first sign of a topcoat degradation on exposure to weathering is a fall in the gloss reading. This usually takes place in the first year or less on Florida exposure. It doesn't signify that the coating has a lifetime of less than 12 months, as it may take a much longer time period for significant film breakdown to occur. However, as a comparison between known 'good' systems and experimental coatings, the gloss retention figures against a standard are handy early indicators of a coatings performance.

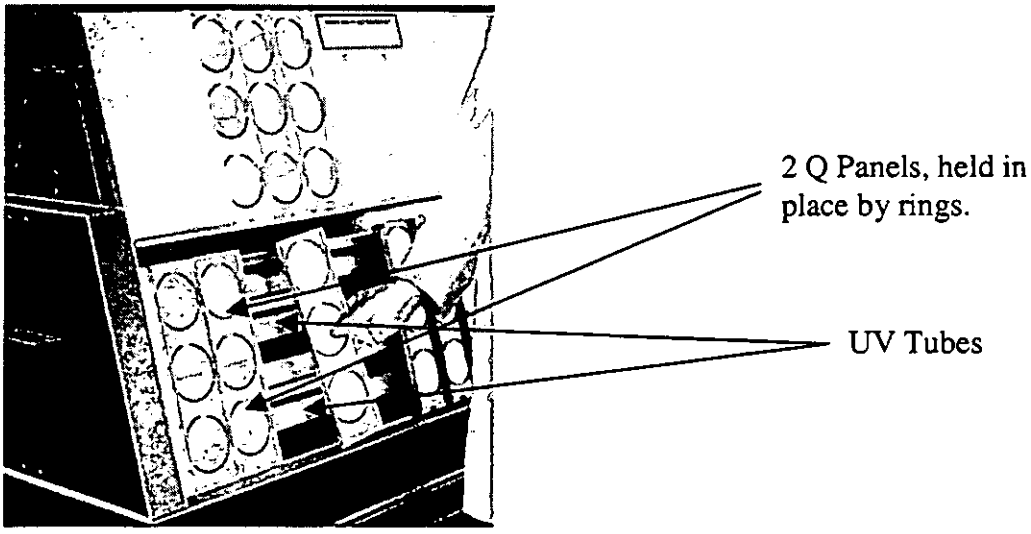
It must be stressed that in any weathering test, the experimental coating must be compared with a standard and that standard must be a similar type of coating – alkyds are compared with alkyds and polyurethanes with polyurethanes. However, to demonstrate the relative performance of alkyds, silicone alkyds and a polyurethane the following schematic of a Florida exposure test is included:



Accelerated Weathering Testing

Due to the long time scales of Florida testing and the expense of Emmaqua, various artificial, laboratory based tests have been developed. Perhaps the most common is the QUV test. (Quick UV). This test method was devised by the Q Panel Company and involves testing coated test panels at elevated temperatures under cycling humidity and UV exposure conditions.

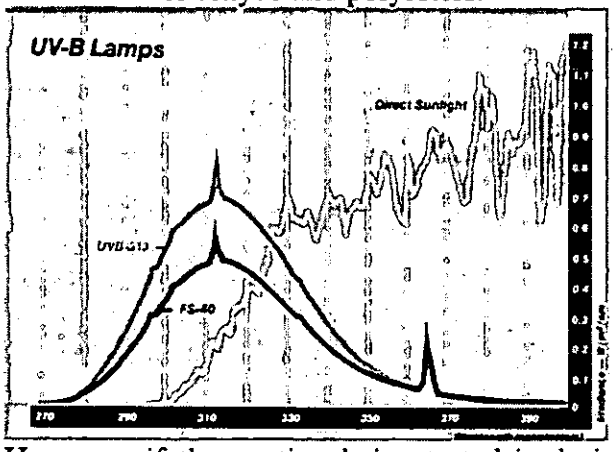
A test cabinet as shown below was devised:



Panels approximately 12cm by 5cm are held in frames and placed in front of UV tubes. The cabinet is closed and the machine switched on. The test regime can be varied considerably and a typical cycle is shown in the table below:

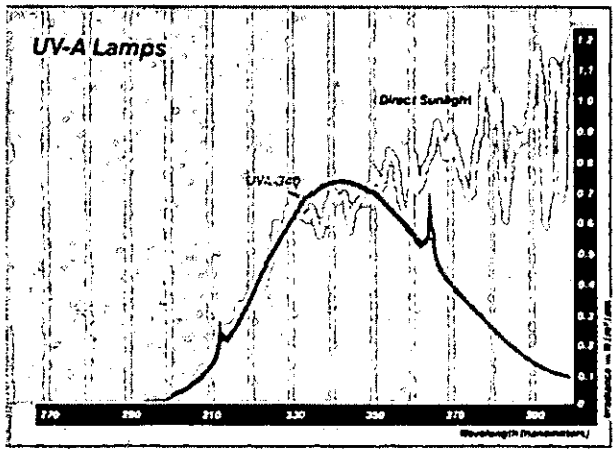
Panel Temperature	60° C
Humidity Cycle	8 hours
UV Cycle	8 hours

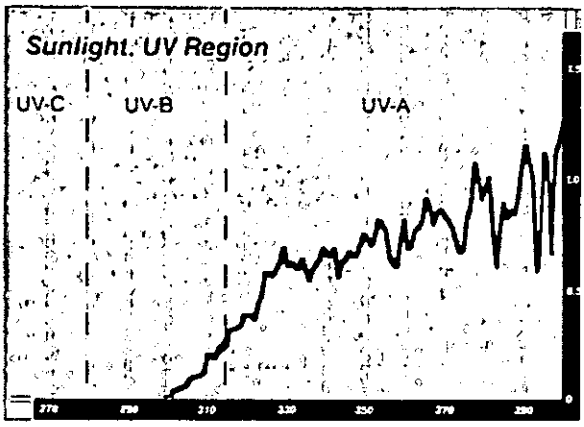
The UV tubes can be of two types, radiating UV A or UV B radiation, depending on the nature of the coating and or the end use of the coating. For example, if the coating is a polyester or alkyd, the UV B tubes have a peak at 310 nm, which attacks the ester linkage in polyesters and alkyds and therefore produces early degradation. Hence, UV A tubes are more often used for alkyds and polyesters.



However, if the coating being tested is designed as an aviation topcoat, then the prevalent radiation at 35,000 feet is UV B, and this would then be the required test regime.

The following two graphs show the UV A spectrum and a comparison between sunlight and the two UV lamp regions.

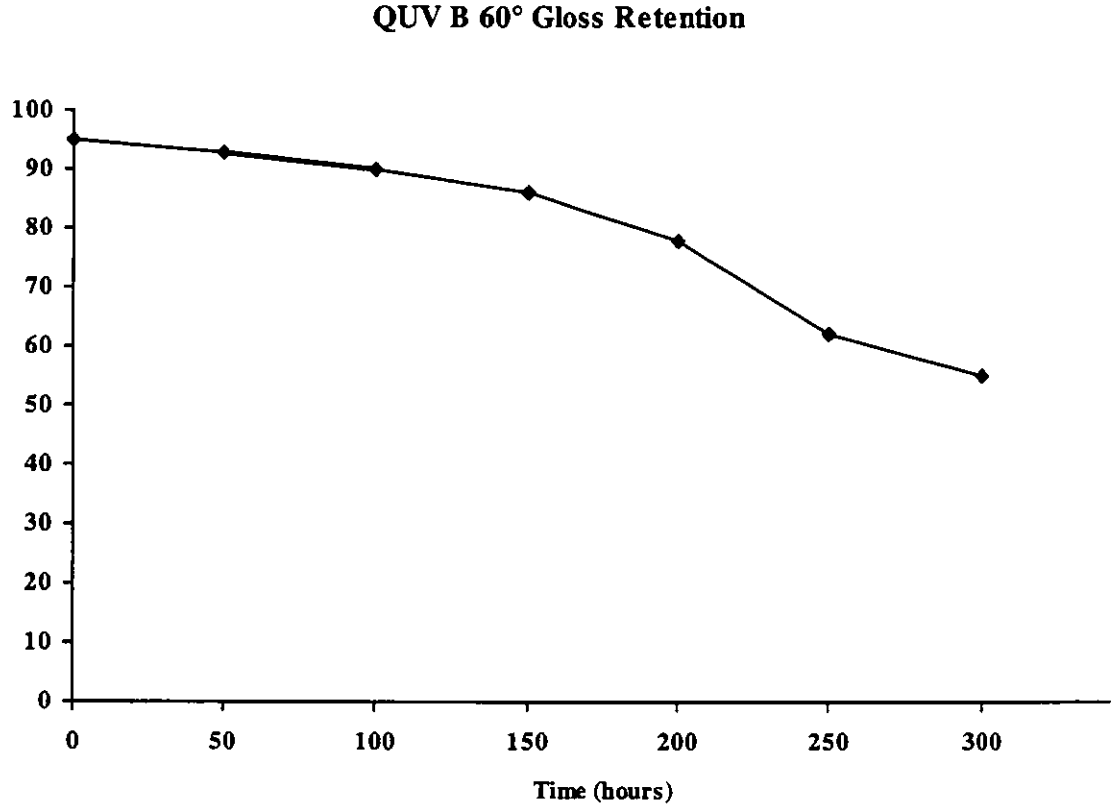




It can be seen that the UV A lamp follows the sunlight spectrum more closely than UV B.

The same issues, of relevance of test to true lifetime for a coating, apply to accelerated testing as to real time natural exposure. Standard coatings of known lifetime performance must be tested alongside experimental coatings for the test to produce meaningful results.

A typical gloss retention graph for a conventional alkyd in a QUV B test is shown below:



As can be seen, the duration of the test is very short to produce significant gloss reduction.

New Coatings Technology and Environmental Testing

The advent of VOC legislation has forced the pace of change in coatings development at a greater pace than any other driver in recent memory. High solids and waterborne technology is now a reality in the marketplace, but how relevant are the existing environmental tests in predicting the lifetime of these new coatings? One thing is for sure; no examples of the new coatings technology have yet been exposed for 15 years or more in real life conditions!

Therefore, claims made by the coatings manufacturers for the predicted lifetime of these new coatings are not based on proven fact, but on extrapolation of test results. The results of tests described above, where it was pointed out that tests were only relevant when known performance controls were used and like was compared with like.

It is, of course, no problem to compare the performance of the new technologies with known real time performance of conventional coatings, but like is not compared with like, so there must be some doubt in the validity of the test results.

This being the case, it is necessary to compare the chemical nature of the new high solids and waterborne coatings with their commercial predecessors. In the case of waterborne systems the comparison reveals that in the majority of cases, the change from solvent borne to waterborne does not usually involve a fundamental change in polymer chemistry. Alkyd emulsions are essentially the same chemically as their solvent borne predecessors, as are the epoxies. The one significant difference to bear in mind when comparing the waterborne/solvent borne alternatives, is the presence of surfactants on the waterborne polymers that can lead to increased water and humidity sensitivity. This sensitivity will show itself up in the existing tests in the early part of the test, so any coatings that have performed well in comparison to their solvent borne 'standards' should go on to perform similarly in real life.

In the case of high solids polymers, the differences in the polymer chemistry are much more significant. In order to produce liquid coatings of significantly lower VOC at the same viscosity as the conventional solids coating, the molecular weight of the polymers must be reduced. This reduction in molecular weight would produce coatings with significantly impaired film performance if other measures were not taken to compensate for this.

These other measures involve ensuring that polymer chain extension and crosslinking is significantly increased during film 'drying'. To accomplish this, new monomers are used and different crosslinking chemistries can and are being employed. These high solids coatings are truly novel and conventional environmental testing may not reveal the true lifetime performance of these coatings. Of course, the coatings manufacturers use their experience to assess the risk of unexpected failure occurring, but at this stage the jury is still out.

Antifoulings

The mainstay of the antifouling market for the last twenty years has been the tin copolymer. As is well known, tin will be banned from use in the near future due to concerns with environmental pollution. A tin antifouling works because the tributyl tin methacrylate copolymer slowly dissolves in sea water by an ion exchange mechanism, releasing minor

amounts of tributyl tin, a biocide, and large amounts of cuprous oxide, the major antifouling biocide, plus a cocktail of boosting biocides.

The excellence of the tin based antifouling is its predictability, it polishes away from the ships hull at an even rate for its lifetime, polishing faster at higher ship speeds and slowly when the ship is docked. 5-year dock to dock cycles are possible with tin antifoulings.

What did we do before tin? The majority of antifoulings before tin copolymers were rosin based. The biocide package was still cuprous oxide and various organic boosting biocides. The rosin-based antifoulings are controlled depletion systems, or CDPs. They function because rosin has a limited solubility in seawater and can gradually dissolve. Unfortunately, rosin does not form a stable film if used as the sole film former and must be combined with other, more stable resins, such as acrylics or vinyls. A typical ratio between rosin and vinyl would be 4:1 for a fast polishing system and 2:1 for a slow polisher.

In a CDP system, the 'supporting' resin does not dissolve or polish off and it remains behind as the rosin slowly dissolves. The result of this is that the cuprous oxide biocide comes out of the antifouling at an uneven rate, very fast at the beginning of the coatings lifecycle and very slowly at the end of the cycle. Antifouling performance will therefore vary and the hull will get rougher instead of smoother, negating another big advantage of the tin copolymer.

CDP systems have been optimised over the years and will offer a viable alternative to tin as the ban comes into effect. However, the 5 year dock to dock cycle will probably not be possible, at least not without some mechanical cleaning at stages of the antifoulings lifetime, to remove the so called leach layer of inert vinyl or acrylic resin.

New technologies are being introduced to offer alternatives to the tin copolymers. One is the non-stick, low surface energy coating that you have discussed elsewhere and so will not be covered here.

The most significant alternative biocidal antifouling technology would seem to be International Paint and Nippon Paint's Ecoloflex. Developed some 10 years ago by Nippon Paint, it is a copper acrylate copolymer that slowly dissolves in seawater by ion exchange, similar to the tin copolymer. The biocide package is cuprous oxide and an organic booster called zinc pyrithione, or ZPT. The performance of the product is certainly excellent in the initial months but may reduce over a period. However, it is certainly better than the CDP systems and has been in service for long enough for some significant, and supported, claims for its performance to be made. Polishing may lead to hull smoothing, unlike CDP systems.

Environmental Testing of Antifoulings

As was the case for topcoats, new antifouling coatings are tested under real time conditions and under laboratory conditions. Unlike the topcoats, the performance attributes being tested under the two types of regime are different. The efficacy of an antifouling can only be tested by real time exposure, i.e. immersion in the sea as opposed to just seawater! There must be animal and weed fouling present to offer a challenge to the antifouling coating. The laboratory testing can, however, measure the release rate of the biocides in the antifouling and the rate at which the coating will polish in seawater.

Efficacy Testing

Two methods are used for efficacy testing. The first is the immersion of coated panels off a raft moored at a suitable test site (static board) and the second is the use of test patches on commercial shipping.

Unlike the case with topcoats, there is no internationally accepted location for the static board testing of antifoulings, although there are commercial test stations, again in Florida. Similarly to topcoat testing, it is desirable to present the antifouling with a suitably severe test and also it is obvious that fouling is a seasonal occurrence. Therefore, test sites are required that are challenging and located in both hemispheres.

On the other hand, a test site must be reasonably accessible to the antifouling chemist, because the assessment of an antifouling test board is somewhat more subjective than a topcoat test panel and is not easily left to less experienced technicians.

International Paint use the Newton Ferrers site because of the reasonable fouling challenge on the UK south coast and its accessibility to their R&D site in the north east. Having had the site for so many years, there is a huge database of results that can be used as comparison for new coatings. Having said that though, it is an accepted fact that no two boards should be directly compared, other than as a broad measure. (A board contains between 4 and 8 test panels).

Antifouling panels are prepared by applying the desired thickness of test coating onto primed panels and affixing the panels to a test board. The test board will have a non-toxic strip to check the severity of the fouling challenge and a standard antifouling to act as comparison for the experimental antifouling.

Panels are immersed in Newton Ferrers for one or multiple seasons and either waterline or deep immersion is used. Panels are assessed for performance every month during the fouling season – April to October. Of course, similar sites exist around the world in order that International can avoid seasonality and check for resistance to multiple fouling organisms.

The method relies entirely on comparisons of performance of experimental coatings with existing proven products and gives an idea of the antifouling performance of coatings under static conditions. This is a useful screening exercise for prospective antifoulings, no more. True efficacy testing of an antifouling is only possible as test patches on ships with real global itineraries and all antifouling manufacturers do this.

Laboratory Testing

Tests for polishing rate and biocide leaching rate are conducted in the lab. To measure the polishing rate of an antifouling, circular Perspex discs are coated with 'fingers' of experimental and standard antifoulings and these discs are then spun at a standard speed in seawater at controlled temperatures. The speed at which an antifouling polishes is determined by measuring the depleted film thicknesses at various positions on the disc, using a laser profilometer. The further along the disc, towards the circumference, the faster the coating is

moving, so a comparison of polishing rate against speed and water temperature can be constructed and comparisons to real life polishing of standard products made. Hence an assessment of polishing rates of antifoulings under real conditions of service can be made.

The leaching rate of biocide, usually cuprous oxide, from a coating can be measured by immersing the coating in seawater of zero copper content and after a suitable period, measuring the amount of copper that is present in a sample of the seawater. This sort of measurement is useful in predicting the performance of an antifouling and for complying with the regulators, who specify the amount of biocide that is allowed to leach out of a coating in a certain time. This type of legislation is becoming increasingly common in various parts of the world.

New Antifouling Technology and Environmental Testing

Because of the nature of antifouling testing, the relevance of the existing tests to the new technology products is less concerning. A test patch is real time testing and so will provide a degree of certainty regarding the likely lifetime of a new antifouling. However, it is essential that an antifouling manufacturer does provide evidence of a 3 or 5 year dock to dock cycle for a new product, there is inevitably much competition presently to demonstrate tin replacement antifoulings!

Chapter 13

The Integration of Prefebrication Primer Coated Steelwork with Modern Ship Construction

R M Hudson

The Integration of Prefabrication Primer Coated Steelwork with Modern Ship Construction.

R.M. Hudson
Swinden Technology Centre,
Corus UK Ltd.
e-mail: Roger.Hudson@corusgroup.com

Abstract

The supply of quality prefabrication primer coated steelwork has become an essential requirement for fast fabrication and construction in modern shipbuilding. Over the years, the paint industry has developed a specific range of prefabrication primers designed to provide adequate corrosion protection during the storage, fabrication and construction stages and to enable satisfactory welds to be achieved without removal of the primer.

The installation of a modern fully automated blast cleaning and priming plant with accurate control over surface preparation and coating application has enabled Corus to supply 'value added' products for immediate fabrication.

This paper reviews the more common types of prefabrication primers and their properties, a description of the automated surface treatment process and the applied technology to ensure consistent product quality.

The results from research projects to examine the properties of traditional and alternative prefabrication primers in response to environmental legislation and their compatibility with laser cutting and welding technology are discussed.

Keywords

Prefabrication primers, shipbuilding, steelwork, paints, welding, environment, lasers, construction, fabrication

1. Introduction

The very competitive nature of modern shipbuilding has demanded improvements in production methods and efficiencies in construction. The industry is adopting new technology and processes to speed fabrication and reduce or eliminate time spent on the preparation of steelwork to an initial condition suitable for down stream operations. It has been recognised that the preparation and coating of the steelwork components is an important factor and needs to by fully integrated in the total construction process. The surface treatment required is usually applied by modern automated plant capable of producing a satisfactory surface condition in terms of substrate cleanliness and profile that is then coated with an appropriate prefabrication primer. To achieve the high quality surface standards suitable for marine paints, shipbuilders can either invest in the installation of on-site modern plant, or upgrade existing equipment if feasible, or source ready treated material from the steel producer. It is the experience of the author that, for a variety of reasons, more shipbuilders are opting to purchase 'off site' treated products that can be immediately profiled and fabricated. This paper describes the benefits of the latter approach and the challenges facing the future of

prefabrication primers brought about by environmental legislation and new laser processing methods.

2. Fabrication and Construction

Ship fabrication and construction has changed significantly over the years to become faster by maximising efficiency and quality to reduce completion times.

In the 1960's and 1970's, the move towards block construction and the introduction of semi automated welding methods found that in particular, fillet welding at high speed was not possible with the range of prefabrication (weldable) primers around at that time. It was then necessary for the primers to be removed locally before welding to ensure that a satisfactory weld could be achieved.

Obviously, such additional treatments were counter productive and that new types of prefabrication primers were developed to be compatible with faster welding processes. The exacting requirements by shipbuilders of prefabrication primers in terms of weldability and durability has highlighted how critically important the primers and their application are as an integral part of the whole fabrication and construction process. The importance of this is reflected in the approach taken by steel producers and suppliers to supply surface treated steel components processed through modern automated plant.

2.1 Modern Automatic Surface Treatment Processes

The successful performance of any coating system depends to a large extent upon the condition of the substrate. The removal of surface millscale, rust and other surface contaminants followed immediately by the correct application of the paint (primer) coating are essential factors. A desirable standard of a coated surface is achieved using modern automated computer controlled 'in-line' abrasive blast cleaning and priming plants.

For many years, blast cleaned and primed plate has been supplied by Corus (formerly British Steel) to customers, primarily in the shipbuilding industry. Until 1994, 'as rolled' plate product was descaled by an abrasive blast cleaning machine followed by the manual spray application of a prefabrication primer to one side of the plate. After the primer was sufficiently dry to handle, the plate was turned over and the second side was coated. This method of operation was labour intensive and required large areas of floor space to allow drying of the paint after application. The time taken to fully paint being dependent upon the shop conditions of temperature and humidity. The size of plates was also limited by the capacity of the handling equipment which sometimes caused localised damage to the coated surfaces.

The installation of a new automatic shot blasting and priming line in 1994, has enabled the surface treatment of plates under controlled conditions by an 'in-line' process. The plant can handle plates up to 4 m wide, 5 mm to 150 mm thick, up to 25 m length and a maximum plate weight of 15 t or 2235 kg/m. The normal maximum operating length is 17 m, but 25 m can be accommodated.

A schematic layout of the plant shows the main units for preheating, shot blasting, painting and drying, as a complete 'value adding' process, Fig. 1.

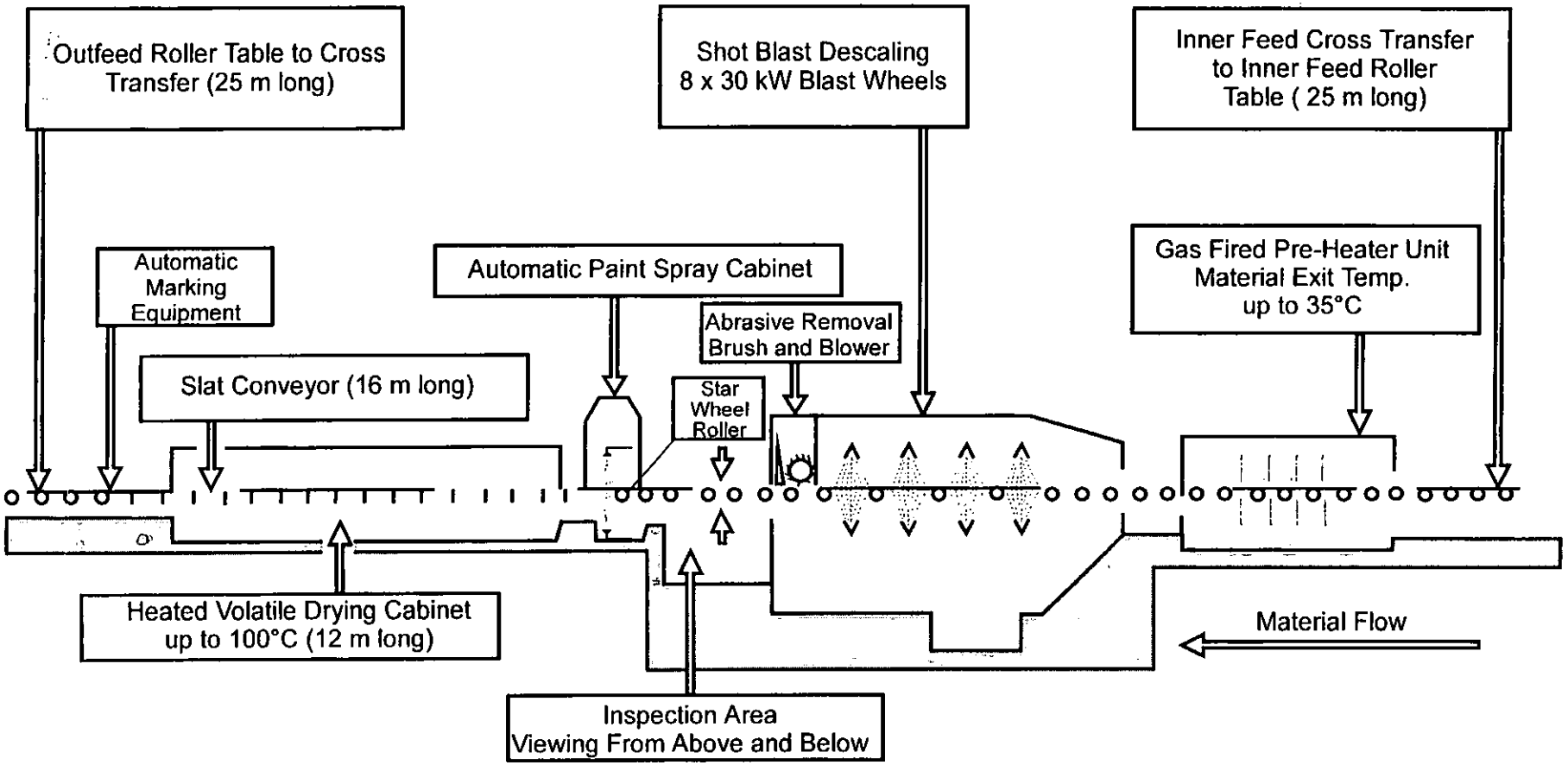


Figure 1 : Schematic View of the Automatic Surface Treatment Plant

The feed stock steel plates generally have a surface condition of either an 'A' or 'B' classification as described in BS 7079 Part A1,1989 (ISO 8501-1) 1988 and abrasive blast cleaning is achieved to Grade Sa 2½ of that standard. A higher standard of cleanliness to Sa 3 is also possible if required. A range of proprietary prefabrication primers can be applied. Each primer specified is applied according to the paint manufacturers data sheets or in exceptional cases to alternative customer specific requirements.

In recognition of environmental legislation, UK Environmental Protection Act, (EPA) and the relevant Process Guidance Notes (PG6/23) applicable to in-house painting processes, the line is designed to operate with either 'compliant' organic solvented based primers or water-borne equivalents. The plant is currently configured to operate with organic solvent based prefabrication primers only which have volatile organic compounds (voc's) contents within the maximum 780g/litre for this category of paint.

The individual units of the line and their operation are described in order of the sequence of processing plate steel product;

2.2 The Pre-Heater Unit

The preheater unit is designed to raise the temperature of the steel from ambient up to 35°C. The thermal shock helps with the descaling process and assists in the acceleration of solvent evaporation after painting. The 6 m long oven has an air knife blower at the entry end to remove any surface water. A series of natural gas fired burners are automatically controlled to adjust to the length and width of the plate.

2.3 The Shot Blast Machine

The shot blast machine consists of three compartments:

- The inlet section fitted with multi-split rubber curtains to ensure an effective retaining seal for the abrasive shot particles.

- The blast compartment fitted with eight 30 kW centre fed centrifugal blast wheels; four above the treated plate and four underside. The position of the wheels is controlled to direct the blast stream to give optimum performance of cleaning.

- The outlet section containing the abrasive removal equipment which comprises a single rotary brush system, working in conjunction with a single air blower.

The machine is fitted with a continuous abrasive handling and reclamation system together with a reverse jet cleaning cartridge type filter unit.

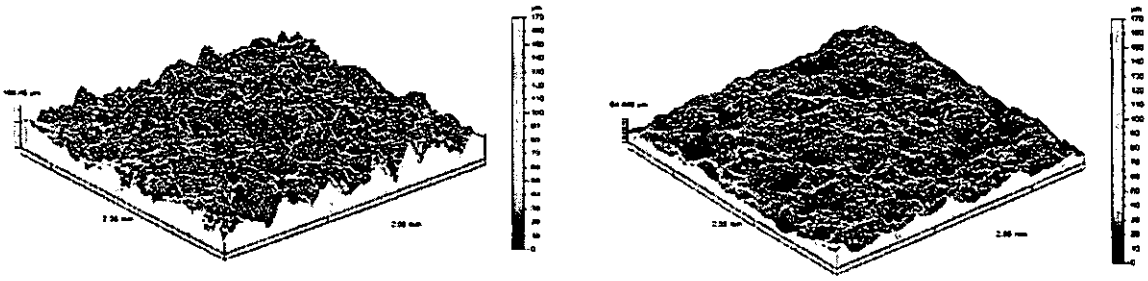
2.3 Plate Surface Cleanliness and Profile

A high level of surface cleanliness and correct profile are necessary to maximise the benefits afforded by prefabrication primers. The type of abrasive used is shot, based upon Type S330 which achieves a standard of cleanliness to Sa 2½ and if required to Sa 3 of BS 7079: Part A1:1989 (ISO 8501-1988). Examinations are carried out on both the

top and undersides of the blast cleaned surfaces in the illuminated inspection area immediately after the shot blast machine. The standard of cleanliness is checked frequently against the BS 7079 Part A1 Standard. The presence of residual contaminants e.g. millscale dust and shot is also checked for on a frequent basis.

The profile produced by the shot is rounded resulting in a surface which is more uniformly coated during the application of the thin primer coating than would be achieved on sharper profiles formed by grit abrasives which can leave the peaks of the profile either very thinly coated or unprotected.

A comparison between the two types of surfaces produced by grit and shot abrasives can be made by reference to the three dimensional surface representational (axonometric) diagrams, Figure 2. The shot blasted surface representation is typical of that produced by the automatic line.



Grit Blasted **Shot Blasted**

Figure 2. 3 Dimensional (Axonometric) Diagrams of Grit and Shot Blasted Steel Surfaces

As the shot is used, it breaks down in size and a 'working mix' is achieved. Control of the shot particle sizes is achieved by regular monitoring and sieve analysis to ensure that an effective working mix is maintained.

The surface profile is measured every operational shift using a calibrated Surface Profile Gauge to ensure that it remains within the specified range 30 to 100 μm; typically 42 μm average.

2.4 The Automatic Painting Equipment

The automatic painting equipment is situated after the inspection area following the shot blast machine. The workpiece is conveyed into the spray chamber on a 'star wheel' to minimise wet paint pick-up on the roller. The spray equipment is contained in an enclosure with a water screen and wash extraction system. Two reciprocating painting heads, one above and one below the workpiece, are fitted with airless spray guns. Automatic work detection sensors ensure that overspray is kept to the practical minimum. The rate of reciprocation of the spray guns is synchronised to the conveyor speed to ensure that a satisfactory overlap pattern is achieved with an even paint thickness. The primed workpiece is carried on a slat conveyor designed to support the painted workpiece

by point contacts on its edges to minimise contact between the wet applied paint and the conveyor.

2.5 The Heated Drying Tunnel

The heated drying tunnel is 12 m long and is situated immediately after the automatic painting enclosure and positioned over the slat conveyor. It is designed to accelerate the drying and curing of the primer paint coating and to extract solvent fumes. The tunnel is heated by a gas fired forced draught burner with a flame tube blowing through two centrifugal fans. The air temperature is variable up to 100°C, selected through a digital controller linked to a thermocouple inside the tunnel. The capacity of the tunnel is designed to dry both organic solvent and water borne primers to be suitable for handling on exit.

2.6 Automatic Marking Machine and Direct Despatch

Upon leaving the drying tunnel, the primed plates are automatically marked by a computer controlled automatic ink marking machine. The Corus logo and an appropriate identification to customer requirements appear in characters from 50 mm to 120 mm in height on the top surface. The identification can be up to 6 lines of the 50 mm characters. The primed plates are then cross transferred to an adjacent bench by lifting from their undersides. To avoid surface damage, the plates are then raised by soft faced (cushioned) vacuum lifts to awaiting road wagons where they are separated with wood battens to minimise surface marking (if required) and sheeted for protection from the weather ready for direct despatch to the customers stated destination.

2.7 Control of the Primer Coating Thickness

One of the most critical factors influencing the successful use of prefabrication primer coated steel is the coating thickness. It has become increasingly recognised that incompatibility problems demonstrated by unacceptable levels of weld porosity are not necessarily directly attributable to the primer. More often, such problems have arisen because of the 'over application' of the primer and not due to the primer itself. The paint manufacturers have recognised that control of the primer thickness is significantly important and have examined ways and methods to measure the thickness of a thin coating on a profiled surface. It is widely agreed that reasonably accurate measurements taken on the blasted and primed treated surface are difficult to achieve consistently. For this reason, a new standard method of measurement on the smooth surfaces of strips of plastic, glass and metal attached to the steel at the time of processing provide a satisfactory acceptable means of control. The majority of paint manufacturers now specify a required or typical dry film thickness (d.f.t.) to be as measured on a smooth surface and this method now appears in the paint data sheets. Usually there is also an equivalent estimated thickness on the processed steel surface which can be calculated with respect to the surface profile and amplitude achieved from the blast cleaning operation.

The most usual nominal thickness specified is around 20μm ±5 μm although thinner coatings are now increasingly required. The method of thickness measurement is based

on a new BS EN Standard 10238:1997 'Automatically Blast Cleaned and Automatically Primed Structural Steel Products.' The thickness is measured using a calibrated electromagnetic induction paint thickness gauge on a smooth steel panel attached to the surface of the blast cleaned plate before painting. (The accuracy of the thickness gauge is verified against a calibrated 25µm plastic shim with its thickness validated according to a Quality Operating Procedure).

The smooth panel is then primed automatically at the same time as the workpiece. The average dry film thickness from 20 individual measurements has to be within the defined tolerance of the nominal specified thickness. Corrective action is taken when unacceptable measurements are found. The data are recorded and the panel stored for future reference.

3. Properties and Requirements of Prefabrication Primers

Prefabrication primers are applied as thin film coatings (15 µm to 25 µm) to blast cleaned steel to provide short term corrosion protection during fabrication and construction periods. The primer may then be overcoated with a compatible paint system or be completely removed and a full protection system applied. It is important that all prefabrication primers meet the following property requirements;

- Suitable for airless spray application by automatic plant
- Quick drying for resistance to damage during handling and transportation
- Provide adequate corrosion protection
- Not affect welding or cutting operations (Welding Certificate)
- Sufficient thermal stability when subject to high temperatures
- Not produce fumes in excess of permitted levels (Health Certificate)
- Be compatible with overcoating systems
- Be compatible with cathodic protection systems, if appropriate
- Require minimal secondary surface preparation

Some of these properties may conflict e.g. a low film thickness facilitates quick drying and minimises the risk of porosity during welding but also reduces the protection against corrosion. Sometimes, there is a customer requirement to apply the primer thinner than that specified in the manufacturers' data sheet to minimise weldability problems.

It is generally recommended that prefabrication primers are tested to establish the tendency to form porosity in welded joints. Standard test procedures, to DVS 0501 'Testing of Pore Formation Tendency when Overwelding Production Coatings on Steel', or similar, are used by recognised test authorities who, upon achieving a satisfactory result, issue a Certificate of Approval.

In addition, there are health and safety requirements relating to the acceptable amounts of hazardous fume, particularly zinc fume released during welding. Similar to the Welding Certificates, prefabrication primers are tested and certificated by recognised authorities. All reputable proprietary prefabrication primers have both welding and health and safety certificates.

4. Types of Prefabrication Primers

The most commonly applied prefabrication primers applied are from one of the following categories:

Etch (single and two pack)

Etch or PVB primers are based on polyvinyl butyral resin reinforced with phenolic resin to improve weathering properties. Phosphoric acid is incorporated which acts as a curing agent and as an etchant to the steel surface. The low volume solids together with the fast evaporating solvents produces a quick drying film. These primers are usually pigmented with iron oxide with zinc phosphate added for corrosion inhibition. The durability of these primers is generally short term. The cutting properties are good, but welding speed is low and the damaged coating at the 'burn back' width has to be removed. This type of primer is not suitable for immersed conditions where cathodic protection systems are to operate.

Two Pack Epoxy

Epoxy based prefabrication primers were introduced to have improved durability and compatibility with cathodic protection systems compared with the PVB types, although similar to the PVB primers, the cutting properties are good but the welding speed is low and the 'burn back' width has to be removed. The zinc rich epoxies, whilst having excellent corrosion resistant properties, have the drawback of reduced speed and quality of welding coupled with the formation of zinc salts during storage and fabrication, resulting in the need for thorough secondary surface preparation. The high organic content of the epoxy primers also makes them unsuitable for double fillet welding at high speed and therefore has limitations with modern fabrication processes. The use of the zinc rich epoxies has markedly declined, also because of the unacceptable volumes of zinc fume produced during welding and a high risk of weld porosity.

Zinc Silicate

The epoxy primers have generally been replaced with zinc silicate primers that have good corrosion protection and can therefore be applied as thin films which in turn have the advantage of good cutting and welding properties at high speed processing. The inorganic nature of these primers gives other benefits including less porosity formed in double fillet welds and there is minimal 'burn back' along the weld edges.

The original zinc silicate primers contained up to 90 % by weight of zinc which caused zinc fume during welding and required a high standard of secondary surface preparation to remove 'white' zinc corrosion products. Subsequently, reduced zinc content primers were introduced as first, second and third generation types containing 60 to 70% zinc, 40 to 50 % zinc and 25 to 35 % zinc respectively. The zinc was replaced with extenders to increase the welding speed and reduce zinc fume and porosity.

Of the main generic types of prefabrication primers, most demand is for the zinc silicate type, particularly the 'third generation' low metallic zinc content types. These are

preferred for their durability during storage and fabrication, high heat resistance, low burn damage, and low porosity risk during most conventional welding procedures. The low zinc silicate types are sometimes applied at reduced film thicknesses (down to 15 μm) and are generally acceptable at a correspondingly lower level of durability to take advantage of the benefit of having good cutting and welding properties.

Most zinc silicate primers are suitable for use with controlled cathodic protection systems.

5. Challenges to Prefabrication Primers

Whilst the range of prefabrication primers commercially available has been continually developed to meet industry requirements, there are two significant challenges to the established products that will have a bearing on their future use.

The acceptance that the volatile organic compounds (voc's) in many existing primers are environmentally damaging and the compatibility of these primers with new fabrication methods provide scope and opportunity for a review of their formulations and properties.

5.1 Environmental Legislation - 'Compliant Coatings'

The ever increasing impact and awareness of the environmental damage caused by volatile organic compounds (voc's) has brought mounting pressure to bear on the paint industry to formulate environmentally friendly paints.

With the introduction of the Environmental Protection Act (EPA) in the UK in 1990, limits were proposed to restrict the amount of voc's released from paints during their application. An original limit of 250g/litre of paint regardless of type was the target figure to be achieved by 1998. However, after representation by the paint industry, the legislation was amended to consider different categories of paint as etch, wash and blast (prefabrication) primers, intermediate coats and finishes with voc limits set as; 780g/l, 250g/l and 420g/l respectively. The voc limits in the different categories and alternatives of achieving 'compliance' for painting processes are set out in Process Guidance Note PG26/3. Reductions in voc emissions may also be achieved by the use of abatement equipment to 'arrest' solvents released at the time of paint application, however, to achieve this would require the installation of specialist plant if not already fitted to the painting line.

In the case of prefabrication primers, the very nature of their formulation with low solids content does not readily allow them to be formulated to have a low voc content although water borne equivalents with identical properties appeared to offer a possibility.

With a view towards the pending revision of the Process Guidance Notes, water borne technology has been investigated and several experimental formulations were obtained by Swinden Technology Centre, examined and compared with the traditional prefabrication primers.

A programme of work to investigate the properties and characteristics of these primers in natural and artificial weathering tests and the weldability of several 'alternative' formulations was initiated in 1994. The results from this work indicated that all of the primers examined had acceptable drying and welding properties however, the environmental exposure test results suggested that their durability, with the exception of water borne zinc silicates, would not be satisfactory when compared with the traditional formulations. To date, there has been limited development and minimal use of water borne prefabrication primers, however, environmental damage control measures are expected to renew interest in these products.

5.2 Laser Cutting and Welding

Modern formulated prefabrication primers are compatible with conventional cutting and welding techniques e.g. oxy/fuel and plasma processes and of these primers, the most widely used are zinc silicates, especially those containing a low zinc content to reduce the risk of porosity in the weld joint.

However, the introduction of laser technology for cutting and welding operations has raised concerns as to the compatibility of the currently applied prefabrication primers with laser processing. It is known that reductions in the normal primer dry film thickness are specified to ensure a satisfactory quality of laser cut edge but less is known about the use of these primers with laser welding. Where laser welding is to be carried out then the primer is normally removed from the weld area to avoid porosity and a poor quality weldment.

Laser welding offers the fabricator a number of advantages over conventional arc welding processes such as Metal Active Gas (MAG) welding. These are principally:

- Low heat input, which minimises distortion and metallurgical changes in the parent material.
- High Productivity, because of the ability to weld thick sections in one run.
- Ability to reach areas that are otherwise inaccessible using conventional welding processes.

Laser welding is being used by an increasing number of industrial sectors such as automotive and shipbuilding. It is understood, that at present, fabricators remove the primer from the weld joint zone before laser welding to ensure that the weld does not produce significant defects. However, this additional treatment contradicts the benefit of fabricating material coated with a prefabrication primer. Such additional processes therefore are counter productive and disadvantageous.

In anticipation of the progressive increase in the use of laser equipment for fabrication in the construction industry, it was considered necessary to determine the limitations of the currently used primers with laser techniques and to explore the formulation with a view to the development of new novel 'laser friendly' prefabrication primers.

Towards this objective, a programme of work was designed to compare the performance of Shipbuilding Grade A, 6 mm thick plate to BS EN 10 025 S275, shot blast cleaned to Sa2½ of BS 7079 Part A1 in the uncoated (as blasted) condition and coated on both plate surfaces with three traditional and two experimental prefabrication primer as follows:

- A traditional zinc phosphate epoxy at 25 μm [(1)]
- A traditional zinc silicate at 13 μm (approx. 55% zinc*)[(1)]
- A traditional zinc silicate at 22 μm (approx. 32% zinc*)[(1)]

  * zinc content by weight in the dry film

- Experimental primer A[(2)]
- Experimental primer B[(2)]

  [(1)] Cutting and Welding [(2)] Welding only

The experimental primers were formulated without metallic zinc and silicate binder in an attempt to reduce the 'volatile elements that are considered to cause porosity in the welds.

The primer thicknesses are expressed as a dry film thickness (d.f.t) as measured on a smooth steel surface and applied in accordance with the paint manufacturers' data sheets.

These panels were then sheared to 0.5 m squares for the cutting and welding trials.

A 25 kW CO_2 convergent energy laser was used to carry out the cutting and welding trials. Metal Active Gas (MAG) conventional arc welding was chosen as a conventional welding method for comparison with the results from laser welding.

5.1.1 Laser Cutting Trials

Cutting trials were initially carried out on uncoated plate under various conditions to obtain the most visually acceptable cut, based on an examination of roughness, dross, drag and melting of the top edge, all of which need to be minimised to improve the quality of the cut edge. Squareness of the cut edge was also visually assessed. From the visual assessment, optimised variables were established for the cutting trials.

The same variables were also used when cutting each of the primed plates.

For the assessment of laser cut quality, the typical parameters that can be considered are:

- Presence of and adherence of dross after cutting
- Quality of the cut edge e.g. squareness and roughness
- Metallurgical changes adjacent to the cut edge
- Distortion due to the relief of residual stress

The parameters considered most important to this investigation were examined after the cutting of uncoated and primed plates, using optimised conditions. The results from the trials indicate that dross was either minimal or absent on the edge and that all conditions

achieved a similar level of perpendicularity when measured using an engineers try square and feeler gauges.
The method of assessment for quality used the methodology outlined in the draft standard ISO/TC 44/SC 8N 663:1999, 'Thermal Cutting – Classification of Thermal Cuts – Geometric product Specification and Quality Tolerances'. (The document is intended to supersede ISO 9013:1992).

The average quality of the cut edges for the uncoated and three types of primers applied is shown in Table 1.

Plate Treatment	Average Drag n (mm)	Average u Perpendic -ularity Tolerance (mm)	U Range ISO/TC 44/SC 8N 663:1999 Figure 13b	Average Ra (μm)	Average Rt (μm)	Average Rz5 (μm)	Rz5 Range ISO/TC 44/SC 8N 663:1999 Figure 13b
Uncoated	0.82	0.14	2	16.81	100.11	29.4	2
Epoxy Zinc Phosphate	0.82	0.14	2	14.65	92.78	23.7	2
Medium Zinc Silicate	1	0.15	2	8.45	56.61	19.94	2
Low Zinc Silicate	0.81	0.13	2	8.55	51.91	18.14	2

Table 1 Average Quality Laser Cut Assessment Readings

Of particular significance was the surface roughness measurements obtained using a traversing stylus instrument.

The results have indicated that none of the prefabrication primers had a significant detrimental effect on the quality of the laser cut edges and that zinc silicate primers, particularly the low zinc content type, appeared to have improved the cut edge quality compared with the uncoated condition, Figure 3.

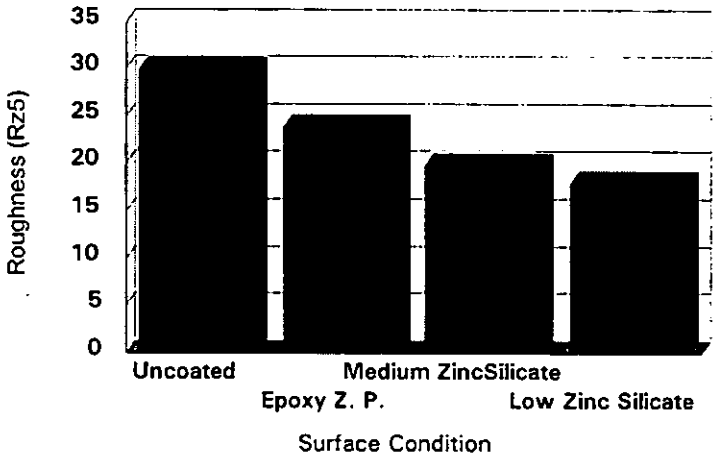


Figure 3 : Average Surface Roughness Measurements of Laser Cut Edges (R_{Z5})

5.1.2 Laser and Automatic MAG Welding Trials

Both laser and Metal Active Gas (MAG) welding processes were used to compare the performance of the primers examined.

Guillotined strips 100 mm wide by 500 mm long were cut from uncoated and primed steel panels for the welding trials which comprised;

Laser butt welds, laser fillet overlap welds and MAG welds.

For the laser welding, the angle of the laser beam was set at 8°, whilst for MAG welding the angle of the welding head was set at 45°.

The laser focal length and power remained unchanged throughout the experiments at 514 mm and 10 kW respectively and the speed was set at approximately 1.4 m/min.

However, in view of the excessive spatter and weld defects observed during the first fillet weld trial on each type of the two experimental primed coated plates, a second trial with a slower speed of 0.96 m/min and higher power of 15 kW was applied. This change in parameters was intended to provide a full penetration weld, thus aiding the escape of volatilised paint from the weld joint.

During MAG welding, all butt welds had a 3.2 mm root gap and a ceramic backing tile was used to control penetration. A 1.2 mm diameter Carbofil 1 solid wire steel electrode, manufactured by Oerlikon, was used with an electrode extension (stickout) of 20 mm and CO_2 shielding gas at a flow rate of 18 litres/min. The power was DC+ve with a welding current of 220-230 Amps and 29 Volts. The welding speed was set at 300 mm/min to give an arc energy of 1.3 kJ/mm.

The weld quality was assessed using non standard impact fracture tests and extraction of longitudinal and transverse sections from the welds.

For the fracture tests, sections 50 mm wide, were extracted from all overlap fillet welds, cooled to -186 °C using liquid nitrogen, immediately transferred to a vice and impacted with a hammer.

Visual examinations of the weld fractures were made, which consisted of an assessment of the severity of porosity in the weldment, Table 2.

Laser Weld Type	Primer	Lack of Cap Fusion	Lack of Root Fusion	Lack of Penetration	Porosity
Butt	None				
Butt	Zinc Phosphate Epoxy				
Butt	High Zinc Silicate				
Butt	Low Zinc Silicate		✓		
Fillet	None				
Fillet	Zinc Phosphate Epoxy		✓	✓	✓
Fillet	High Zinc Silicate		✓	✓	✓
Fillet	Low Zinc Silicate		✓	✓	✓
Butt	Experimental Primer 1				
Butt	Experimental Primer 2				
Fillet(1)	Experimental Primer 1			✓	✓
Fillet(1)	Experimental Primer 2			✓	✓
Fillet(2)	Experimental Primer 1		✓	✓	✓
Fillet(2)	Experimental Primer 2		✓	✓	✓

(1) 10kW at 1.4m.min (2) 15kW at 1.0m/min ✓ Presence of Defect

Table 2 Observations of Transverse Section of Laser Fillet or Butt Weld

Longitudinal and transverse sections were cut from each weld, mounted in bakelite, ground, polished to 1μm, etched in 2 % Nital for macroscopic examination.

The presence of defects for laser and MAG welds are characterised according to the presence of cap and root lack of fusion, lack of penetration and porosity .

Cap and root refers to the top and bottom of the weld respectively. No defects in longitudinal laser butt welds, sectioned in the cap and root, were observed.

5.2 Assessment of Results from Laser Cutting and Welding Trials

The results from this programme of work and the assessments of the quality of laser cut edges and laser welds examined have provided an indicated of the compatibility of a range of prefabrication primers with laser techniques.

It is encouraging that laser cutting of plate coated with zinc silicate type prefabrication primers had a superior cut edge quality compared with either the zinc phosphate epoxy primer coating or the uncoated condition. The fact that the zinc silicate types are more extensively used today than other types of prefabrication primers provides an unexpected benefit in the fabrication process.

In the laser welding trials, it is evident that joint geometry is a significant factor in the formation of porosity in the joints. None of the primers tested caused unacceptable butt

welds in terms of porosity, however, in the laser fillet joints, there was lack of penetration and unacceptable levels of porosity. This result was consistent with both the traditional and experimental primers, although there were indications that the two experimental primers produced less porosity in the fillet joints that the traditional primers. An increase in laser power in an attempt to obtain full penetration of overlap fillet welds still produced defects but to a lesser extent and this suggests that modifications to the formulation to remove 'reactive' components may be beneficial. However, it would also be necessary to determine the durability of such primers during the storage and fabrication stages of construction.

The MAG welds did not produce any porosity or defects in the uncoated or traditionally primer coated tests except for some lack of root fusion in the butt welded zinc phosphate epoxy primer coated panel. However, this defect was not observed in the MAG welded panels coated with either of the two experimental primers.

6. Summary and Conclusions

The progressive increase in the supply of quality processed prefabrication primer coated steel by modern automatic plant to the shipbuilding industry has provided significant benefits. The traditional commercially available prefabrication primers have been developed and modified by the paint industry to meet the exacting requirements of modern fabrication processes. It has become increasingly apparent that coating thickness is a critical factor in the successful welding of prefabrication primer coated steel. A new standard method of measurement has enabled control within a tight range and reduced problems during fabrication.

Anticipated changes in the restrictions imposed by environmental legislation has necessitated an examination of alternative formulations including water borne primers. The results form the testing of a range of experimental water borne prefabrication primers has indicated that of the primers tested, only the water borne zinc silicates can meet the requirements of suitability for application and drying, weldability and durability.

The progressive introduction of laser technology for cutting and welding operations led to the initiation of an investigation in to the compatibility of traditional prefabrication primers and experimental types without reactive constituents. The initial results have indicated that the quality of laser cut edges is not affected by the presence of a prefabrication primer and that there is an indicated benefit introduced by zinc silicate types.

The risk of producing defects, mainly porosity, during laser welding has been shown to be influenced by joint geometry. Generally, all of the prefabrication primers examined including two experimental types, caused unacceptable porosity in overlap fillet type joints whereas butt welds joints are visually acceptable.

Further studies into the development of laser friendly primers would be justified if the shipbuilding industry is to significantly increase the application of laser welding in fabrication and construction processes.

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Chapter 14

Time and Cost Effects of the Coating Process

Dr M Raouf Kattan

Time and Cost Effects of the Coating Process

Dr M Raouf Kattan
Managing Director
Safinah Ltd
2 Wraysbury Court
Newcastle upon Tyne
e-mail : Enquiries@safinah.co.uk
Tel/fax: +44 (0)191 286 7559

Abstract

This chapter will review both the pre-production and production factors that influence the shipbuilding process in shipyards. It will identify those areas where shipyards commonly have problems in managing the coating process and describe some of the opportunities they have for improvement of these activities.

Historically the painting process has been seen at best as an inconvenience to the real task of building ships from steel and outfit. The coating process is often afforded little weight in the planning process of building a ship.

Most paint mangers and their personnel often have a very clear idea of the problems they encounter during the coating process but often their communication is not treated with any weight during the planning of the next vessel.

Coating selection is all too often more a function of good selling and low price, with a guarantee of quality of course, rather than a systematic analysis of the yards needs to match process and programme requirements.

It is important that the coating process, which accounts for an increasing percentage of man-hours and re-work, should be given a clear voice at the pre-production stage of the vessel to prevent unnecessary problems in production.

Keywords

Shipbuilding, marine coatings, painting, pre-production, paint, marine paint, ships paint

1. Introduction

This chapter sets out to review the some of the pre-production and production problems faced by many shipyards in managing the coating process at new building and the impact of this process on the time and cost to build a ship.

It describes some of the problems common to many yards and suggests some possible solutions that could improve the way the vessel is coated to reduce costs, man-hours and administration and improve quality of the finished product.

The solutions adopted by any one yard will depend on the cost structure, in particular labour costs of the yard and its achieved levels of productivity.

The process of properly integrating the coating process into the new building process is becoming more and more important as owners demand more from the coating process and classifications societies take a greater interest in its through life performance. This, combined with increasing environmental and legislative pressures on the coating process (including surface preparation), is creating a bottleneck in the production process, where the costs of error are often becoming unacceptably high.

2. Historical perspective

" .....The method of surface preparation will be shifted from the mechanical process of shot blasting to a chemical treatment of spraying acid or rust removing chemicals from now on. It is being studied whether to perform this operation after subassembly or after completion of hull blocks. The hand spraying method of painting, which is current practice, may be replaced in the future by Electro static spray or flow on painting conducted after subassembly or completion of hull blocks, or by submersion of hull units or blocks in a tank of paint. Another treatment system under study is to pour paint into the ship's tank to be coated. In any case, development of new paints themselves and the large quantity of paints to be stored still remain a problem to be solved." ...I Takezawa, 1972 (1)

This is the first significant evidence of thinking about the coating process at new building. Just 3 years before a milestone paper was presented by Kawasaki Heavy Industries (2), which considered future shipbuilding methods, in which no specific mention was made of coating.

It is interesting to consider the implications of the statement made by Takezawa in 1972 and to compare that with what is happening in the coating field today.

It is clear that the solutions being sought by Takeazwa, recognised the need for reducing manpower and the selection of the best time to coat the steel structure was being viewed from both a low cost and a low labour requirement approach. He does not however dwell on the need to match coating attributes with process requirements.

The methods of surface preparation were clearly being reviewed from a productivity point of view. With the rise in environmental concerns and Health and Safety issues, the proposed solutions may not be entirely suitable under current conditions, the reasons for wanting to make a change however remain as valid today as they did nearly 30 years ago.

The method of application has by and large not changed since 1972, although the pump and delivery systems have had to adapt to plural component products with lower viscosity. Some attempts have been made to adopt electrostatic application and Hitachi (3) have recently launched a coating robot.

The problem of managing the stock, issue and handling of paint containers was clearly identified at that time and remains a problem for many yards, with a uniform cost effective solution evading the coatings industry as a whole. Today this is compounded by the problem of managing the waste and other sources of pollution from the process.

From 1972 there was long gap until the late 1980's and early 1990's when several papers, were published regarding the problems faced by shipyards in managing the coating process (4,5 and 6). The recent interest has been steadily increasing with a number of projects both in Europe and then USA increasingly focusing on environmental and productivity issues.

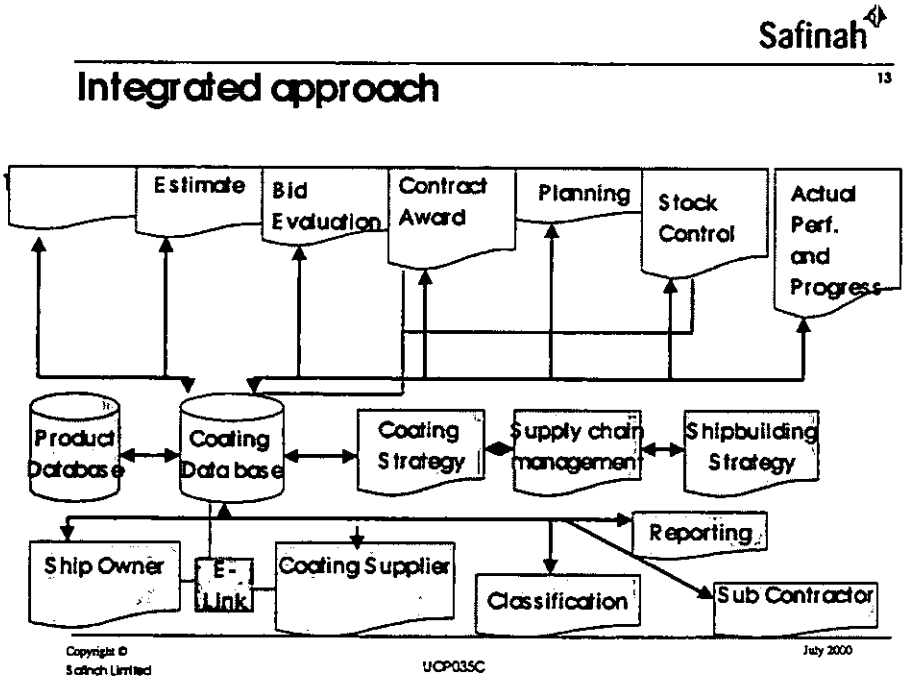
3. Pre-production activities

These include the following activities:

- Tendering
- Estimating
- Coating Strategy
- Planning
- Purchasing
- Stock control
- Health and Safety
- Environmental protection and management
- Use of Sub contractors.

The inter-relationship of all these activities is shown in figure 3.1 below.

Figure 3.1 The pre-production activities



The relatively low first cost of purchasing paint materials for the contract usually means very little attention is paid to the coatings activities at this stage. An indication of this can be provided from an analysis carried out over 3 years in one shipyard (7).

Cost of Paint as percentage of price of ship	1%
Cost of Paint application as percentage of price of ship	7%
Coating man-hours as a percentage of total man-hours	20%
Coating Re-work man-hours	60% of total coating hours

The low first costs, tends to make shipyards ignore the coating process at pre-production or at least afford it little planning time. This is a mistake, evidence from audits carried out by the author, shows that those yards that do apportion adequate pre-thinking to how they are going to manage the coating process tend to be more productive.

The total man-hours for coating are increasing relative to steelwork man-hours as more and more of the steelwork process is automated.

The level of re-work would be unacceptable in any other activity in the shipbuilding cycle and reflects the relatively low perception of the added value created by the coating process, yet the cost implications are considerable in terms of total man-hours.

3.1 Tendering

At tendering, a broad budget is generally allocated to coating, this despite the fact that many shipyards tend to now build similar ships. The data collected for analysis and use in future bids tends to vary from reasonably comprehensive to almost nothing. This is often reflected by the reliance of shipyards on Paint companies or contractors to provide area calculations. Certainly in a number of Japanese yards, quite comprehensive data does exist on paint consumption by vessel type, size and area of the vessel, enabling more accurate tenders to be generated.

The yard should build up a database of consumption to enable a number of factors to be considered:

- Total consumption
- Area estimating data base
- Performance of selected products at new building
- Performance of selected products through life (potentially at least a 5year in service history).

The yard should also be in a position to ask the paint company to tender against very specific performance parameters, such as drying time, volume solids, VOC emissions for the package, extent of use of brush/roller application etc.

To do this a yard should have a well-developed coating strategy document as outlined later in this paper.

3.2 Estimating

At estimating, a more detailed cost breakdown is required for the yard to put together budgets for each department and to confirm costs in the contract documents to the customer. The two key elements to be balanced here are material costs and labour costs.

For Coating activity the material cost is a much smaller percentage than the overall labour costs. Yet often, little attention is given to factors in coating selection that could impact on material cost. The pressure faced by yards generally results in them trying to minimise first cost by controlling material costs. This is a false economy. As bids are often evaluated on price alone, rather than the totality of the package of benefits or costs they may offer.

For example, one common theme from all yards is the need to have coatings that dry quickly and a perennial cry is for the use of winter grade products year round. Yet often in evaluating bids, the yards do not specifically look at the drying times of products on offer, assuming them to be all about the same. This is not the case and a yard could inadvertently create problems for its own production schedule by focussing on the first cost rather than the attributes of what they require.

One of the most common oversights in presenting the budget for the tender, is that the small volume coatings are usually overlooked, or small areas, for example the matt black required to paint navigation light boxes.

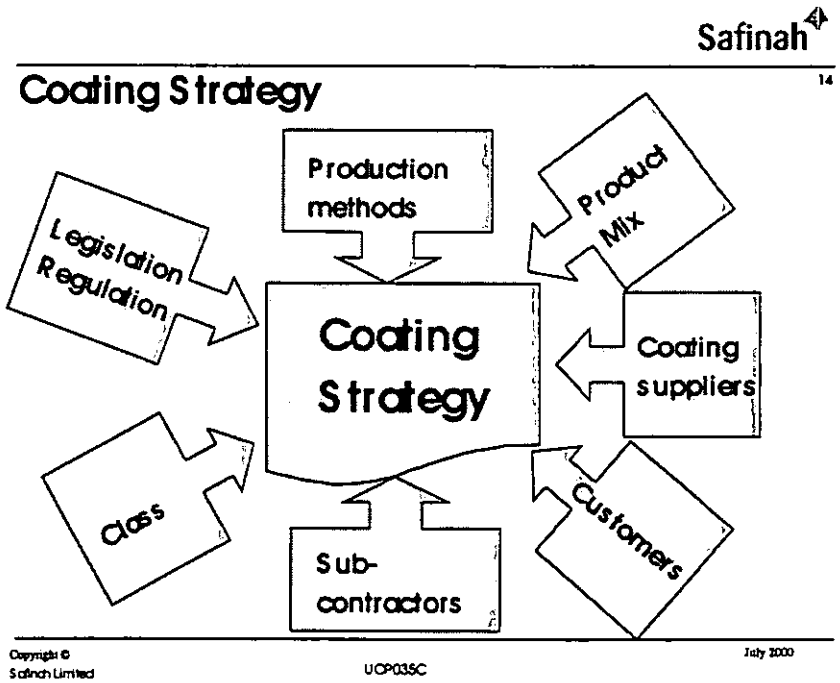
The development of a yard database that could be built up over a number of vessels would very quickly overcome these problems and enable parametric measurements to be developed to help with the tendering process. The potential to standardise this, so that data could be exchanged between yards, would of course increase the potential benefits of such a database.

3.3 Coating strategy

Many yards have a broad coating strategy, that is they have decided when and where they should carry out their coating activities for the majority of key areas. The decision is often based on facilities, climate, cost, and previous experience as well as whatever pressure a customer can bring to bear upon them for a particular contract. In reality, many yards find that they are unable to adhere to their own defined coating strategy and procedures because of schedule pressures resulting from poor planning of the coating process or poor control of other production activities.

What is clear is that on the assumption that the coating process is properly controlled, then the earlier you can coat the lower the labour costs, as productivity is generally higher. However, this broad statement does not reflect the specific needs of different shipyards, different ship types and different customers. The factors that influence the coating strategy are shown in figure 3.1.

Figure 3.2 Development of a coating strategy.



In yards with good craneage and a relatively large unit/block size, coating on unit or block makes sense, In yards with small block size coating after erection makes sense. If the vessel being constructed is complex with a long outfitting time, there is an increased chance of hot work damage thus; delaying coating can reduce overall costs, even though productivity is lower.

Any coating strategy adopted would tend to lead a yard to standardising particular aspects of the coating process. In the extreme this results in standardising on a single paint manufacturer. Alternatives would be to standardise on curing time, number of coats in the scheme for each area etc.

If one takes this to the extreme, then what the yard is really looking for is the best match to its production process for each area of coating, depending on when and where it is to be coated, together with the performance required to satisfy the ship owner.

The difficulty with adopting an approach to standardise the production process is that owners' requirements are increasingly being voiced in particular in the area of anti-fouling and ballast tanks as they come under operational and regulatory pressure to ensure adequate performance through life.

The Coating strategy should include the following:

- The System based specification for coating the vessel
- The breakdown of the vessel into coating tasks by unit/block, area or zone
- The specific production attributes required for each task
- The location where the work will be carried out for each task
- The time when the work will be carried out for each task
- The time required for the work to be carried out for each task
- The preferred method of carrying out the work
- Inspection timings
- Re-work/touch up plan and timings
- Alternative approved strategy (in the event of schedule pressures).

These should take into account:

- The needs of the particular contract in hand, and its interaction with other contracts.
- Any special equipment requirements
- Any particular transport of services requirements.
- Any special owners requirements
- Any specific issues raised by this contract

The above should then be developed with the coatings to be used in mind. For example, if work is to be carried out in situ for the engine room. Then the ideal pack size should be considered, to minimise handling problems, or the paint should be suitable for long spray lines. Will the work be carried out by airless spray or by brush and roller, in which case the appropriate paint should be supplied or the method of application stated when the paint is ordered at the start of the contract.

It is only by taking this methodical approach of ensuring adequate time and effort is afforded by the yard to minimise the problems associated with coating work.

There is, as with any such development, an initial time investment required to collate the information, however the strategy once developed will only change slightly from vessel to vessel to reflect particular contract needs or any facility development/changes to the over all build strategy.

3.4 Planning

In general the planning of coating activities is usually based on the blocking of a period of time (shifts or days) for the coating activity. The time period does vary from summer to winter, reflecting the effect of temperature and humidity on coating activities. However, the paint department is subject to the planning control of the steelwork and the berth erection cycle.

It is not unusual for the coating process to be used as the buffer to compensate for delays, or poor planning in either the steel or erection cycle. Consequently, the time that the department may have to coat a particular block or area can be changed at relatively short notice.

This often means that the time the paint department has gets changed at fairly short notice. In addition, as the time allocated to the department is done without reflecting coating attributes (eg. Drying time),

event he time allocated may mean that short cuts have to be taken to carry out the work, or that the work is not progressed as far as it should be at that stage, leading to extra time and cost penalties later on.

Also, the time allocated by planners often assumes that coating activities take place 24hrs every day, and hence make no allowance for dew point or humidity, or other climatic and seasonal factors, which practically limit the total time available.

For yards coating on block in paint cells or even outside, there is often inadequate scheduling and materials handling capability, often resulting in Paint Cells being blocked because of lack of transport to move the unit/block out. Often the transport needs of the paint department are secondary to those of other activities.

For yards that carry out coating in situ after erection, one big problem is the clash between coating work and other activities that have to be carried out on board.

Poor planning of the work. Or delaying of the work to later stages of production can increase conflicts with other trades and in extreme cases impact on the energy loads that the yard services need to deliver to the berth or outfit quay.

Here poor scheduling of the coating work can lead to access problems for other trades, in particular this tends to show itself when Deck Coating takes place as this cuts off movement to many parts of the vessel. There is a clear need for planners and the paint department to work together to come up with an acceptable strategy.

It is essential therefore, that adequate time and effort is given to the proper planning of the coating processes, with proper thought out plans to handle the problems that will arise in the early stages of such a change. In the long term the target must be to plan and develop the work process so best suit the yards over all strategy. In the short term, this may not be possible to achieve and thus the target in the short term is to better manage and resource the process itself.

3.5 Purchasing

The purchasing process at new building is increasing in complexity, because of the increased interest of the ship owner in the process and the need for yards to control production costs against in a market of declining selling prices for ships.

The purchasing process should take into account the following key factors:
- Quality of the product to meet the specification (fitness for purpose)
- Delivery to meet production requirements
- Compatibility with defined production process attributes
- The potential of single source supply for the entire vessel
- Finally of course, first cost

Yards should consider that the market for coatings is extremely competitive and opportunities exist for benefiting from multi-vessel contracts. This process can of course be de-railed by a ship owner with a strong preference for one particular manufacturer. One possible approach would be to actually let a ship owner who does have a particular preference for one paint company to supply the coating free issue to the yard, this would reduce the inherent negotiating problems when 3 parties are involved, and the reduce the potential for misunderstandings. There are potential benefits to the owner as well in adopting this process as his interest in the paint extends beyond the normal yard guarantee period.

Of course the owner would need to ensure that the supplied products match the coating strategy or else pay the additional required to adjust the normal methods of working of the yard. What is important is that the yard should be in a position to identify the penalty for deviating from the options that best suit its desired coating strategy.

Cost control is always critical, as the yard must meet its own target budget for the coatings. The degree to which they can fix the price enables them to make their bid as competitive as possible. The more uncertainty they have to reflect in their bid/tender, the greater the chance they have to loose the contract. As far as possible they are trying to minimise their own risk. This has tended to result in more and more yards using sub-contractors for coating activities and hence retaining less and less in house knowledge on coatings (all the more reason for the development of a suitable coating strategy).

3.6 Stock control

Stock control is a time consuming process for yards, because paint is supplied to them in pallets by system, rather than by how they intend to paint (by unit/block/area/zone etc.).

In recent years paint companies have started to adopt bar coding at their factories. The bar codes are primarily used for the Paint Company's own stock control requirements and thus only contain very basic information. The yard should consider developing appropriate systems that can capitalise on the availability of the bar code to manage their own stock, issue and consumption in a more labour efficient manner.

The use of the bar code could be extended by the adoption of non-standard bar codes that could carry much more information with the product (such as data sheets and H&S information). The technology to insert a microchip into the label of the product already exists and can provide real opportunities and benefits to the yard and the Paint Company in terms of keeping control of stock and documentation.

Yards that develop a single source supply strategy can benefit by adopting e-commerce solutions to the ordering, delivery and stocking of paints as well as payment (8).

3.7 Health and safety

Health and safety is becoming more and more important. The regulations and legislation on the use of hazardous air pollutants is increasingly controlling the exposure of workers to toxic products. This is not only leading to improved paint formulations but also to careful consideration as to how the physical coating processes is carried out.

The physical handling of paint containers has come under scrutiny in a number of yards. In particular in warehousing, yards should consider the adoptions of systems that either reduce the overall manual handling required or adopt products that can be delivered through suitable delivery systems to over come these problems.

3.8 Environmental protection and management

The biggest burden that environmental protection and management will impose on the yard is the need to keep proper records for:

- VOC and other emission management
- Waste management

There is an increasing need to compare tenders not only on the usual factors of price, quality etc. but also on the emission package and the total waste likely to be generated. The waste in the form of liquid waste is the more critical and is directly related to the pack size that is used and the vessel type being built.

As more and more pressure is put on yards to properly manage these activities, then the workload on the paint department will increase. Thus, the obvious solution will be to develop appropriate computer

software that can automatically compare bids on this basis and manage both the waste and emission processes properly.

A number of US yards did develop a system for this purpose but found that the labour input required to feed the software was adding an excessive burden to already stretched coating departments and the system is now largely unused.

Any system developed will need to rectify the problem of data entry and data base management and make the most use of the information available form the yard and the paint company, while ensuring compliance with the reporting requirements of the legislation/regulations.

3.9 Use of sub-contractors

As discussed earlier, many yards are making use of sub contractors. The use is usually in one fo 3 forms:

- Supplement the existing shipyard work force at periods of peak demand
- Focus on special/critical areas (tanks etc)
- Complete management of the coating processes with the exception of procurement
- Complete management of the coating process including procurement.

Most contractors are on a ship by ship contract, and this tends to limit the amount of investment they are willing to make, as the payback period of one contract is inadequate.

The reliance on the contractor to purchase material is acceptable as long as the requirements of the coating strategy are met. The coating strategy therefore serves as a suitable document to mange the contractors activities and method of work.

The degree of supervision required to be provided by the yard of the contractors activities will tend to reduce if the contractor and yard develop a longer term working relationship. The yard should consider carefully the allocation of exclusive contracts as these could tie the yard in to a specific way of work and level of investment. For each contract the yard should work with the contractor to identify ways of continually improving the process

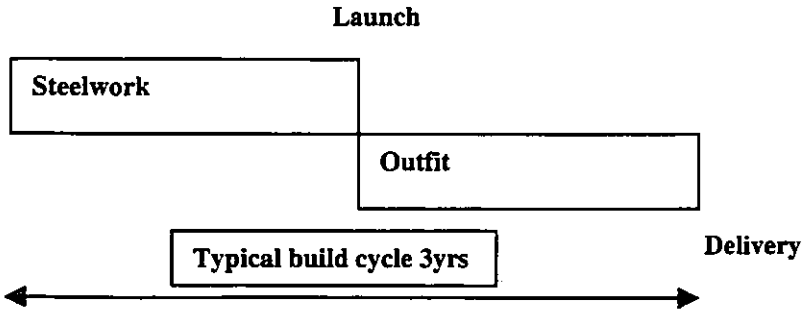
4. Production

4.1 Review of the production process

To examine the influence of the coating process on the production cycle, it may be helpful to briefly review the development of production technology over the preceding 5 decades to understand the integration required today between coating activities (ref 9).

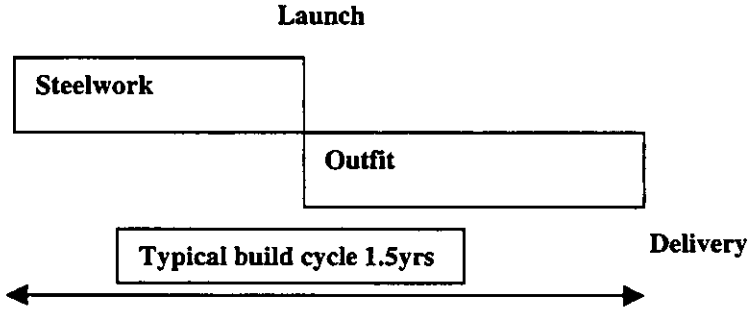
In 1940's ships were built sequentially using the "layer" method of construction. This led to long build times with steel work carried out pre-launch and the outfitting carried out afloat and finally painting as shown in figure 4.1.

Figure 4.1



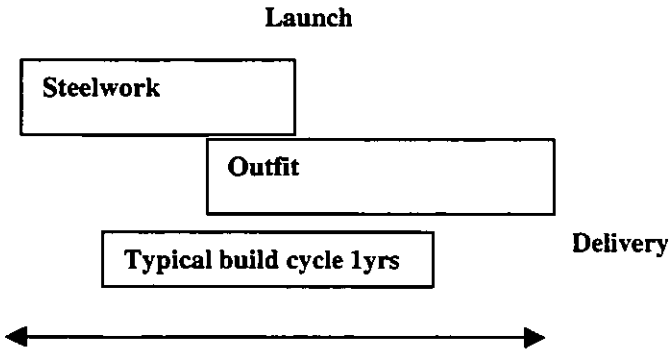
With the introduction of welding in the 1940's and automated cutting shops in the early 1950's, steelwork time was reduced considerably and the use construction of sub-assemblies and unit assemblies (with the appropriate crane capacities), more work could be carried out in fabrication sheds under cover. However little improvement if any was made to outfitting activities. The Build cycle reduced as shown in figure 4.2.

Figure 4.2



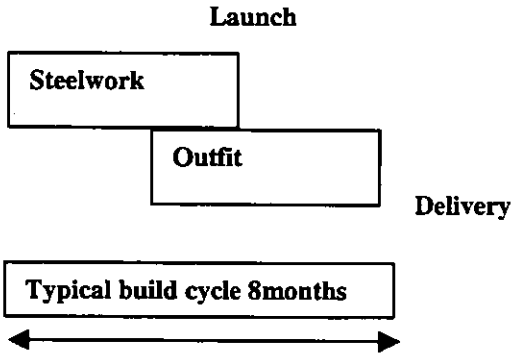
By the late 1960's and early 1970's, improvements in welding, material handling and the increasing size of ships, saw the first panel lines and twin skin lines introduced and the advent of advanced outfitting. This approach was dominated by the Swedes and the Japanese in Tanker construction and enabled them to further reduce the steelwork times and bring forward some of the outfitting activities. The integration of the activities was at last given some thought in Japan with the adoption of the "Integrated Hull Outfit and Painting" method (IHOP, ref 10). The improvements are shown in figure 4.3.

Figure 4.3



With the relentless pursuit of improved productivity yards have steadily improved on this process by improved steelwork times, improved outfitting through better design and modularization and hence less time to carry out the actual painting process without interfering with other activities as shown in figure 4.4.

Figure 4.4



In the 1990's pre-outfitting techniques have meant that by the time units and blocks are erected at the building dock or berth, many of the outfitting activities have been completed and cycle times are down to 3 months in the best yards.

It is true to say that these developments have probably impacted far more on the construction of large ships rather than smaller more complex vessels. However the principal coating problems are the same for all ship sizes.

The reduction in the build cycle time and the overlapping of steel and outfit activities coincided with considerable investment in steelwork automation and hence a reduction in steelwork manning levels and man-hours (manpower in steelwork has been reduced by about 2/3rds since the 1960's). This has resulted in an imbalance in most facilities, relatively high productivity steelwork being followed by labour intensive and relatively low productivity coating and surface preparation activities. This has caused a bottleneck in the production process at the coating activities and especially at the unit/block stage where 80-90% of coating is carried out in larger yards.

4.2 Steelwork, Outfit and coating

In the past the coating process has been viewed as more of an unwanted necessity by shipyards and of less importance than steel and outfit work. The foundations of this may lie with the fact that the steel and outfit work is usually in conflict with the coating activities. When coating takes place all other work must stop for both practical and health and safety reasons. The steelwork and outfit activities also tend to cause damage to the previously applied coating unless great care is taken (not very often).

The following activities typically comprise coating activities during production in a shipyard.

- Shop primer line
- Shop coat application
- On unit/block coating
- Post erection coating
- Post launch coating.
- Touch up and re-work

Table 4.1 identifies the possible sources of damage to the paint system during the build cycle.

Table 4.1 Causes of paint damage.

Process	Surface preparation	Paint Application	Cause of Damage
Stockyard			Variation in quality of steel from supplier
Treatment Line	Wheelabrator	Shop primer application	Low DFT, poor material handling, poor curing, poor surface profile.
Cutting			Burn damage, material handling, marking, immersion in water, cut edge condition
Sub and panel assembly	Wire brush/grinding	Shop coat	Usually inadequate mixing of the product
Unit Assembly			Hot-work damage, fumes, material handling and fairing
Unit Painting	Either mechanically prepare surface or sweep blast or full blast	Either a holding primer or full or part of scheme applied, feathered to the edges.	Low DFT, high DFT, holidays, dust, poor curing, poor equipment, transport
Block assembly			Hot-work damage, fumes, material handling and fairing
Block Painting	Either mechanically prepare surface or sweep blast or full blast of damaged areas and seams/butts	Full or part scheme application, feathered to the edges	Low DFT, high DFT, holidays, dust, poor curing, poor equipment, transport
Dock Erection			Handling, hotwork, fairing, lifting lugs
Painting in dock	Either mechanically prepare surface or sweep blast or full blast of damaged areas and seams/butts	Full or part scheme applied, cosmetic scheme pre-launch.	Outfit hot work, abrasion, equipment moving, staging, access
Outfit alongside	Either mechanically prepare surface or sweep blast or full blast of damaged areas and un-coated areas	Full or outstanding scheme applied plus more cosmetic coats	Hotwork, damage, accesses and conflicts resulting in poor application and short cure times.

4.3 Cost Penalties

Labour costs - The increase in coating process man-hours due to re-work will lead to an increase in direct labour costs and, therefore, the indirect labour costs associated with the co-ordination of these activities. The coating process will account for about 5-10% of the price of the vessel depending on the vessel type (Ref 11 and 12). With up to 60% of the coating man-hours being utilised for re-work (for a VLCC priced at $85 million USD this would add $1 million to the price).

The direct labour costs associated with coating re-work are easily identified but do not account for all the costs incurred by the shipyard and ultimately passed on to the ship owner. Costs associated with

increase requirements for facilities, energy, consumables (including paint), equipment and supervision must also be assessed.

Facility investment - areas must be set aside for re-work to be undertaken. This may require the addition of an extra paint cell(s) depending on where repair work is to be carried out. Usually the cost of coating is cheapest at the paint cell, where it can be up to 3-4 times cheaper than carrying out the work later on in the production process. Alternatively additional areas could be set aside, although these would have to take into account weather protection and environmental issues as well as access of both men and equipment.

Environmental costs - if surface preparation and coating is to be undertaken in external areas then it may be essential to protect both the unit from the environment and the environment form the surface preparation and coating activities. I.e. spent blast media, Volatile Organic Compound (VOC) emissions, noise and liquid and other waste. The temporary covering of a unit to may cost in the region of $40,000. Additional costs would be incurred as a result of the required clean up and disposal of the supplementary consumables required to perform the re-work. The additional disposal costs for a VLCC can amount to $10,000.

Equipment costs - with an increase in surface preparation and coating man-hours of up to 60% for the re-work, additional equipment has to be supported and purchased.

Energy costs - These will rise in accordance with the additional work being carried out and can result in high levels of demand on services at critical points in the build programme (this is common if a lot of re-work is undertaken in dock, or alongside).

Material Costs - the increased consumption of blast media and paint due to re-work will be an additional expense.

An estimation of total cost of coating re-work for a VLCC (excluding energy and small plant costs) can be obtained from the following data:

Direct labour	= $1million
Indirect labour	= $0.25 million
Additional facilities	= $0.08million p.a. (1 paint cell)
	= $0.02 million per ship (assume 4 ships p.a.)
Additional consumables	
Blast media/ship	= $6,400 consumption
	=$6.500 disposal
Paint/ship	= $1,432,900
Total per ship	= $1.4 million or approximately 1,7% of the ships price and a cost of almost $6 million per year for a yard building 4 ships p.a.

It should be noted that VLCC's are relatively simple vessels with relatively little outfitting, these figures could more than double for more complex ships.

4.4 Time Penalties

The direct cost of coating re-work has been identified above. However this figure does not tell the whole story. The economic survival of a shipyard is governed by the amount of revenue it can achieve. The more ships it can build in one year the less the proportion of overheads each ship contract has to carry. Typically yard cost structure is usually split as 60% materials, 20% direct labour and 20% overheads.

Thus the more vessels the yard can produce per year the better its chances of survival. We have seen earlier how the steady improvement in steelwork production technology has resulted in a bottleneck at

the coating process in the paint cells. Thus any time lost at the bottleneck is time lost for the whole facility. (Ref 13, 14).

The time penalties of coating re-work often lead to a requirement for large areas to a t as a buffer store for the units leaving the steel facilities and for the coating work to be completed. This adds overhead and causes delays to the production process and hence reduces the revenue earning potential of the yard as a whole.

5. Improving the coating process

5.1 Types of Improvement

Improvements can be made both at pre-production and production. There is no doubt that the first step is to improve pre-production activities along the lines and in the areas outlined earlier.

The first step must be to raise the perceived value of the coating. When a part of the ship has been coated, value has been added and hence the coating needs to be protected.

It is difficult to lobby for improvements when the cost of the paint is often less than 1% of the price of the ship, however it is one of the few areas where improvements can be easily and readily made. Typically up to 60% of coating man-hours are used on re-work and touch up, in no other part of the shipbuilding process would this be acceptable.

The first step is to properly integrate the coating process into the shipbuilding cycle and to that end the development of a coating strategy should help to achieve this.

To properly integrate the process the following key areas should be addressed:

- Ship design
- Facilities, equipment and technology
- Production management
- Paint system selection

5.2 Ship design

The design of the vessel must take more account of the needs of the coating process at new-building and the need for the coating to perform well through the life of the vessel. The performance of the coating should be considered as an integral part of the structural performance of the vessel through life. Premature failure of the coating could lead to corrosion and in turn premature failure of the ship structure (Ref 15).

The ship design should recognise the requirements of the coating process and by so doing create a production approach that affords the coating process equal footing with steel and other outfit work.

The design should ensure adequate access and ventilation possibilities for coating work to be carried out as well as subsequently cleaning operations.

One of the biggest challenges has been the increased water ballast tank area resulting from OPA 90. This has created problems both at new building and in service as access for proper coating work can be quite difficult to achieve.

Hitachi have recently launched a coating robot and there is no doubt that the vessel design swill have to be modified to enable the robot to perform effectively.

Another weakness is often in the drainage of tanks, with much complex geometry leading to flat surfaces which can often encourage water pooling.

The designer should be aware of the basic principals of good design for corrosion and of the in service problems of present designs. Sadly not many good data bases exist in the public domain.

Perhaps the key is to focus on the use/developemnt materials/designs that would reduce the need for edge grinding.

Vessel designers should look at the use of other non-corroding materials for many of the outfit items such as pipes, door etc. as this would reduce the overall through life coating costs.

5.3 Facilities and equipment

The timing of when coating work is to be carried out is critical. It should not always be assumed that the best place is the paint cell (although it is the most efficient). Different yards face different problems and so the selection of when and where to paint different areas will depend on how the yard works and what are the more common forms of damage as well as what levels of investment the yard has for facilities and equipment.

The aim is to balance the activities to match the throughput requirements of the facility as a whole. This means scheduling paint-work to fit in with the production process and this in turn will dictate facility and equipment requirements.

Often even basic items such as proper high-pressure hoses and couplings are not used thus reducing productivity in this bottleneck area. The technology of the equipment is changing and environmental pressures are making yards look at alternative surface preparation strategies. However in most cases the new technologies are not as productive in terms of man-hours, thus all the more reason to ensure that re-work is minimised by proper integration of activities.

For the surface preparation activities techniques currently employed are:

Open air dry blasting using abrasive
Ultra High Pressure water jetting
Slurry blasting
Mechanical treatment
Vacuum blasting
Etc.

The total cost of the operation should be considered including man-hour costs, time penalties and waste handling costs.

For paint application, airless spray still dominates although in smaller yards, brush and roller are still heavily used. At present apart from automation of this process the basic process remains the same with bigger pumps and plural component equipment being introduced to handle the newer materials and the higher solids required today.

5.4 Production management

This can cover a very broad scope of management systems from financial control and budgeting to training and education. The build strategy and approach to ship building by the yard is the corner stone of all these activities and all the major pre-production activities have been discussed earlier.

However one key system should be mentioned:

Quality systems - The use of a quality system to identify, quantify the occurrence of re-work and to systematically mange it and eliminate it is critical. Juran and Deming have advocated systems based on statistical tools for many years amongst others. Yet very few yards seem to use these in earnest even to monitor DFT on a primer line.

The use of variable and attribute control charts to monitor the occurrence of things such as:

Runs
Sags
Heat damage, dft, and profile
Productivity
Curing time
Etc

Can be readily established and can reap rewards in a short period of time.

5.6 Paint scheme selection

Talking to a number of yards it is always clear that a number of items are very high on their list of desirable features of a paint scheme:

Examples include:

- Fast drying products in tanks and on deck
- Low surface preparation requirements
- Low VOC
- Minimum number of products
- Minimum number of coats

Yet often when the decision is made to select one tender or another only two criteria are considered:

- Price
- Supplier

It is no longer true to say that the lowest bid always wins, but it is still quiet common. The technical support and reputation of the supplier is also very important. In fact one can say that it is quite difficult for one supplier to dislodge another form a particular customer. Often the incumbent supplier has to make a large mistake before sufficient momentum to make a change can be developed.

Thus, even though many yards know what they want, they are not very good at ensuring they get exactly what is required.

The whole area of paint supplier and shipyard relations is undergoing a gradual change in line with the general trend to improve supply chain logistics in industry as a whole.

CONCLUSIONS

It is clear that careful thought should be given to the pre-production activities and their impact on the coating process. Often by the time production starts, many of the problems that will be encountered have been set in place by inadequate thinking at the pre-production stage. The development of a coating strategy would make the best use of the limited resources to develop a proper set of rules and guidelines for the coating process in a yard. For pre-production the basic steps are:

- Audit the coating process and extract from the audit the key elements of the coating strategy
- Develop the coating strategy.
- Feed the information back to the designers and production planners in a form that they can use to improve their processes.
- Structure the information required for tendering and estimating
- Streamline purchasing and stock control together with delivery and consider the use of e-commerce in making this a low labour intensive activity.

- Ensure compliance with H&S and Environmental issues. Use of computer based systems to manage and keep track of these activities is the simplest form as long as it does not lead to excessive man-hour requirements to maintain the system.

For production activities the following should be considered:

- The designer needs to understand the coating process and its problems.
- Detailed design for coating manuals or standards should be developed.
- Use of statistical tools to monitor and guide the improvement in quality should be more widely adopted.
- Each yard needs to analyse its own cost base to identify the best method of application and the best schedule to suit its needs.
- The yard must define what it is looking for from the paint scheme to best integrate it into its method of production and look at the total cost of the scheme rather than price.
- The total cost should consider both time and money elements.
- The environmental burden of the process needs to be evaluated and options to reduce this considered.

There is no doubt, that many of the problems encountered at the production phase could be mitigated by careful planning at the pre-production phase, and by the development of a suitable coating strategy that encompasses all the major aspect of the coating activity at the yard. This may include surface preparation and staging also.

The coating process has to now be awarded greater time and effort to ensure it is properly integrated and thus not a bottleneck or an inconvenience to the production process as a whole.

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Chapter 15

Afloat Maintenance, the Control of Marine Fouling and the Care of Coatings Underwater

Dr David Jones

Afloat Maintenance, the Control of Marine Fouling and the Care of Coatings Underwater

David Jones
Chairman, UMC International Plc.
Warrior Close, Chandlers Ford, Hants.,SO53 4TE
e-mail: djones@umc.co.uk

Abstract

This lecture estimates the cost of a rough hull to a ship owner and reviews the options for controlling marine fouling and maintaining hull coatings beneath the waterline during a five year docking cycle. Current underwater ship husbandry techniques are described and future developments are predicted with especial reference to environmental restrictions on biocides in antifouling paints.

Underwater inspections, hull roughness surveys, hull cleaning, underwater painting.

Introduction

Paint coatings applied to ships' hulls beneath the waterline fall into two distinct categories depending upon the function that they are designed to fulfil, either antifouling or anticorrosive. Anticorrosive coatings are applied to bare steel and may be assisted by cathodic protection systems; antifoulings are applied on top of the anticorrosive coatings and are not assisted by any other system on the ship. Although there have been attempts to combine both of these functions into a single coating these have not proved successful and generally speaking the marine paint industry treats anticorrosive and antifouling paints separately. Anticorrosive and antifouling coatings may detach or cease to function from time to time and it is not always possible or desirable, to postpone attention to the next scheduled docking.

In this chapter I shall point out why the maintenance of a clean, smooth hull is important to a ship owner and go on to deal with the care and maintenance of both types of coating afloat. How can fouling be removed once it has formed on a dysfunctional antifouling? Should the treatment be varied depending on the type of antifouling? Is it possible to repair areas of detachment underwater? I shall also review various options for the control of marine fouling and suggest how the combination of environmental and financial pressures may shape the future.

The Effects Of Hull Roughness

International Paints were the first manufacturer to introduce self-polishing antifouling coatings in the mid-1970s. By definition they offered ship owners a smooth hull and it was imperative to the successful marketing of the product to have facts and figures available to explain the benefits. It was important to be able to measure hull roughness and to quantify the benefits of a smooth hull in terms of fuel savings. The British Ship Research Association (BSRA) had produced a hull roughness analyser that consisted of a small, wheeled trolley that was pushed over the hull and measured maximum peak-to-valley roughness over a sample

length of 50 mm. Initially this was only available for use above water where it was extensively used to measure average hull roughness before and after hull painting in dry dock. This proved very popular because for the first time ship owners had a definitive method of assessing the quality of a paint job. However, a great deal of other information could be derived from a hull roughness survey, but it came too late if it had to wait until the vessel entered dry dock. For example, areas requiring spot blasting could be identified and the results incorporated into the dry dock specification, thereby avoiding the dreaded 'extras'. BSRA therefore produced an underwater version of the analyser and divers soon became adept at carrying out the surveys afloat. Each survey comprises some 10,000 readings taken in a specified pattern over the hull. In fact underwater surveys are much quicker and easier to carry out because a diver does not require scaffolding or the use of a 'cherry picker'.

For merchant ships the predominant component of hull resistance is viscous drag, which may represent 75% - 90% of total drag. Unfortunately, it is difficult to separate the effects of propeller roughness from the effects of hull roughness and it is also difficult to measure speed, engine power and propeller thrust accurately. Therefore the viscous component cannot be determined from measurements taken on board ships and these can only provide an indication of a trend. It was therefore hoped that hull roughness surveys would provide a method of measuring the fuel penalty derived from an increase in AHR. However, although the BSRA gauge proved simple and convenient to use, it only measures peak-to-valley roughness whereas viscous drag also depends on the 'quality' of the roughness, which includes other parameters such as frequency (peak-to-peak distance), the frequency distribution and the shapes of the various elements that go to make up the roughness. Hull roughness surveys alone do not provide much of a guide to fuel savings and it was left to Marintek, formally the Ship Research Association of Norway, to take the science one step further.

Marintek produced a series of replicas taken from actual ships in service and measured the hydrodynamic effect of the roughness in a specially constructed test rig. Using these replicas, the power / fuel penalty of a rough hull compared to that of a well-painted new ship, can be estimated. Table 1 applies to a ship of 200 m. waterline length steaming at 13 knots and it illustrates how much the 'texture' of the surface affects drag and how misleading it could be to rely on AHR alone. For example, the table shows that two identical ships, both with an AHR of 400μ suffer widely differing fuel penalties, one of 27% and the other only 7%. The answer lies in the 'quality'of the roughness. The replica with the high hydrodynamic drag in column 5 had the characteristics shown in Fig.1, whereas the replica with the lower drag had the surface profile shown in Fig.2.

Table 1

REPLICA	2	6	4	5	3	7	8	9
AHR (μ)	150	220	250	350	400	400	450	500
Power Penalty	2%	3%	2%	4%	27%	7%	8%	19%

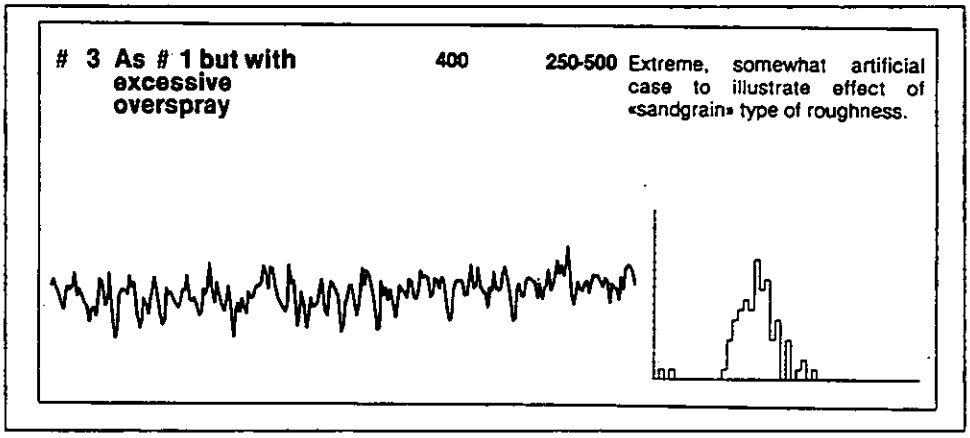


Figure 1

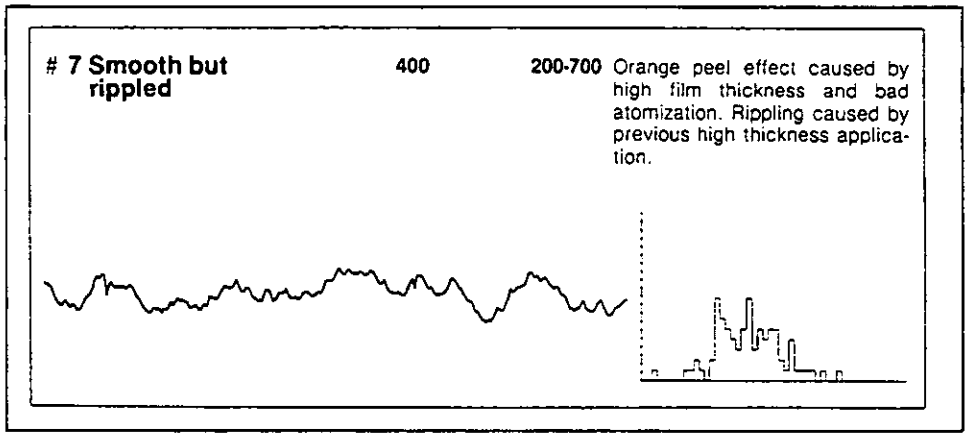


Figure 2

Of course, the table does not take account of marine fouling and efforts to produce smooth coatings are dwarfed by hull fouling if the paint fails. Here again, the effects are difficult to quantify and have been analysed more fully in previous chapters, but it is generally accepted that a really heavily fouled hull can suffer a fuel penalty of up to 40%. In any case this illustrates how important it is to maintain a smooth, clean hull and why so much money and effort is invested in the search for effective antifouling coatings.

Fouling Control, The Traditional Approach

Some means of controlling marine fouling on ship's hulls has been considered essential ever since the earliest days of marine transport. It has been estimated that without any attempt to control fouling shipping would require 40% more power, equating to about 75 million tonnes of additional fuel burnt annually costing in the region of $6 billion. Without an effective antifouling system today's marine transport industry would undoubtedly grind to a halt, not just because of the increased cost of bunkers but because ship propulsion systems are not installed with sufficient reserves of power. Whilst there is general acceptance that some means of fouling control is essential, this is difficult to reconcile with ever-stricter controls on the biocides used in antifouling paints.

The conventional approach to improved fouling control has always relied on the identification of increasingly potent biocides, which were incorporated into antifouling paints with ever

more sophisticated release mechanisms. The aim has been to provide a reliable level of protection for as long as possible, against as wide a range of marine organisms as possible. In recent times the industry has been remarkably successful at realising the expectations of ship owners. This was demonstrated in 1974 when the introduction of the first tributyl-tin (TBT) self-polishing antifouling lead directly to a rule-change which allowed certain classes of ship to stay afloat for up to five years in between Special Surveys. This linkage between the time that an antifouling will keep a hull clean and the time that a ship owner can keep his vessel afloat is important. So long as the life of the antifouling matches the in-service period of the vessel all is well, but ship operators cannot tolerate steaming with any significant degree of fouling on their hull. As soon as bunker consumption begins to rise they will look for a solution and the only alternative to a premature dry-docking is to have the hull cleaned by divers.

TBT antifoulings fulfilled these criteria admirably. However, at the 42nd meeting of the International Maritime Organisation (IMO) it was finally agreed that the application of organotin antifoulings will be banned throughout the world by 1st Jan. 2003 and that a complete ban on the presence of these antifoulings on ships hulls will be in place by 1st Jan. 2008. What is more, the legal instrument that the IMO Marine Environment Pollution Committee will develop will have the ability to ban other biocides if they are proved to have unacceptable effects on the environment. Since it goes without saying that for a conventional antifouling paint to be any good it must be toxic, then the future of these compositions looks bleak. There is an obvious dilemma. Ship owners have become accustomed to their vessels entering dry-dock virtually free from visible fouling, so can their expectations be met in the future?

Fouling Control - Emerging Technologies

Various solutions are being considered aimed at deterring marine fouling without the use of toxic biocides. These include the use of ultra-sound to deter organisms from settling, electrical systems that ionise seawater and low surface energy paints that provide a surface they cannot stick to. It is this latter approach, which appears to be meeting with success. These low surface energy silicon based paints are extremely difficult to "wet out" and as a consequence they provide an inhospitable surface for marine organisms to adhere to. Weed and shell fouling will settle and grow, but they will only be lightly attached. For example, fouling can be removed by low pressure water washing in dry dock, or removed underwater with a wipe of a diver's hand, or it may be washed off if a vessel's passage through the water is fast enough.

Naturally, a self-cleaning hull is an attractive proposition and this is why most of the applications so far have been to high-speed craft. However, some backup in the form of underwater cleaning will almost certainly be required, particularly on vessels with a service speed of less than 20 knots, which includes the world's fleet of tankers and bulk carriers. This poses a problem because the paint relies entirely on the integrity of its surface for its antifouling effect. If the surface is abraded or scratched fouling will become firmly attached. Any cleaning, whether it is carried out underwater or in a dry dock, must be carried out very carefully and gently. If any damage is inflicted on the coating, fouling will soon grow on the affected areas requiring more rigorous cleaning next time, thereby causing more damage, resulting in more fouling and so on. Excellent results can be maintained over an indefinite

period, but the antifouling properties of the coating can easily be compromised by one unfortunate episode such as an uncontrolled underwater clean.

Underwater Cleaning Low Surface Energy Antifouling Paints

Some years ago we embarked on a development programme to fulfil a military requirement. Most navies apply a special type of rubber cladding to the outer surfaces of submarines in order to make them more difficult to detect (Fig. 3). Like any other vessel they foul up and need cleaning. Here we have an obvious similarity, both requirements involve underwater cleaning a delicate substrate where the consequences of accidental damage would be severe. The machine we produced to meet the military requirement we named Mini-Pamper (Fig. 4) and this, or its variants, will provide support to the new antifouling coatings. At this point it may prove helpful to explain how divers clean ship's hulls underwater.

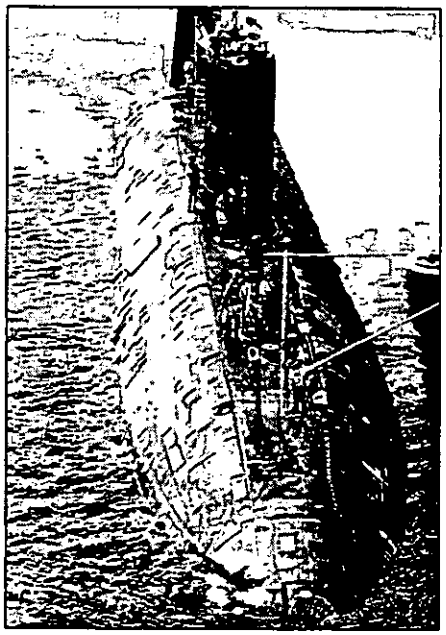


Figure 3: Courtesy, British MoD

A Vessel Having a Delicate Coating Suffering Some Detachment!

All the machines currently in use take advantage of a very helpful physical characteristic; if a face brush is rotated in way of an underwater surface a low-pressure area is created beneath the brush with the result that the brush clings to the surface being cleaned. The effect of this is that a diver does not need to press the brush on to the hull he is cleaning, it holds itself on. Typically, a suction force in the region of 200 kg. is created under a brush of say 400 mm diameter rotating at about 800 rpm.

Unfortunately, this creates its own problems. The brush must have robust bristles otherwise they will not support the suction force and anyway, in most cases, stiff bristles are required in order to clean effectively. In practice stiff polypropylene bristles are used which would certainly damage a low surface effect antifouling.

Mini-Pamper comprises a wheeled chassis fitted with two rotating brushes as shown in Figure 5. In between the brush mountings and the chassis is a sensitive restraining mechanism that off-loads the suction pressure on to the chassis and thence to the wheels. The vehicle can then be driven and steered whilst the cleaning is accomplished entirely by sideways motion rather like a rotary lawn mower. It is this restraining mechanism that allows the brushes to respond to uneven surfaces such as weld seams, whilst ensuring that virtually no brush pressure is applied to the surface being cleaned. The Mini-Pamper machine cleans at a theoretical rate of 1250m² per hour. In practice we achieve rates of 600 m² - 700 m²/hr on the job when diving conditions are taken into account. The machine steers and drives on the rear wheel that makes it extremely manoeuvrable and it is fitted with both forward and reverse drive. In order to ensure that the brushes can never "dwell" on the surface they automatically lift clear whenever Mini-Pamper is stopped or put into reverse.

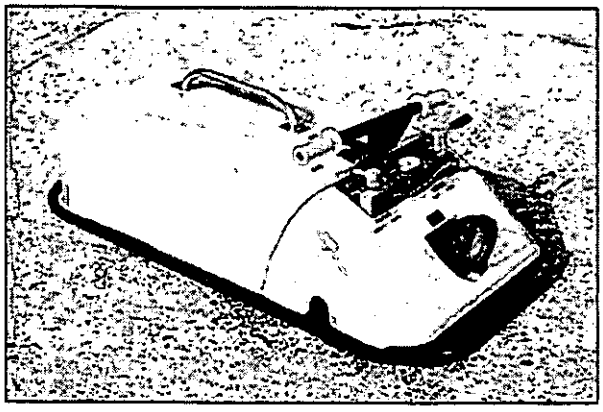


Figure 4

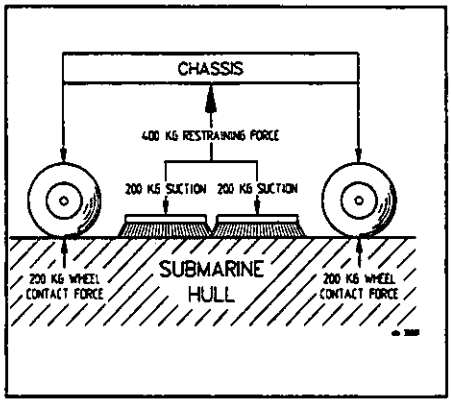


Figure 5

A Concept For The Future

In the words of the song, "the farmer and the cowman should be friends", or in our case "the diver and the paint man should be friends". Not so long ago the idea of divers underwater cleaning ships was an anathema to the marine paint companies who saw it as a threat to their antifouling compositions. Now times are changing. A more flexible approach in which antifouling paint and underwater cleaning are marketed together as a package is almost inevitable; otherwise the expectations of customers will no longer be satisfied.

Let us see how the cost of underwater cleaning compares with applying antifouling paint.

The first generation of tin-free antifoulings are considerably more expensive than their TBT equivalents at around $13 per litre and their performance has been somewhat disappointing. They retain some roughness throughout their life, are prone to cracking and flaking and their life is limited to about 36 months. The next generation of tin-free coatings are rumoured to be more promising but cost over $20 per litre. It would appear that ship owners must reconcile themselves to paying a great deal more for their fouling protection.

Referring to the table below, it costs around $15 m² to apply two coats of a first-generation tin-free antifouling in dry dock and this will provide about 36 months protection. Therefore, assuming underwater cleaning may be required at four monthly intervals, six underwater

cleans at $1 per m² may be required in order to 'top-up' to 60 months. In the case of a second-generation tin-free antifouling, no underwater cleaning is required (in theory) and the total cost of 60 months protection is slightly more. In the absence of any antifouling paint underwater cleaning may be required at four monthly intervals. This means that a ship could be maintained afloat for five years, which fits the maximum 5 year permitted docking cycle, using underwater hull cleaning for considerably less than the cost of a tin-free antifouling system.

Table 2
COMPARATIVE COSTS OF PROVIDING 60 MONTHS FOULING PROTECTION

36 MONTH TIN-FREE ANTIFIULING + UNDERWATER CLEANING	
	$ Per m²
HP water wash in dry dock	0.85
250 μof antifouling at $13 per litre with a practical spreading rate of 1.1 m² per litre	11.82
Application cost (2 coats)	1.90
TOTAL COST OF ANTIFOULING APPLICATION	$14.57
Add cost of 6 underwater cleans at $1 per m²	6.00
TOTAL COST OF 60 MONTHS FOULING CONTROL	**$20.57**
60 MONTH TIN-FREE ANTIFOULING SYSTEM	
HP water wash and application costs as before	2.75
250 μof 'second generation' antifouling at $ 21 per litre with a practical spreading rate of 1.1 m² per litre	19.09
TOTAL COST OF 60 MONTHS FOULING CONTROL	**$21.84**
60 MONTHS CONTROL USING UNDERWATER HULL CLEANING	
TOTAL COST OF 60 MONTHS CLEANING (13 CLEANS)	**$13.00**

However, at the moment underwater hull cleaning is only used as an occasional expedient because it is a relatively primitive process. It requires the ship to be stationary at a time and in a place where divers can operate. In practice, this means during daylight hours and at a location having reasonable underwater visibility with no currents of more than about 1 knot. Ever since the advent of TBT based antifouling paints there has been very little development of underwater hull cleaning systems because TBT provided a clean hull from one docking to the next.

Some vessels, particularly those on liner trades, may opt to use underwater cleaning as the primary method of fouling control, in which case they need only apply a good hard anti-corrosive coating. However, for some years to come I think it is safe to assume that most ship owners will wish to apply some form of antifouling coating in dry dock, which will afford them a measure of protection against marine fouling. Legislation is now steering them away from toxic paints and the most promising approach at the moment appears to be the low surface energy "non-stick" coating. This in turn will almost certainly need underwater hull cleaning to provide backup protection, but just as development money is being directed into non-polluting antifoulings, so development money should now be directed into improving underwater cleaning systems. The world market for antifouling paint has been estimated at 25 million litres costing the shipping industry in the region of $200 M, so there would appear to be some scope for investment.

Underwater Hull Cleaning In The New Millennium

What is required to elevate underwater hull cleaning to the point that it becomes an efficient, reliable means of fouling control?

The single most important factor is that the ship owner must be able to rely on the service being available when and where it is needed and for that to happen a machine that does not require a diver to operate it must be developed. The environment is not user friendly towards divers. They are expensive and difficult to deploy and as we have seen from the figures already quoted for Mini-Pamper, the "human element" effectively halves the output of a mechanical cleaning device.

There are two different ways of achieving this aim that are currently under consideration. One is to produce a remotely operated vehicle (ROV) for underwater cleaning, as shown in Fig.6. The other is to build a large installation along the lines of a car wash as depicted in Fig.7. It is the brainchild of Orca Marine in New Zealand and would operate rather like a floating dock by submerging beneath the ship to be cleaned and then travelling along the hull using an array of brushes to remove the fouling. Both systems would need to embody technology that enables them to clean without damaging the substrate and we do not consider them to be competing systems. The ROV provides a flexible approach, able to operate more or less anywhere, whilst the "car wash" would be installed wherever large concentrations of shipping justified the capital investment.

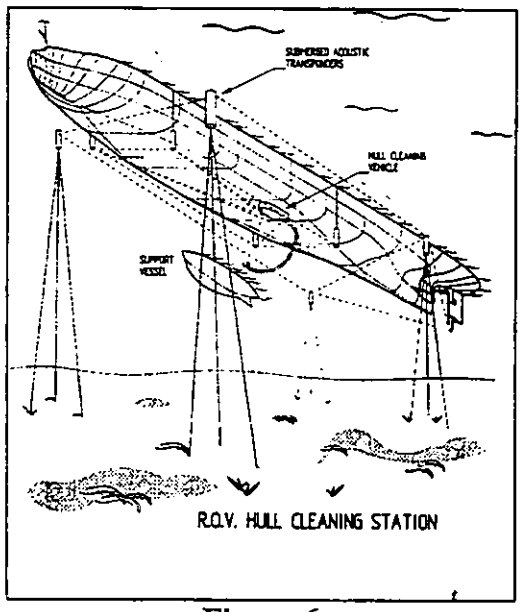


Figure 6

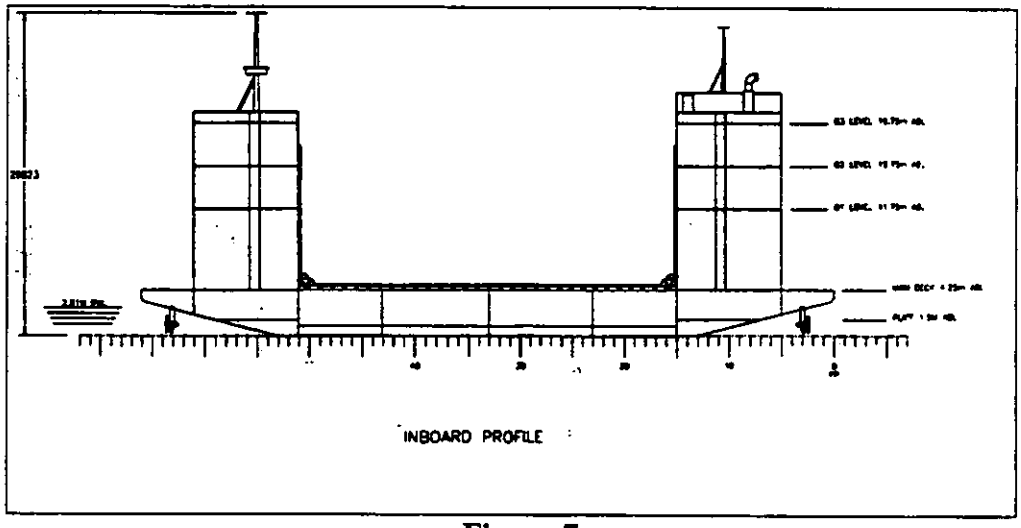


Figure 7 Courtesy, Orca Marine Co.

Environmental Considerations

There is a growing level of concern, present in virtually all levels of society, to protect the natural environment and the resultant pressure manifests itself in the form of major international agreements such as the ban on tributyl-tin and regulations to control emissions from ship propulsion systems. Indeed, one of the arguments put forward by the pro-tin lobby was that TBT based antifoulings reduced fuel consumption by an estimated 4% equating to about 7.4 million tons annually, thereby reducing the emission of greenhouse gases.

Until recently, approximately 10,000 tonnes of tributyl-tin were used in the manufacture of antifouling paints annually. The ban on tin will, in the short-term, merely result in an increase in the use of copper to an estimated level of 20,000 tonnes. Copper is also harmful to the

marine environment and as such it is likely to be included in the list of banned substances so far as antifouling paints are concerned. Certainly the development of alternative, non-polluting methods of fouling control will facilitate future legislation.

A non-toxic antifouling combined with an efficient robotic underwater hull cleaning system is likely to provide a way forward.

Repair Of Coatings Underwater

So far all the discussion has been concerned with antifouling coatings. To a certain extent this is inevitable because the antifouling paint is the last coating applied to a ship's hull and is therefore encountered by divers carrying out maintenance tasks. Anticorrosive coatings are out of sight and only become of interest when they detach, exposing areas of bare steel. Underwater maintenance work is confined to replacing them using underwater painting techniques.

Various special coatings capable of being applied underwater by divers have been marketed from time to time. These are normally epoxy compositions, which cure chemically rather than by solvent evaporation, which is not an option underwater. Presumably they must also contain wetting agents to aid application. They have not met with a great deal of success, partly because the divers seem to get more paint on themselves than on the job and partly because they have one thing in common, they are expensive. The process that I understand and am qualified to discuss relies on a technique that my company developed some twenty years back.

This relies for its success on a conditioning process that converts the steel from a low-energy surface, which is difficult to wet out, to a high-energy surface that is extremely easy to wet out. In other words, the exact opposite to the new 'fouling release' antifouling paints that are low surface energy and present a surface that marine organisms find difficult to adhere to. We call this process Sacrificial Pre-Treatment (SPT) and it consists of laying down platelets of hydrocarbon by high-speed brushing in which some of the brush material is deposited on the surface of the steel. After the paint is applied this material is absorbed into the paint coating (sacrificed) so that it is no longer present to form a weak link in the adhesive chain.

The application of SPT means that it is not imperative that the paint is especially formulated for underwater application. For example, the most successful anticorrosive coating that we apply is a standard wet-deck epoxy which is readily available at a reasonably price. The initial surface preparation before the application of SPT is carried out in the same way that it would be in air, either by grit blasting or disc sanding after which the paint is applied by means of a hand-held applicator in which the paint is fed through the back of a porous pad. The whole process is slow, but it is ideal for touching up isolated areas of bare steel. A team of four divers can prepare and apply two coats of anticorrosive paint to about 20 m^2 per day.

Because modern anticorrosive coatings properly applied are extremely durable, underwater painting on ships is generally limited to touching-up. However, occasionally it may be necessary to coat larger areas on structures that are designed to stay afloat for very long periods. For example, the Royal Navy owned a floating dock in the Clyde that was used for docking nuclear submarines. The dock last dry-docked in 1973 and by the mid-1980s

underwater surveys showed that the original hot-tar coating was beginning to break down. From then until the dock was sold in 1997, it was maintained in pristine condition by regular underwater painting. The specification comprised an annual underwater clean followed by touching up with two coats of an epoxy anticorrosive. Towards the end of its life the dock bottom, amounting to about 5000 m^2, was also coated with a tin-free antifouling paint that provided three years protection. This more than paid for itself by removing the need for any other maintenance during the life of the coating.

Underwater Ship Husbandry

If a vessel is on a 5 year docking cycle many other tasks that would normally be carried out in dock have to be accomplished afloat. A whole new industry developed as a result of three events that all occurred more or less at the same time, in the mid-1970s. These were the closure of the Suez canal, the advent of TBT self-polishing antifouling paints and the rule change that allowed 5-year docking cycles. The combined effect of these events resulted in an acute shortage of repair docks just as new technology became available which facilitated extended docking cycles. As a direct result, it is now possible to carry out permanent repairs to shell plating underwater, propellers are polished to surface finishes better than 1μRa. and a host of underwater engineering tasks can be carried out afloat, all reducing the dependency of vessels on dry docks.

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Chapter 16

Coatings for Corrosion Protection

David Deacon

COATINGS FOR CORROSION PROTECTION

David H Deacon, FICorr, FTSC
S P C Co UK, 6 Atherstone Court, Two Mile Ash,
Milton Keynes, MK8 8AE. UK
e-mail : deacon.s-p-c.co.uk@virgin.net

Abstract

Paints and coatings have been used for very many years in the protection of iron and steel as well as non ferrous structures to prevent them from degrading and corroding to return to their original natural state. This paper concentrates on the importance of successful maintenance painting of existing coatings on structures, to ensure that the optimum performance of the newly applied coatings is achieved and costly repetitive regular maintenance is prevented.

Coatings have developed over the past five decades from oil based, through synthetic resins mixed with oil up to complex chemical materials all containing corrosion retarders, either as anti-corrosive pigments or assisting in forming impermeable barriers in the resin/binder matrix.

It has been established by the author's company that failures prior to 1992 were assessed as over 90% being caused by application or surface preparation and not the coating system applied.

However, significant changes in paint technology due to enforced environmental protection legislation on a world wide basis has resulted in paint manufacturers making changes in the complex paint formulation to meet these requirements. These changes and the improvements with the application and understanding of surface preparation has resulted in a significant change in the author's companies experience, in that since the legislation was first introduced and finally implemented by the 1st April 1998, failures undertaken have changed to over 80% being caused by the paint or coating, either formulation or a lack of understanding by the specifier or the applicator in the requirements of the newer types of materials.

It is important to understand the question "what is paint". The fact is that paint is a complex engineering material and is a mixture of raw materials, each having an effect on the application properties and ageing of the applied film. Solid particles of pigment are dispersed in a liquid binder, that can be applied to a substrate and convert to a solid protective film where the adhesion to the substrate should be greater than the cohesion of the material. The basic ingredients of a typical paint comprise a binder, (the resin/vehicle/medium that holds the materials together.

A pigment which may incorporate an extender, a complex balance of solvents, a plasticiser or other additives and with two pack materials, a curing agent. Paints can be generally classified into two types, convertible and non-convertible.

Convertible paints are those paints which go through an irreversible change during the drying period, such as oxidation from the atmosphere as in oil paints or a chemical during process as in two pack synthetic resin mixtures.

Non convertible paints dry purely by the evaporation of the solvent from the coating and the resultant film can at any time in the future be re-dissolved in the original solvent and converted back to a similar paint system. Typical convertible paints are alkyds which dry by reacting with the oxygen in the atmosphere which is the basis of gloss paints for decorative purposes. Convertible paints are also the two pack types, for example epoxy or polyurethane which are chemically cured by the use of an additive. Non convertible paints are vinyls, bitumen solutions or chlorinated rubbers etc., which dry entirely by evaporation of the solvent.

There is significant confusion by manufacturers, specifiers and users of paints in the jargon of paint names. Solventless and solvent free coatings, some of which contain solvents are misleading and MIO or zinc paints are meaningless since they only describe the pigment. There has also been a range of compliant surface tolerant, moisture tolerant, winter grade paints produced by different paint suppliers, all of which have different properties and again can result in confusion and failure by misunderstanding the properties of these systems.

There are a range of maintenance paint systems, from the new stable of coatings, which have been produced by manufacturers since the EPA "watershed" in 1998. Many of these coatings can produce 20-25 year maintenance free repaint lives, provided the existing paintwork is carefully surveyed and assessed to select the appropriate material which will be compatible with the existing surface.

The importance of surveying of paintwork was reflected by the Department of Transport when they had approved approximately 250 painting inspectors to inspect and supervise the application of wet paint to well prepared surfaces and implement a specification and of those 250 they had less than 10 who could be used for paintwork surveys to produce specifications for maintenance purposes.

An experienced paintwork surveyor should be a trained and qualified paint technologist who has experience in examination and assessment of weathered paint films. They should be familiar with the knowledge of paint formulations and the ageing and degradation properties of the raw materials contained in the type of coating present on the surface.

Clearly a knowledge of surface preparation, application methods and the likely defects that may occur for one or more of these parts of the application and formulation process should also be understood. A paint surveyor would carefully select the areas to carry out this initial assessment of the structure, identifying both typical areas and possible weak areas on the structure to be examined.

The site tests undertaken would fall into two categories, non destructive and destructive. The non destructive tests would generally be visual with the aid of low power illuminated magnification and an angled mirror to observe areas which are not easily visible from normal access. General dry film thicknesses can be taken with non destructive instruments and

pinhole testing with a 90 volt wet sponge pinhole will give an indication of any porosity present in the paint film at vulnerable points.

The destructive tests are the most important during any survey, so access must be provided to the surveyor at arms length from the surface of the structure. Initially an abraded test patch is prepared to expose all of the individual coatings present on the surface. Cross cut adhesion tests and angle cut cohesion tests are carried out, an instrument is used to measure the thickness of each of the individual coats on the surface.

The abraded test area is subjected to small droplets of solvents to ascertain the likely compatibility of each one of the coatings with the typical solvents to be used in the specified maintenance coating. Tests for toxic materials, in particular lead, on older types of paint should be carried out and the surveyor will remove flakes of paints from this destructive test area to carry out laboratory examination of the individual coatings removed.

Once the surveyor has established the condition of the existing coating, a draft specification must be prepared to outline the surface preparation, extent of removal of the existing coating or whether it should be retained and the coating system that can be applied over this surface. The surveyor should be looking at a maintenance free period of at least 15 - 20 years before further work is carried out, so the decisions taken at this stage are of the utmost importance to ensure reliability and prevent disastrous failures occurring in the life of the protective coating applied.

The UK's Highways Agency call for a short feasibility trial to be carried out after the draft specification has been prepared to ensure that the specification can be implemented as part of the contract document, so claims for extras by the successful bidder during the main tender work will not be able to be substantiated. This short clause in the Highways Agency specification has prevented many claims from being agreed and strengthens the hand of the engineer in controlling the standards of the contract being undertaken.

A wide selection of maintenance paints are available to apply over the variable coatings that have been weathered over many years. The findings of the survey will narrow the possible choice of coatings to be considered from single pack to two pack. The type of structure and timing of the contract will decide whether moisture cured or moisture tolerant materials should be specified. It is not the purpose of this paper to carry out a detailed listing of all the coatings available, but only to emphasise the importance of establishing the condition of the previously painted surface to accept and provide a compatible base for the application and performance of a maintenance coating system.

Remember, would you ever build an expensive long life house on untested and untried foundations.

Reference:-

"Surface Preparation of Weathered Paint Systems for Successful Maintenance" – International Protection Coating Conference at PCE, The Hague, 1997.

Appendix:

Categories of Failure (from BD/18/83)

The UK Department of Transport (DTp) has set down certain procedures in order to achieve maximum economy with maintenance painting of highways bridges. A paint survey is required first in order to establish the extent and type of any coating failure and to establish the condition of the paint system.

Various categories of failure have been listed by the Department of Transport and these are the criteria for determining the extent of the maintenance required.

Categories of Failure (from BD/18/83)

CATEGORY I Local failures only. Finishing coat otherwise sound, such that a repaint of the whole Structure is not necessary.

CATEGORY II Normal weathering of finishing coat, e.g. chalking, surface affected by deposits, with some small areas of local failure. Adhesion generally sound that such that, after cleaning down, the system can accept local build up of undercoats and overall coating of the whole structure with an undercoat and finish similar to that of the previous system.

CATEGORY III General failure of the finishing coat at or before the expiry of its expected life. Some local failure of the last undercoats but otherwise first undercoats appearing to be still sound.

CATEGORY IV General failure of system, with disruption of undercoats and primer. Widespread corrosion varying from heavy rusting of the substrate to spot rusting on the surface of the paintwork. In some cases considerable areas of which corrosion products may be visible on the surface, probably denoting extensive corrosion of a metal coating or of a zinc rich paint.

For all categories of failure a pre-specification overall survey is generally recommended by the DTp.
In the case of Category III and IV a specialised surveyor is appointed from a list maintained by BES Division (DTp).

The purpose of this survey is to establish the extent, intensity and methods of surface preparation to ensure satisfactory performance of the remedial paint system.

Chapter 17

Design, Control and Operation of an Underwater Robot for the Automated Cleaning and Surveying of Marine Structures

Dr Manuel Armada
P González de Santos
T Akinfiev

Design, Control and Operation of an Underwater Robot for the Automated Cleaning and Surveying of Marine Structures

M. Armada, P. González de Santos, T. Akinfiev

Instituto de Automatica Industrial, CSIC
Arganda del Rey, Madrid, Spain
e-mail: armada@iai.csic.es

Abstract

In the last ten years the Automatic Control Department of the IAI-CSIC has been researching in the area of climbing and walking robots for hostile/hazardous environments. Apart from theoretical investigations, several practical realisations dealing with climbing and walking robots intended for performing remotely supervised welding operations in the shipbuilding industry have been successfully undertaken. The next step in this framework of shipbuilding and repairing industry is to provide an automated solution to the problem of cleaning and inspection of ship hull. For doing so a new project, funded under the EC Fifth Framework Programme, named AURORA, has been organised. This paper presents in general terms the sea adherence problematic and the preliminary ideas for the automation of cleaning&inspection tasks using an underwater climbing robot.

Keywords

Shipbuilding and repairing, underwater robots, climbing robots, sea adherence.

1. Introduction

All kind of ship's (passenger ships, ferry boats, bulk carriers, tankers, chemicals, cruises, roro, etc.) underwater hull, including flat bottom, vertical side and boot-top become overgrown with sea adherence (weed, barnacles) very fast. World fleet fuel expenditure is about 180 millions of tons/year, that at a medium cost of 100 euro/ton yields to an expenditure of 18.000 M euro. Taking into account that a hull with sea adherence can raise consumption of fuel up to 40%, this means burning of an extra figure of 72 millions of tons per year. But economy is not the only problem: raise of fuel consumption implies freeing atmosphere an extra amount of 210 million tons of CO_2 (incrementing greenhouse effect) and 5,6 million tons of sulphur dioxide (acid rain), apart from deterioration of ability of ship's control. This situation becomes important even after six months of ship activity. For recovery of ship's required operational performance, it is necessary for Ship-Repairing and Conversion Industries to dry dock a ship and proceed to cleaning. This procedure is very time consuming and of high cost, but it is the only available solution nowadays for SRYs. On the other hand, this cleaning activity is the first to be done when a ship needs maintenance and/or some repairing, being the last the main activity of SRYs. So hull treatment is required and, at present time, is done manually in dry-dock using different adapted methods like grit blasting or water jet, and it has to be noticed that, in itself, it is a very contaminant operation (dust contains always painting particles), it is harmful for human operators health and it is a very uncomfortable job. By other side Classifying Societies Surveys obliges to inspect ship hull steel two times every five years, with a maximum delay of three years between two inspections. This is mandatory for certifying ship's conditions and sea adherence must be generally cleaned before inspection.

Normally that inspection is performed in dry-dock, although there are in the market instruments that provides underwater thickness gauge for steel structures along with in water cctv & photo inspections, but they are handled by human operators.

Appart from ships there are other kinds of marine structures that presents similar problems (i.e. stationary drill-ships and FPOs) like those commented above. However although the goal of our research concerns the full problem of marine incrustations we are focused mainly in this paper on ship hulls. In any case the starting premise is that there is a proven need of sea adherence clean off and ship hull surveying.

The first difficulty we encounter when trying to automate cleaning or inspection tasks to be carried out on ship hull is its huge dimension. Generally speaking the problem of accessing to more or less remote job sites presents major difficulties and prevents automation. There are, reported in the literature, interesting solutions to this situation, for example very long reach manipulators. Other, not less interesting approach, is to provide a transport mean for the tele-manipulator. Such a transport mean includes wheeled or tracked vehicles, and more recently, legged-machines.

The Automatic Control Department (Industrial Automation Institute – Council for Scientific Research, IAI-CSIC) has been carrying out research and development projects in the field of robotic systems for more than twenty years. Since late seventies this activity began with the realisation of industrial robots, what provided the research team with a wide experience and reputation in robot kinematics, dynamics, mechanical design, and control systems. After some successful developments in that field, the department focused its interest in the area of robots for hostile/hazardous environments, like those posed by some nuclear engineering applications. In these kind of environments it is necessary to carry out a variety of tasks, what implies human operators are exposed to high radioactive doses. Also there are a great number of potential applications that cannot be performed directly by human operators because of difficulties in reaching working positions in a proper and safe way. This situation yields, in a natural way, to the utilisation of remotely controlled devices, where tele-robots can be considered as the most advanced and promising solutions. Doing so a number of advantages will come: improved working conditions, improved safety, improved quality, automation of repetitive tasks, and opening the possibility of providing innovative solutions to new applications.

Our activity in the field of robotics for hazardous environments, by the end of the 80's, was addressed to the research and development of climbing and walking machines. These are very innovative locomotion systems that presents a number of advantages over the other more classical ones, being the basic idea of providing transport to manipulation devices and/or to special instruments, sensor equipment and specialised tools, with the medium-term goal of industrial applications. During the last years, in our department there has been developed several climbing and walking robots for both basic research and industrial application purposes (Armada and Gonzalez, 1997).

In the field of industrial applications, and taking into account that nowadays shipbuilding, repairing and conversion industry is being forced to adapt its production means to new technical specifications, two new robotic systems (climbing and walking robots) has been developed by us, in the last five years, especially tailored for automatic welding in ship

erection (dry-dock). Both robotic systems have been developed within the framework of European Commission funded projects (Brite/Euram BE 7229 Rower 1, Esprit Pace Pr 212 Sacon) (Armada *et al*, 2000). Our next step in this framework of shipbuilding and repairing industry is to provide an automated solution to the problem of cleaning and inspection of ship hull. For doing so a new project, funded under the EC Fifth Framework Programme, Growth 99, named AURORA has been organised. The project partnership brings together 6 partners from 3 EU countries with complementary roles: the Industrial Automation Institute (IAI-CSIC) which is the Project co-ordinator, two ship-repairing yards, T. Kalogeridis&Co. Inc. and Unión Naval de Barcelona, Algosystems S.A., the Division of Robotics, Department of Mechanical Engineering, from Lund University, and SAIND, manufacturer and vendor of equipment for shipyards.

This paper presents in general terms the sea adherence problematic and the preliminary ideas for the automation of cleaning&inspection tasks underwater. The content of the paper is as follows. First the main features of marine incrustations will be revisited. Next a short explanation on how advanced mobile robot solutions can help shipbuilding industry is presented. Then the interest and state of the art in underwater robots for related applications will be shortly described, and that description will serve as a basis for the final discussion of the potentiality of such kind of machines for the automated cleaning and surveying of marine structures.

2. The problem and characteristics of marine incrustations

Although marine structures are provided with coatings to protect them against the incrustations, in practice it is only possible to delay the development of the micro-organisms during a certain time. However if the layer of marine life develops in a too significant way on the hull of the structure, roughness will increase and thus a number of problems like those just mentioned above, are originated. To understand the situation several studies on the formation of this layer on the hull have been carried out with the final goal of protecting both the marine structures and the environment.

It can be considered that the layer of incrustations is divided into three parts:

- Primary under-layer: it consists of silt or more or less hard mud, as of plants in low density.
- Secondary under-layer: composed of plants in stronger density (algae).
- Tertiary under-layer: constituted by molluscs.

The primary under-layer of mud can measure from one-half to several millimetres. Major part of the scale-preventing painting do not manage to prevent its appearance, but rather its later development, even if on the 100000 various species of silts only one tenth can be fixed by anti-incrustation paintings.

The appearance of the secondary under-layer is at the origin of a significant increase in roughness and resistance to the advance of the ships. Moreover, the rigidity of the algae, which can reach up to 150mm length and their forms, also plays a role.

Shells constitute the tertiary under-layer and there is no doubt that by its irregularity and its rigidity it contributes in a prevalent way to the increase of resistance to the advance of the

ship. The modern scale-preventing coatings, during their effective lifetime, prevent the appearance of this type of incrustation. Nevertheless, in the event of passage in tropical water and of navigation at low speed, it can arrive that these incrustations are fixed on zones not having protection anymore. The fixing of the larvae of these molluscs occurs in less than 48 hours. Typical dimensions of these molluscs are 10mm in diameter and 5mm height. However one can meet specimens of 50mm height and 100mm of diameter. As a consequence the ship's roughness can be multiplied by 4 only by the action of these incrustations.

There are two main factors influencing the development of the marine organisms: temperature and salinity. Temperature is one of the factors, which influences more the speed of development of the incrustations, which are of vegetable or animal origin. Of course, the effect of the temperature depends on the species considered, because there are characteristic species in cold water. Besides, it is necessary to take into account that some cargo liners transport liquid products at high temperatures and that the protection against the incrustations must be reinforced. On what respects salinity, this parameter exerts a less influence in the propagation of the incrustations. Just like the temperature, when salinity is significant, the speed of development is increased, but in general, the hot water zones correspond to water in low content saltworks. Moreover, there are zones like the ports and the estuaries where salinity combines with the pollution, which exerts apparently the same role. By other side salinity influences more the type of species which will appear than on the speed of development.

To solve the incrustation problem some protection counter measures can be taken. The most economic means to protect the hull from the marine organisms remains scale-preventing paintings (anti-fouling paint). Putting toxic substances in painting, like elements containing copper carries out protection against the incrustations. Painting releases then small quantities of these toxic elements and prevents the marine life from developing on the hull of the marine structure. The scale-preventing layer must adhere suitably to the anti-corrosive layer, which it covers, and must be compatible with this one.

The ideal processing would be to renovate the scale-preventing layers regularly so that there are not zones of paintings without toxic substances. These restorations would take place according to the exploitation of the ship, i.e. according to the number of days in port, the speed of navigation as well as the temperature and the salinity of water in which the ship navigates. Scale-preventing paintings available on the market can be classified into two families: traditional or "self-cleaning". The first category can itself be separate in two parts: conventional paintings and those of higher quality.

3. Climbing and walking robots for welding automation in shipbuilding

In the field of shipbuilding there are three main stages in the ship erection process. The first activity consists of the construction and assembly of huge ship blocks. This work is performed in highly automated workshops with a relatively good productivity, which is being increased by current research in this area. After the transportation of the blocks, which is performed in the second stage, the third involves joining two consecutive blocks by welding together all the longitudinal reinforcements and all the vertical bulkheads. For environmental safety reasons most ships, especially tankers and bulk carriers, are built with a double bottom and double hull so the cargo will not spill out if the hull is breached. This double structure

forms cells all along the ship's hull. A typical tanker bottom cell can be up to 10 meters long, 4 meters wide and 3 meters high. To allow workers inside, cells have an opening ("manhole") measuring about 0.8 x 0.6 meters.

There are two main welding problems in ship erection: butt-welding in position along the near-flat external hull surface, and butt/fillet welding for joining double bottom cells. In the last years IAI-CSIC has been involved in several projects dealing with welding automation in shipbuilding. Two main results are briefly reported herein: one six-legged climbing robot for butt-welding of ship hull, and one four-legged mobile platform for double bottom welding tasks. Both robots have been equipped with industrial welding units.

The REST climbing robot (Armada *et al*,1998) has six reptile-type legs with three degrees of freedom each one, actuated by dc motors through appropriate gearing. Feet at the end of legs are provided with special grasping devices based on electromagnets, securing the robot to ferromagnetic-material walls with intrinsic safety. The climbing robot carries on board his control system that consists on an industrial PC that serves as a master for a bunch of slave processors that controls in real time the 18-degrees of freedom. REST weights 220 Kg. and has been designed to carry on high payloads (100 Kg.) both on vertical/inclined walls and on ceilings.

Figure 1 illustrates the experimental testing of the REST six-legged climbing robot. Different gaits and control algorithms has been implemented and evaluated.

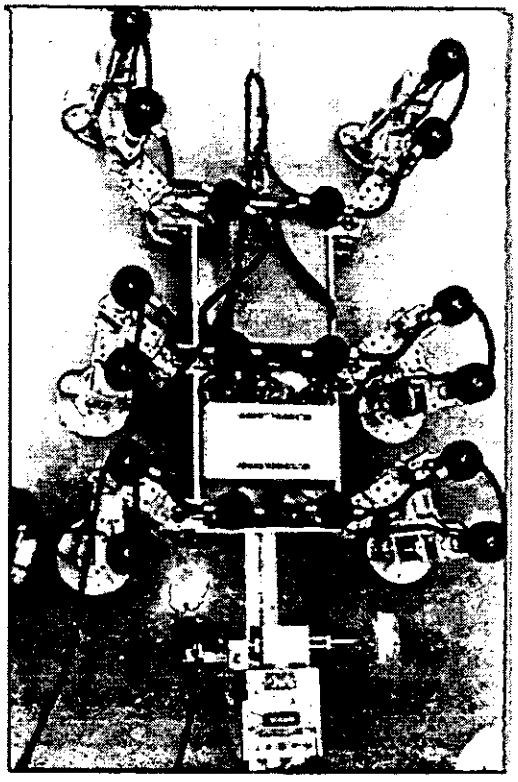


Figure 1 REST 1 system performing welding tasks.

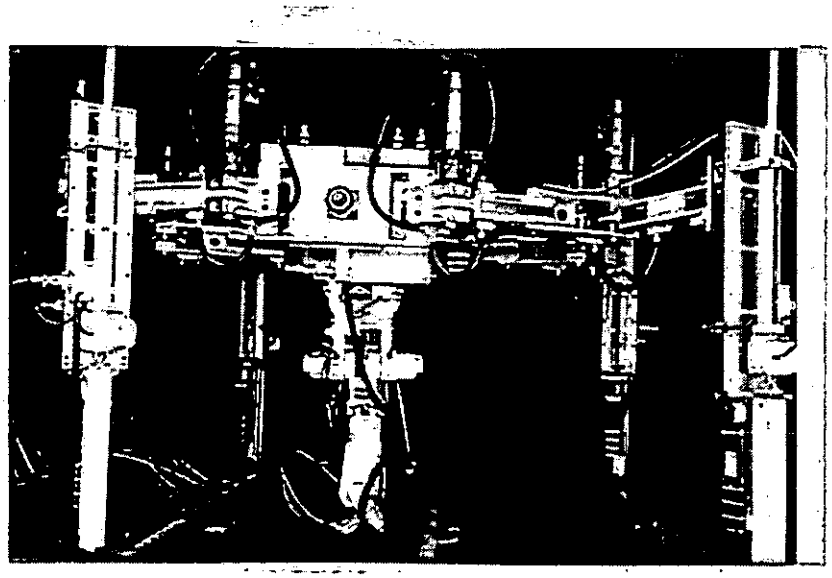


Figure 2 ROWER 1 system deployed inside double-bottom cell at shipyard.

The second development was intended for solving the problem of welding automation inside the double-bottom cells. The complexity of the working scenario and the system mobility requirements made a walking machine the best choice for this application. Different machine configurations were investigated in the light of the end users' strict requirements, such as total weight, dimensions, payload, and assembly/disassembly capabilities. Finally, a four-legged machine able to walk by grasping cell stiffeners was envisaged as the best choice for our application. The ROWER 1 solution was required to be modular and the presence of manhole was very important for its design, because the volume of each subsystem should be constrained to the manhole's dimensions. Another constraint was that the weight of each subsystem (manipulator, welding system, mobile platform, vision system, etc.) should be less than 50 kg due to labour regulations on systems carried on by operators. This is the reason why the mobile platform was divided into different parts and assembled inside the cell.

The full ROWER 1 (Gonzalez *et al*, 1997) system comprises the four-legged mobile platform, which provides 12 degrees of freedom for displacement plus 4 degrees of freedom for "grasping" up/down the stiffeners, along with an industrial welding manipulator, stereo vision unit, and welding equipment. The ROWER 1 system is controlled remotely (around 30 m far from the robot) by means of a control unit located outside the double-bottom cell. Very complex software was prepared for this system. Figure 2 shows ROWER 1 mobile platform inside double-bottom cell at the shipyard.

5. AURORA: Auxiliary Climbing Robot for Underwater Ship Hull Cleaning of Sea Adherence and Surveying

All known technical solutions on ships' hull cleaning are mainly based on the use of dry dock. The use of dry dock is very expensive, so ships' hull cleaning from sea adherence is not made very often usually, something like every three years. By that time, usually, there is a necessity of repairing of protective coat. Therefore, during the dry dock cleaning process a ship is being cleaned both from sea adherence and old protective coat. So, a ship operates having a lot of sea adherence during a long period of time, which worsens its operational characteristics (dotted line in Figure 3). Sea adherence that has been got in warm seas could decrease speed

of a ship considerably (about 10% in a short time: six months). Moreover, a presence of large amount of sea adherence leads to more intensive destruction of protective coat.

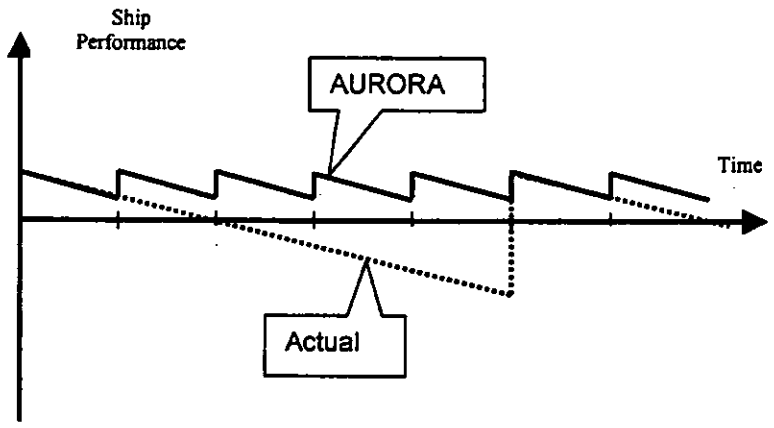


Figure 3 Ship performance improvement with AURORA concept.

In contrast to above mentioned, the use of proposed technical solution allows to clean a ship from sea adherence without the use of expensive dry dock. In this case it is possible to clean a ship much more often, for example, twice a year (solid line on the figure) and a ship could be in a much better state at all times. Even in the case when it is necessary to make inspection, repair or restoration of protective coat of a ship in a dry dock, it is possible to make a ship's hull cleaning out of a dry dock first, which would allow to use dry dock more efficiently than now.

5.1 The AURORA scenario

There are, reported in the literature, many and excellent examples of underwater robots. However most of them are intended for sub-sea exploration and manipulation (Ura and Suto, 1991) where important technological advances are present. There are also some works oriented to perform specific tasks like cutting and cleaning (Haferkamp et al, 1994, and 1995), and also some results dealing with underwater welding, but this activities are not very much widespread.

The AURORA scenario consists in the underwater hull that after some time, as it was explained before, is plenty of marine incrustations. That scenario presents large dimensions and exhibits some areas of very difficult reach-ability. The presence of water adds also another category of technical problems. In fact the surface to be clean off from sea adherence is not very much suitable for a legged robot to climb under it. So we are focusing a complex technological problem.

Figure 4 shows one example of ship underwater hull and the area to be covered by the robot for performing cleaning and inspection. It will be necessary to steer the robot all along the hull, which, at the end, is a very long distance, because for technical reasons the robot dimensions can not be very big. Figure 5 shows a closer view of the climbing robot design.

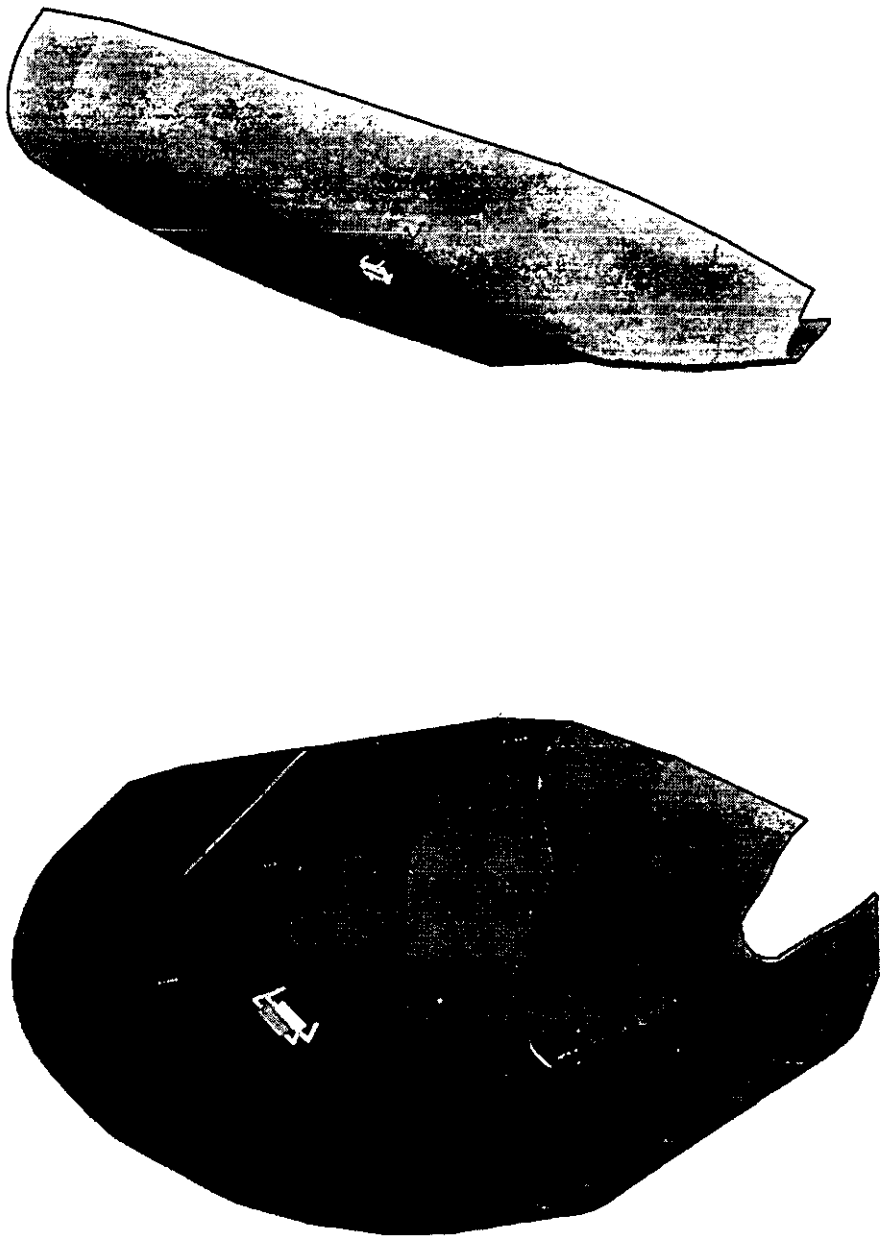


Figure 4 Underwater ship hull and AURORA robot

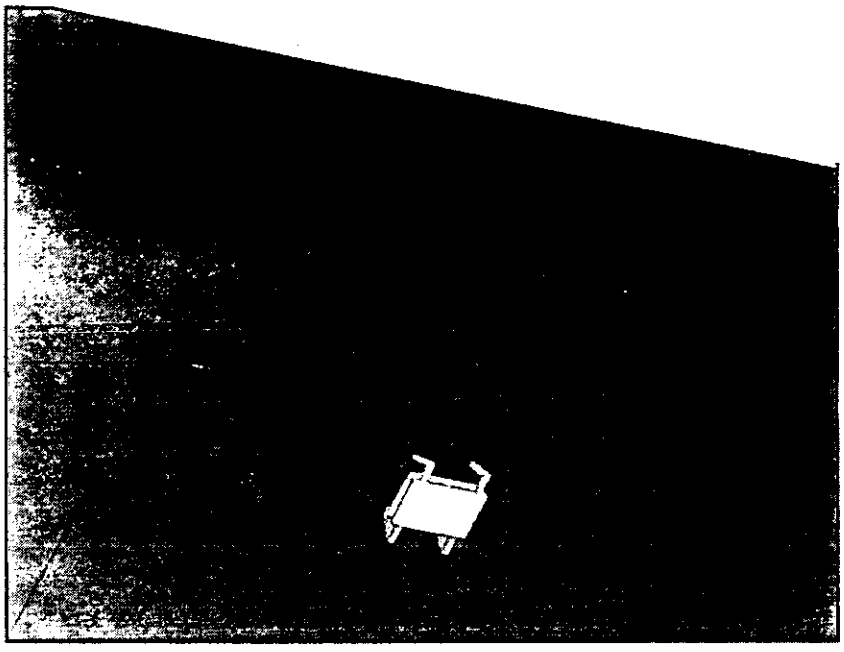


Figure 5 Detail of the climbing robot design

5.2 Control system and operator interface

As it has been conceived the underwater climbing robot control is a human-in-the-loop process. Human-Machine Interface (HMI) or User Interface (UI) design takes this into consideration whether using direct control or supervised control. From tele-operation to just "blind" control, the HMI can be more or less sophisticated. It can be said that all climbing and walking robots (CLAWAR) have a common basic functionality because they are locomotive vehicles (Armada and Prieto, 1999). A simple man-machine interface will be used to facilitate the steering of the AURORA robot. This interface includes a control command set used to select the machine trajectory and a graphic representation used to get information about the robot and its environment.

We differentiate between two main modalities of robot control, direct control and supervised control. Direct (or manual) control requires a different approach to HMI compared with supervised (or semiautomatic) control. Direct control deals with detailed attention to robot parameters and considers the user (person) a vital part in the loop. Here, detailed real time magnitude feedback and control flexibility is of prime importance. Supervised control assumes the robot is able perform a group of tasks by its own or autonomously. The user is more devoted to just monitoring and taking high level decisions when appropriate. The supervision HMI should be more task-oriented with general views of the robot operation and the ability to intervene in order to stop or launch orders. HMI specifications have been discussed from the monitoring and manipulation standpoints:

Magnitudes: The interface should provide the ability to monitor and manipulate useful magnitudes at different levels:

- Joint magnitudes
- Leg trajectory level
- Body movement level

- Gait control
- Overall machine

Views: AURORA HMI should have a "Scene View" of the machine's state together with the environment and a "Magnitude View" reflecting the evolution of selected parameters. Both parts should be customisable by the user at least in form of persistent configuration files from session to session. The most desirable property should be the online reconfiguration of views as the operating conditions recommend switching to a better monitoring view.

User interaction: From the operation standpoint, a "Main Control Panel" should exist in order to give operational orders to the robot. This panel should also be re-configurable and flexible according to the context and level of control. Another desirable property of operation is to use, when possible, specific peripherals.

Simulation: The need for better situation awareness and what-if operational testing justify the addition of simulation capabilities during run-time. Of course simulation integration could also allow for debugging and fine-tuning during design and construction before the actual vehicle is in place. Training and task planning alternative evaluation could also benefit from simulation-HMI integration.

The peripheral context of those GUIs is to use typical I/O computer devices: screen, joysticks, mouse, keyboard, teach pendant and video camera.

The objective of the control system is to allow a human operator to drive the robot in real time, just paying attention to the trajectory of the machine, giving simple and intuitive orders by keyboard as if the robot were a wheeled vehicle. An omni-directional free gait and a spin gait can be easily combined to follow a trajectory or to reach a point of the underwater ship hull. The operator can make use of the following controls in real time to drive the machine:

Crab angle selection: The crab angle can be increased or decreased in five-degree steps by hitting two different keys (this increment can be programmed). This is useful to make small corrections in the trajectory of the robot or to steer it along a smooth trajectory. Another four keys allow the operator to select four pre-determined crab angles. These angles are 0, 90, 180 and 270 degrees, so that the robot will move forward or backward along its X-axis or Y-axis.

Spin gaits: A clockwise or a counter-clockwise free spin gait can be selected with the left and right cursors. The omni-directional gait is recovered by hitting any of the crab angle selection keys.

Pause: This key stops the movement of the robot momentarily, keeping some information such as present gait, next leg to lift, crab angle, etc.

End: Stops the movement of the robot finishing the gait algorithm.

There are simple commands allowing the operator to determine some parameters, such as the total distance to walk, the angle the robot must rotate, the number of steps to make, or the crab angle, before the walking algorithm begins. This provides an accurate way to follow some simple defined trajectories, releasing the operator from an exhaustive vigilance of the

machine. Previous simulations and experiments carried out on earlier developments (Jimenez and Gonzalez, 1996) showed that just with these controls, it is possible to drive the robot following desired paths, using both rotations and changes in the crab angle to change the trajectory.

6. Conclusions

Sea adherence problematic and the preliminary ideas for the automation of cleaning and inspection tasks underwater have been presented. The main features of marine incrustations were briefly outlined and an explanation on how advanced mobile robot solutions can help shipbuilding industry was presented. The interest and state of the art in underwater robots for related applications were shortly described, and that description served as a basis for the final discussion of the potentiality of such kind of machines for the automated cleaning and surveying of marine structures.

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Chapter 18

Classification Societies Perspective of Marine Coating

Sille Grjotheim
Erik Askheim

Classification Societies perspective of Marine Coating

Sille Grjotheim and Erik Askheim
Section for Material/Production Technology, Det Norske Veritas AS, Høvik, Norway
e-mail: Sille.Grjotheim@dnv.com

Abstract

Ships' structural integrity as well as economical and environmentally safe operation depend on effective, durable corrosion prevention. Due to historical events and technical developments, some ship owners and Maritime Authorities now desire more involvement from the classification society concerning protective coating of seawater ballast tanks, cargo tanks and cargo holds. DNVs approach towards the desire so far, is mainly reflected in our new Rules. Additionally class notations on voluntary basis represent an option to owners wanting an especially high coating standard (COAT notation) for ship new buildings, and for those owners wishing and environmental class, CLEAN AND CLEAN DESIGN Notations have been introduced.

DNV is also approaching the request for more involvement by offering various advisory services within coating/corrosion prevention such as; Pre-contract specification review, advice re. bacterial corrosion, testing of coating/sacrificial anodes, R&D re. flexibility of tank coating, auditing shipyards coating activities, corrosion/coating course, arbitration services, area calculations for tank coating, Life Extension Programme, Life Cycle Cost analysis and Condition Assessment Programme.

Keywords

Coating, Corrosion Prevention, Rules/Regulations.

1 Introduction

The classification societies have traditionally kept a low profile regarding corrosion protection of ship newbuildings. Coating related aspects has been a matter of agreement between shipowner and shipyard. During the last few years, however, classification societies have been encouraged to take a more active role. Briefly, it is due to increasing market awareness of the importance of effective, durable corrosion protection for ships'

- structural integrity
- economical operation and
- environmentally safe operation.

Seawater ballast tanks are most demanding of effective corrosion prevention systems, although also cargo tanks, cargo holds and void spaces need to be well protected.

Steps have been taken by individual classification societies, IACS, IMO and SOLAS towards a more comprehensive classification society involvement in corrosion prevention [1], [2], [3], [4], [5], [6].

The DNV Rules for Ships [8] have currently been updated in order to comply with new regulations and the market. Voluntary class notations COAT are also focusing on corrosion prevention.

As a part of DNVs' approach towards increased involvement in and focus on corrosion prevention, DNV offers various advisory services within the same area.

2 History and Motives for Increased Focus on Corrosion Prevention

Great changes in ship design and shipbuilding practice that took place during the late 1960's and early 1970's strongly influence everyday ship operation and maintenance even today.

Increased ship size and structural optimisation

New shipyards were established in Europe and East Asia with large dry docks and improved production facilities in order to meet the demand for bigger ships. In mid 1960's the maximum size of tankers was about 100,000 dwt. Ten years later, tankers exceeding 500,000 dwt had been built

With the introduction of computers in the late 1960's, direct calculation methods for structural optimisation were developed. The optimisation often focused on minimising the steel weight of the ship, and use of high tensile steel became standard practice. The amount of high tensile steel has been brought up to 80-90% of the steel weight in extreme cases.

Improved production facilities and control at steel mills resulted in steel being delivered with minimum specified thickness without the traditional thickness variations providing extra reserves earlier.

A combination of optimised local scantlings and use of high tensile steels lead to larger strains on local structures. When the structure is increasingly strained, the protective coating tends to crack and exposes the steel for corrosive attack. Rust and scale, which forms a protective barrier, flakes off. As the material is wasted, the stress level increases. And so the process accelerates resulting in possible holing and cracking of the structure with potentially serious consequences for the ship hull integrity and ability to contain polluting cargoes.

Requirements to direct strength calculations of girder structures, and separate fatigue requirements for critical details (by means of Finite Element Methods), are included in DNV's Rules for ship of today.

Hull Damages

A combination of operational factors and human error causes most ship losses. Grounding and collisions are the most common serious hull damages. Hull failures as the initiating event account for about 15 – 17 % of serious casualties, according to statistics comprising the whole world fleet for the period 1978 – 95. Failures caused by corrosion are included in this figure. For bulk carriers, corrosion of cargo hold structures has contributed to the loss of a number of ships and lives during the last decade. Corrosion of ballast tanks is often the reason for scrapping of ships.

Several studies have been made on corrosion rates in ships' seawater ballast tanks, including segregated and non-segregated ballast tanks. However, prediction of corrosion rates for the respective structures and plating is difficult since the rates on ageing ships vary greatly. Corrosion additions on steel plate thickness in accordance with DNV Rules [8] are based on many years' experience with existing ships that are properly maintained.

In general, those areas which are usually most difficult to protect with coating, typically welds, edges and details with difficult access, will be the first to be exposed to the corrosive ballast water due to early coating breakdown. Early coating breakdown can frequently be traced back to substandard steel surface and edge treatment. Accelerated corrosion can occur on these anodic areas due to galvanic effect from large cathodic surfaces with intact coating.

Structural details should accordingly be designed with due regard to

- easy access for surface preparation, coating application, inspection and maintenance
- good drainage and avoidance of pockets and areas where water and dirt can accumulate
- using bulb profiles instead of L profiles
- avoidance of sharp edged details and intricate cut-outs.

Segregated Ballast Tanks and Double Hull influence the Corrosion Pattern

Public concern regarding accidental pollution from tankers as a result of collision or grounding, resulted in Marpol 1973 limitations for oil tank capacities depending on their location, i.e. center or side tanks. Segregated ballast tanks, i.e. tanks for carrying ballast water only, became mandatory in 1978 as defence against oil spills. Carrying oil and ballast water in the same tanks was also prohibited, reducing the risk of discharging of oily ballast water into the sea.

The US Oil Pollution Act adopted in 1990 requires all new tankers intended to be operated in US waters to be built with double hulls. Transport of oil is not allowed in the double hull.

The above two pollution prevention regulations both have great influence on the corrosion pattern. The former practice of carrying crude oil and ballast water in the same tanks created a particularly corrosive environment in these tanks. Corrosion was severe in the ullage space underneath the deck where the temperature may be high and the structure is frequently washed by ballast water. Severe corrosion occurred especially on horizontal surfaces, such as bulkhead longitudinals and deck girder face plates where water was trapped.

After the introduction of segregated ballast tanks, the corrosion in oil cargo tanks is mostly observed in the bottom plating and other horizontal surfaces due to foul, sulfur containing water precipitated from crude oil. Pitting and grooving corrosion may be extensive.

The large ballast tank surfaces in double hull ships are likely to increase the demand for maintenance work on coating as well as steel structures in general.

Cargo Tank Bottom Pitting Corrosion – a Safety Hazard in Double Hull Tankers

If oil cargo tank bottom corrosion is not kept under control, pits may penetrate the bottom plating.

In single hull tankers, pit penetration can result in oil cargo polluting the sea. In double hull tankers, pit penetration will primarily imply a safety hazard due to the hydrocarbons entering empty ballast spaces. In addition, there will be a pollution effect when the ballast water is pumped into the sea.

Microbial Corrosion/Bacterial Corrosion

tends to become an increasingly severe problem in cargo tanks and can also occur in ballast tanks. Double hull ships are more susceptible to microbial flourishing due to prolonged period of elevated oil cargo temperature (thermos bottle effect). Regulations imposing restrictions on the release of ballast tank water may also promote biological activity here.

The microbial corrosion process, when occurring, causes an additional corrosion effect superposed on the normal electrolytic corrosion. The resulting corrosion rate may be formidable, e.g. pitting rates up to about 2 mm/year and 7 mm/year has been reported for ballast tanks and cargo tanks respectively.

Steel Renewals

Extensive steel renewals have been undertaken due to corrosion, especially in ballast tanks.

A main problem with steel renewals is that new steel is welded against a corroded structure. Welds between the new and the corroded structure may contain flaws, and cracks may be generated in the heat affected zone of the old plating during cutting and welding. The coating of old plating may be damaged and not patched up later.

Corrosion of the adjacent old plating may be intensified, and stress levels and stress concentrations in the whole structure may become offset due to changes in local thickness, for example new plates versus old corroded plates. Incidents are known where parts of the ship side have been lost into the sea.

Coating is Cost Effective

Rather than being a safety problem, corrosion is commonly an operational problem causing trouble for the owner, sometimes with severe cost implications.

A good coating applied on a well prepared surface at the newbuilding stage is the most effective means of avoiding corrosion. Coatings will have varying useful lives in ballast tanks, from a few months to more than 25 years, depending largely on steel surface and edge preparation, application conditions and degree/level of maintenance.

Sacrificial anodes will be useful as a support to the coating but can not replace it.

Coatings applied by crew or in repair yards on ships in operation will often have rather short useful life compared with coatings applied at the new building stage. This is because the surface preparation and strict control of temperature and humidity conditions necessary for a good result, are not obtained. Semi hard or other coating types especially developed for the ships in operation market and intended for application on non-blast cleaned surfaces are interesting in this context.

In recent years calculation procedures have been developed to estimate life cycle costs LCC. They indicate the cost effects of different corrosion protection systems applied on the ship new building, maintenance strategies adopted by the ship owner, future steel renewals and off-hire costs. LCC analyses carried out by DNV confirm earlier assumptions that:

The application of high quality coating in seawater ballast tanks at the new building stage is cost effective compared with upgrading by means of steel renewals later on.

The application of increased corrosion margin (coating of steel with steel) is not cost effective compared with improving the coating quality.

Flexibility of Coating

An important contributing factor to coating degradation is the increasing brittleness and loss of flexibility with time, causing cracking and disbonding at structural hot spots, typically in deckhead structures. The coating may be flexible enough when newly applied and a few years afterwards. Then, due to different factors such as cyclic temperature variations, depletion of volatile, low molecular weight constituents in the coating due to evaporation or washing by ballast water, oxidation and other chemical changes of the coating constituents contribute to the gradual loss of flexibility.

The tendency to loss of flexibility of coatings depends on the type and quality of its constituents, i.e. its raw materials such as binder (typically epoxy resin and curing agent), extenders and flexibilisers (e.g. coal tar), pigments, etc.

It is due time that the shipping industry together with the paint/coating manufacturers start investigation of how coating flexibility changes with time due to ageing processes. The behaviour of coatings under simulated ballast tank deckhead conditions is primarily of interest. DNV has undertaken a preliminary study, and laboratory investigations of coating flexibility as function of ageing which started in year 2000 [9].

The Role of Class in the Coating Business

The market generally wants ships to be in good shape, nice looking, safe and economical in operation. Surface protection, including steel preparation, coating materials and their application, adds considerable cost to the ship, so an optimal coating quality at an acceptable cost must be aimed at.

Ship yards have a fundamental interest in building ships quickly and effectively. Since steel surface treatment and coating application operations are cumbersome and demanding of man-

hours, a conflict of interest between yard and owner is often implicit in a newbuilding situation.

The classification societies have long traditions of being the 3rd party, taking a neutral role and always aiming at obtaining the best quality possible. So far, however, the class involvement is mainly limited to paper work only, implying that coating specifications, anode specifications, calculations and drawings of cathodic protection if installed, are to be submitted for information. In addition, DNV offer various advisory support within the area corrosion prevention.

3 Regulatory Framework (IACS, IMO, SOLAS)

The condition of coating in water ballast tanks on existing ships has become part of the classification scope of work due to the IACS Unified Requirement UR "Hull Surveys" [1] introduced in 1990. Based on this UR, the ballast tank coating condition is to be evaluated by the surveyor and categorised as either

GOOD, FAIR or POOR.

The coating conditions GOOD, FAIR and POOR are assigned based on visual inspection and estimated percentages of areas with broken down coating and rusty surfaces.

If the tank in question is found with

- the coating in POOR condition
- without coating, or
- coated with soft coat only

the ballast tank in question will be subject to an annual survey. The potential cost implications of annual surveys is a considerable incitement to the owner for keeping the ballast tank coating in GOOD or FAIR condition.

IACS introduced Unified Requirements to "Corrosion Protection Coating for Salt Water Ballast Spaces" on new buildings in 1990 [2] and to "Corrosion Protection Coating of Cargo Hold Spaces on Bulk Carriers" in 1992 [3].

The background for these IACS UR's was several severe accidents involving oil tankers and bulk carriers.

IMO "Guidelines for the Selection, Application and Maintenance of Corrosion Prevention Systems of dedicated Seawater Ballast Tanks", Resolution A.798 [5], were issued in 1994 and adopted in 1995.

The SOLAS Amendment Ch.II-1, Reg. 3-2 "Corrosion prevention of seawater ballast tanks" [6] applies to oil tankers and bulk carriers constructed on or after 1 July 1998 and gives direction to include corrosion protection of ballast tanks in oil tankers and bulk carriers within the scope of classification, by stating:

"All dedicated seawater ballast tanks shall have an efficient corrosion prevention system, such as hard protective coating or equivalent. The coatings should preferably be of a light colour. The scheme for the selection, application and maintenance of the system shall be approved by the Administration, based on the guidelines adopted by the Organization* (* above mentioned IMO Guidelines). Where appropriate, sacrificial anodes shall also be used."

DNV [8] has developed the Rules for Ships in accordance with this amendment, i.e. by giving detailed recommendations re. corrosion protection. In general, more focus and attention is given in this respect, see below chapter.

Finally, an IACS Unified Interpretation SC 122 was issued early 1998 [7] and was agreed upon and is incorporated in the amended DNV Rules.

4 Class Rules

Market demands for more information and focus regarding

- coating technology in general
- specifications of coating systems, especially concerning steel surface preparation
- follow-up of steel surface preparation and other coating related operations

resulted in the development of the DNV Guidelines for Corrosion Protection of Ships [4]. The Guidelines are primarily for voluntary use as an advisory document. Three target durability levels for coating is defined; approximately 5, 10 and 15 years durability, respectively, with emphasis on coating of water ballast tanks and cargo tanks.

The DNV Rules for Ships [8] have currently been developed in order to comply with regulations and market needs, as described below.

4.1 Main Class 1A1

Requirements to corrosion prevention systems in the DNV main class (1A1) Rules for Ships are given for seawater ballast tanks only, i.e. tanks for ballast water are to be protected by an effective coating or equivalent protection system. The coating specification and anode specifications, calculations and drawings are to be submitted for information. The recommended content of the coating specification for seawater ballast tanks can briefly be summarised as in the below Table 1. The Rules are in compliance with the IACS Interpretation UI SC 122 [7] of SOLAS Amendment Ch. II-1, Reg. 3-2 [6]. The Society's involvement concerns the contents of the specification only and does not imply any approval of the surface preparation or coating as applied. The Rules are applicable for tank and bulk carriers, newbuildings constructed on or after 1 July 2000.

The IMO Guidelines [5] and IACS [7] indicate the contents of the coating specification, including details of a coating inspection procedure, as reflected in the DNV Rules as per the below Table 1. The left column refers to the SOLAS [6] scheme for selection, application and maintenance of coating, and the right column items 1)–9) comprise the contents of the IACS UI [7].

Table 1: Contents of Coating Specification	
Scheme for (ref. SOLAS Reg. II-1/3-2)	***Items to be described in specification***
General	The yard's, owner's and coating manufacturer's agreement on the specification
Selection Of Coating	1) Coating type, material and manufacturer's data sheets concerning below items 2) – 5)
	2) Definition of coating system, including number of coats and minimum/maximum variation in dry film thickness
Application Of Coating	3) Surface preparation, including preparation of edges and welds, and surface cleanliness standard (e.g. blast cleaning to Sa 2,5)
	4) Coating manufacturer's safety data sheets
	5) Maximum allowable air humidity in relation to air and steel temperatures during surface preparation and coating application
	6) Yard's control and inspection procedures *) including acceptance criteria, and - tests/checks (e.g. surface cleanliness, film thickness, air humidity, temperature controls) - handling of deviations from specified quality
	7) Details of anodes, if used
	8) Evidence of Yard's experience in coating application **)
Maintenance Of Coating	9) Coating Manufacturer's recommended procedure, preferably alternative procedures, for future maintenance of coating on the ship in operation

Supplementary descriptions of the items in Table 1 are given in other papers [17].

Guidance notes:

*) The items listed below should be described in the control and inspection procedures (and thus included in the coating specification) for the ship new building

a) Organisation of operators, inspectors, facilities, equipment and procedures
b) Working conditions, e.g. access, staging, illumination
c) Conditioning of steel temperatures and relative humidity
d) Methods of conditioning of steel temperatures and relative humidity, e.g. indoor facilities for blast cleaning and coating, heating/drying equipment, etc.
e) Storing of coating materials and abrasives
f) Preparation of sharp edges
g) Blast cleaning and any other surface preparation
h) Cleaning, including removal of abrasives after blast cleaning
i) Cleanliness with respect to chloride content on surfaces to be coated, oil, weld smoke, dirt, etc.
j) Shielding off painted surfaces from blasting operations
k) Blast cleaning equipment and type of abrasive
l) Coating application equipment and methods
m) Curing times for individual coats in relation to temperatures
n) Dry film thickness of individual coats
o) Total dry film thickness
p) Coating repairs in case of damage, and handling of coated surfaces
q) Installation of anodes, if specified.

**) Re. item 8): Minimum evidence will be a reference list stating (some or all) ships coated by the Yard. Other relevant evidence may be for example technical reports on the performance of coatings applied by the Yard, e.g. inspection reports on coating condition in ballast tanks after a number of years, or a quality system certificate for the Yard's coating application division or subcontractor. It is essential that the evidence is acceptable to the Owner.

4.2 COAT Notations

The DNV main class, 1A1, defines a high quality standard sufficient for ships operating world wide within normal trading patterns, however, when it comes to corrosion prevention, in brief, the class requirement is that tanks for ballast water only are to be protected by an effective coating or an equivalent protection system.

If the owner want additional safety margins by improving the coating system, and are interested in advice and stating this officially, a new, additionally class notation COAT is offered to the market on voluntary basis, tailor made for these ships.

The COAT notations define coating systems and in which category spaces they are to be applied. The coating systems are described in a Classification Note (No. 33.1) and reflect three different quality/durability levels, ref. DNV Guidelines No.8 [4], in accordance with well known and available corrosion prevention technology.

The COAT notations aim at obtaining adequate protection of areas regarded as critical with respect to corrosion control on board ships, in order to obtain long useful lives of ships. For instance, in double hull tankers, bottom pitting including bacterial corrosion has been experienced as problematic. The COAT notations therefore specify cargo tank bottoms to be coated. Similarly, the ullage space underneath deck in oil cargo tanks shall be coated due to experienced corrosion and cost demanding access if coating is to be carried out at a later stage.

During construction, the yard, owner and coating manufacturer can utilise the coating system specification to ensure that the intended quality is obtained. Documentation of deviations from the specification shall be submitted to DNV. DNV will, however, not perform inspections for the coating application unless upon a special agreement.

The three coating systems specified are all on epoxy or similar basis, deviating in quality mainly due to different requirements to steel surface preparation.

Coating System I is a relatively simple specification. The steel plates are blast cleaned and primed before being used in production. Damaged primer on the built structure is mechanically cleaned by power tooling or similar before application of one coat with thickness 200 microns. Coating system I is not recommended for ballast tanks.

Coating System II is a good specification, well suited for ballast tanks. The steel plates are blast cleaned and primed, and damaged shop primer on the built structure is blast cleaned before coating. Two coats of totally 300 microns are to be applied.

Coating System III is a very good specification, well suited for ballast tanks. The built structure is blast cleaned and primed before being used in production. The built structure is

blast cleaned before coating. The salt content on surfaces to be coated is to be below a given limit. Two or three coats of totally 300 – 400 microns are to be applied.

There are two degrees of COAT notations, COAT-1 and COAT-2. A summary is given in the below Table 2.

Table 2: Summary of COAT Notations			
Ship	**Location**	**Coating System**	
		COAT-1	**COAT-2**
Crude Oil Tanker	Ballast water tank	II	III
	Inner bottom in cargo tank	II	II
	Upper part of stringers and deckhead in cargo tank	I	II
Bulk Carrier	Ballast water tank	II	III
	Cargo hold, upper part	I	II
Other	Ballast water tank	II	III

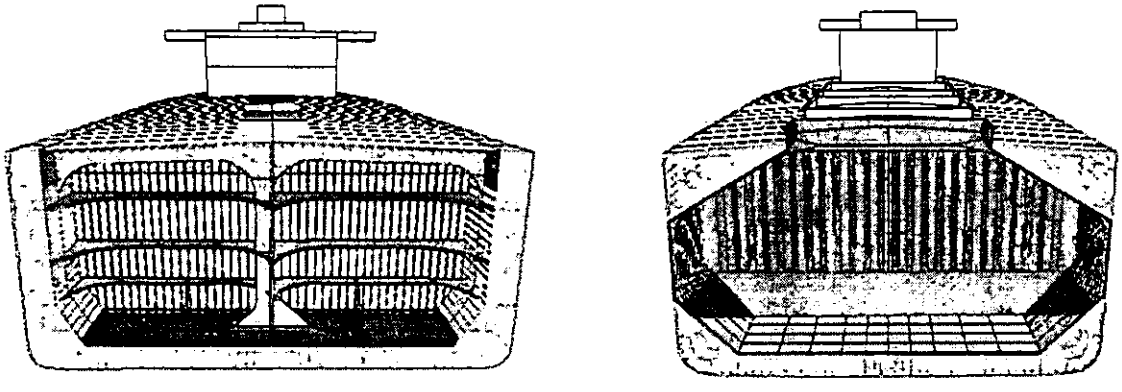


Figure 1. Coating requirements for COAT notations, as per the above Table 2
Left: Tanker; Right: Bulk carrier

4.3 CLEAN AND CLEAN DESIGN Notations

The general request for more environmental friendly ships has introduced the voluntary environmental class notations: CLEAN and CLEAN DESIGN, comprising three main areas: emissions to air, operational discharges to sea and accidental discharge to sea. For both notations, restrictions to the use of TBT antifouling is given, CLEAN DESIGN being the stricter, implying non-TBT antifouling.

A summary of the requirements to paint/antifouling only, is given in below Table 3:

Table 3: Summary of CLEAN/CLEAN DESIGN notations w.r.t. paint/antifouling		
Subject	**Class Notation**	
	CLEAN	**CLEAN DESIGN**
Paint/antifouling	Flat bottom: Non-TBT. If TBT on sides, maximum leaching rate: 4μg TBT/cm^2/day	All antifouling shall be non-TBT

The class notations CLEAN and CLEAN DESIGN can be applied on most ship types.

5 DNV support

In line with DNVs' approach to increase the involvement in and focus on corrosion prevention, DNV offers various advisory services.

Pre-contract specification review

A review of and advice regarding coating specifications is a service offered in order to improve the quality, and possibly avoid conflicts between the owner/yard/coating manufacturer at a later stage.

General advice regarding coating/Arbitration services/Bacterial corrosion

DNV may offer advice and highly technical competent support within the subject corrosion prevention upon markets request, including 3d party inspection and arbitration, if requested.

Especially, the topic bacterial corrosion/microbial corrosion has been highlighted due to the introduction of double hull ships, elevated temperatures and restrictions to release of ballast water that may promote the biological activity, ref. Ch.2, above. The corrosion rate can be rather high, e.g. pitting rates up to 7 mm/year have been reported in cargo tanks compared to an average ballast tank corrosion rate of approximately 0,2 mm/year.

Testing and classification of tank coating, shop primers and sacrificial anode alloy materials

DNV offers standardised testing of protective coatings, shop primers and sacrificial anode alloy materials. Fixing methods for sacrificial anodes can also be evaluated.

Protective coating:

Testing/Documentation of performance
Coatings should be selected that have documented good performance in actual service. Classification societies offer "type approval" of manufacturers' products, usually on a voluntary basis. The concept and technical requirements of type approval (TA) have changed over time, and may differ from one classification society to another. DNV currently uses a 1991 ISO definition, which states that TA is approval of conformity with specified requirements on the basis of systematic examination of one or more specimens of a product representative for the production. TA of protective coating systems is issued to the

manufacturer for the coating material in liquid form on the can, while the technical requirements for TA are primarily concerned with the applied coating in its cured condition. A DNV TA [12] may be issued based on independent reports from real life, field tests, or realistic laboratory tests. Realistic laboratory tests include the tank coating test cycles established by MARINTEK (seawater laboratory, Sandefjord, Norway) and the NORSOK pre-qualification test series for coating materials.

MARINTEK, Sandefjord was closed down in 1999 and DNV took over the test equipment and responsible personnel.

As mentioned in Ch. 2 above, a basic idea of the DNV Guideline no.8 [4] is to relate the useful life (≈ quality ≈ durability) of protective coatings directly to the newbuilding contract specification. The Guideline is referred to in DNV Rules and used as a guidance/advice document.

The DNV Guidelines No. 8 are currently undergoing revision and will be harmonised with the Class Note No. 33.1 [11].

Identification
A fingerprint (IR light) may be used in order to identify the coating. DNV is offering fingerprint testing. The test is relatively simple and quick and may for instance ensure that the chemical composition of the coating on the cans delivered to the ship is the same as the chemical composition of the coating tested in the laboratory/field tested.

Flexibility
Ref. Ch.2 above, as the flexibility of a coating may have fundamental influence on the lifetime of the coating in a ship, DNV has currently undertaken a preliminary study, and laboratory investigations of coating flexibility as function of ageing is ongoing [9].

Shop primers:

Shop primers used as initial protection of steel plates prior to production/assembling are normally applied thin, i.e. 15-20μm. However, in accordance with assembling and welding of the plates, the shop primer may have negative influence on the finished weld, i.e. by introducing pores. In order to verify that the shop primer has no detrimental effect on the finished weld, a TA may be sought for. The DNV TA [13] is based on an internally developed test procedure, based on a German DVS test [14] and the previous DNV test method.

Sacrificial anode alloy materials:

The sacrificial anode alloy material may be type approved in order to document a certain level of quality [15]. TA of sacrificial anode material is normally not required by the classification societies, however, the fixing details are to be of an approved type according to the DNV Rules for Ship.

TA is based on survey and testing of the alloys/fixing details. The testing of anode alloy is based on a long term (normally 12 months) testing submerged in seawater according to a

recognised test procedure, i.e. NORSOK Standard M-CR-503 (1994). The TA programme [15] has currently been modified.

Additionally, fixing details for anodes may be evaluated upon request.

Life Cycle Cost Analysis (LCC)

LCC is in brief, a method for evaluating the detrimental effect of general corrosion on distribution of maintenance costs related to coating and steel renewal longitudinal strength of tank and bulk carriers [16]. The assessment takes into account the expected life of coating applied in ballast tanks at the newbuilding stage, and how this coating is maintained during operation. A probabilistic corrosion rate model based on available statistical data collected for oil tankers and bulk carriers is used for estimating corrosion damage. By using the LCC program, the overall maintenance cost savings as a function of target lifetime of the vessel, may be estimated. The additional off hire, tank cleaning, survey and supervision costs may also be included in the analysis.

Area Calculations for Tank Coating

Through the DNV Nauticus Hull 3D model, a class notation based on an advanced computer tool, the area in the tanks can be estimating more correctly than before. Accordingly, the owner may save considerably amounts of money by reducing the amount of coating and coating application work needed. Examples have shown that area may be estimated wrongly by 100%, accordingly, the tool may be of great value.

Auditing Shipyards Coating Activities

The audit is offered to the market in order to rate/range the coating activities in the yard. The audit will comprise i.a. planning of surface treatment and coating, control of subcontractors, processes related to coating and surface preparation, communication lines, procedure for avoidance of damages, production accordance with specifications, environment, safety and health. The audit will result in a point score and percentage score for the respective activities of decisive importance for the quality and durability of the coating. Weak links in the process will be identified. The audit results can thus constitute a basis for improved quality of the end product; coated steel surface.

Training Course in Corrosion Prevention of Ships

A course focusing on corrosion prevention on ships is currently being developed by DNV. The course will probably be held first time autumn 2000. The course is intended for internal personal and Owners'/Yards' inspectors/technical management, and will be built as modulus that can be held separately upon request, presented from a practical point of view. The course will briefly contain lessons re. WHY coating is applied and HOW coating is applied, including some corrosion technology, practical tools for inspection, typical corrosion problems on ships etc. The motive for the training course is to increase the competence both internally and externally and market DNV as a competence centre on coating and corrosion prevention.

Life Extension Programme (LEP) & Condition Assessment Programme (CAP)

Life Extension Programme (LEP) is used as a tool to predict steel renewals for the future based on today's condition, i.e.

- A survey report stating the condition of the steel and corrosion protection system(coating, anodes), e.g., CAP survey or similar,
- Thickness measurements imported in DNV's Nauticus 3D model

The Condition Assessment Programme (CAP) consists of an extensive survey, mapping the condition of the steel and the corrosion protection system of the ship. Hull strength and simplified fatigue calculations are carried out using Nauticus Hull Sections Scantlings programme. Use of Resonance Thickness Measurement (RTM) technology will simplify data input to CAP significantly as thickness measurements can be directly imported into Nauticus Hull for visualisation and processing.

6 Conclusions

DNV main class (1A1) Rules comply with regulations given by IMO and SOLAS. Briefly, the Rules applicable to tank and bulk carriers constructed on or after 1 July 2000 state that

- Coating specifications are to be submitted for information, and
- If installed; anode specifications, calculations and drawings are to be submitted for information.

DNV will not carry out any survey or inspection of coating related operations in ship yards unless upon special agreement. Additional class notations on voluntary basis represent options to owners wanting an additional safety margins by improving the coating system (COAT notation) for newbuildings.

DNV have the intention to increase the general knowledge within the subject corrosion prevention on ships and do offer various advisory services such as:

- Review of and advice re. coating specifications – pre-contract specification review
- General advice re. coating and especially re. bacterial corrosion which has got increased attention due to double bottom hulls
- Testing, classification and type approval of tank coatings (performance, identification, flexibility), sacrificial anode materials, shop primers
- Life Cycle Cost Analysis (LCC)
- Area calculations for tank coating (Nauticus, paint areas/steel weights)
- Auditing shipyards coating activities
- Voluntary class notations CLEAN/CLEAN DESIGN
- Training course in corrosion prevention on ships
- Arbitration services
- Various programs to establish the condition of the ship including coating and predict some of the future for the vessel, e.g. Condition Assessment Programme (CAP) and Life Extension Programme (LEP).

7 References

[1] *International Association of Classification Societies IACS Blue Book. Unified Requirement UR Z7* "Hull Classification Surveys" introduced 1990, and Z10.1, Z10.2 and Z10.3 "Hull Surveys ... of Oil Tankers, Bulk Carriers, Chemical Carriers", with several revisions during the later years.

[2] *IACS. UR Z8* "Corrosion Protection Coating for Salt Water Ballast Spaces", introduced 1990, last rev. 1995.

[3] *IACS. UR Z9* "Corrosion Protection Coating of Cargo Hold Spaces on Bulk Carriers", introduced 1992, last rev. 1996.

[4] *Det Norske Veritas DNV. Guidelines No. 8*, "Corrosion Protection of Ships", Askheim, rev. 1996.

[5] *International Maritime Organisation IMO. Resolution A.798 (19)*, adopted 1995.

[6] *SOLAS. Amendment, Chapter II-1, Regulation 3-2*, "Corrosion prevention of seawater ballast tanks", MSC 66/24/Add. 1, ANNEX 2.

[7] *IACS. Unified Interpretation UI SC122*, Corrosion Prevention in Seawater Ballast Tanks, 1998.

[8] *Det Norske Veritas DNV. Rules for Classification – Ships*, January 2000.

[9] *Det Norske Veritas DNV.* Flexibility of Tank Coatings. *Preliminary Report No. DTP365/EASKH*, August 1999.

[10] *Det Norske Veritas DNV*, "Classification Focus on Protective Coating", *Paper Series no. 98-P009*, rev.1.0, 1998.

[11] *Det Norske Veritas DNV. Classification Notes no. 33.1*, "Corrosion Prevention of Tanks and Holds", July 1999.

[12] *Det Norske Veritas DNV. Standards for Certification No. 2.9, Type Approval Programme 1-602.1*, "Protective Coating Systems", August 1999.

[13] *Det Norske Veritas DNV. Standards for Certification No. 2.9, Type Approval Programme 1-602.2*, "Shop primers for corrosion protection of steel plates and sections", July 1999.

[14] *Guideline DVS 0501*, "Testing of pore-forming tendency when over welding production coatings on steel", March 1976.

[15] *Det Norske Veritas DNV. Approval Programme No. IOD-90-TA1*, " Type Approval of Sacrificial Anode Materials", rev.2, September 1996.

[16] *Det Norske Veritas DNV*, "Life Cycle Analysis of bulk carriers subject to general corrosion", *Paper Series no. 99-P001*, 1999.

[17] *Det Norske Veritas DNV*, "New Class Rules for Protective Coating", Askheim et al, *Paper at the 8th ICMES/SNAME New York Metropolitan Section Symposium in New York*, May 2000.

Chapter 19

Corrosion Prevention in Sea Water Ballast Tanks

Bill Woods

CORROSION PREVENTION IN SEA WATER BALLAST TANKS – "BACK TO BASICS"

Bill Woods

Milbros Shipping AS, Strandveien 50,"Godthaab"
1366 – Lysaker, NORWAY
Telephone: + 47 67 11 1000
Fax: + 47 67 11 1010

ABSTRACT

Prevention, or at least control of corrosion is now an important consideration in the design, fabrication and operation of most major constructions anywhere in the world, whether those constructions are static in the case of buildings, or dynamic in the case of ships. This was not always the case.

In the last decade, certainly in the case of ships, we have seen the emergence of a more fundamental "Back to Basics" approach to corrosion prevention. Prior to this last decade, the "Basics" invariably had to take a back seat in a highly competitive market.

This chapter looks at the evolution of Corrosion Prevention measures in sea water ballast tanks, the positions taken by the various interested parties up to the present day, and explores the problems and challenges which will need to faced in the future.

INTRODUCTION

In the mid 1960's when the writer first entered the marine paint industry, the painting of ships at the newbuilding stage was a decision usually arrived at between the shipbuilder and the shipowner, and essentially boiled down to a basic issue of cost. The involvement of other parties such as Classification Society, Paint Manufacturer, and Applicator generally only served to complicate the decision making process – the shipyard were building the ship to a cost, and the owner was prepared to pay an agreed price for it.

The protection of sea water ballast tanks was considered only as part of the normal painting specification for the ship – no special attention was paid to them. In fact, quite the reverse often happened. Sea Water Ballast Tanks (SWBT's) were usually the last, or nearly the last, location to be painted, and in some instances the SWBT's were being closed after being sprayed only a few hours prior to delivery of the ship. In fact I know of a number of newbuildings where sprayers were completing the coating of ballast tanks on the ship's maiden voyage! Such was the importance attached to paint and painting.

Paint was viewed as a necessary evil, largely used for cosmetic rather than protective qualities, and was generally considered to be a nuisance, not a necessity. Who put the PAIN in PAINT?

Things have changed in recent years, and now as we enter the new millennium, paint is still viewed as a nuisance, but a very necessary nuisance.

HISTORICAL PERSPECTIVES (1970 – late 1980's)

As mentioned earlier, the key decision makers in the selection and application of coatings for the SWBT's were the Shipyard and the Shipowner. However, as we all know from experience other parties were also involved, and influenced those decisions. Those other parties were the Classification Societies, the Paint Manufacturers, and the Coating Applicators. Most shipyards started with their own "in house" painting department, which did all paint work, including surface preparation and painting. In later years shipyards slimmed down their painting departments, and sub-contracted elements of the painting activities to specialised applicators, who concentrated on coating of cargo tanks and SWBT's. The paint company I worked for throughout the 70's and 80's (Camrex) pioneered the "Supply and Apply" approach to painting of SWBT's and cargo tanks. That particular concept was embraced by both Shipowners and Shipyards for many years before falling from grace in the late 80's early 90's. Now the concept appears to have found favour again with paint manufacturers, with at least two companies taking on the applicators, as well as the suppliers role.

We can learn a lot from the things we did correctly in those days, but perhaps more from the things we did wrong. Lets take a look at the motives and driving forces, which influenced the various interested parties in those days. The interested parties were;

The Shipowner
The Shipbuilder
The Applicator
The Paint Manufacturer
The Classification Society

SHIPOWNERS PERSPECTIVE

Considerations	Views & Influencing Factors
Type of Paint	No real preference expressed by majority of owners. If the paint was approved by one of the Classification societies to enable scantling reductions, it was generally acceptable to the owner. Soft sticky coatings were tolerated, but not preferred. Upgrading to Tar/Pitch Epoxy was preferred by owners, but this usually resulted in an "extra" cost to the owner, and was therefore a "disincentive" to upgrade.
Paint Specification	Limited interest expressed by majority of owners. Provided shipbuilder guaranteed for 1 year at least, owner usually accepted yard's choice.
Surface Preparation Steelwork (sharp edges, weld defects, laminations etc)	Owners preference was to have these treated, but this was not always specified in the Yard's Technical Specification. This usually resulted in many disputes on the necessity and extent of steelwork repairs, and the relevant standards.
Paint Performance	Reference lists of other users, testimonials, and approvals by Classification Societies were the main influencing factors. There was no recognised industry independent test body established. Track records, and case studies were of interest to owners, but were generally not requested by them.

SHIPBUILDERS PERSPECTIVE

Considerations	Views & Influencing Factors
Type of Paint	From the yard's point of view, the paint had to have Classification approval for scantling reductions, and had to fit in with yard's cost, which was built into the price of the ship.
Paint Specification	Yard interest was primarily focused upon the cost of the paint. It must be cheap, with the least number of coats to keep application costs down, and it must be tolerant of minimal surface preparation.
Surface Preparation 1. Steelwork Prep. 2. Secondary Surface Preparation	1. Paint companies who proposed steelwork repairs were considered less attractive by yards. Steelwork repairs increased man/hour consumption, and slowed down steel fabrication and construction. 2. Yards preferred paints that would tolerate minimum standards of surface preparation – ST1 or ST2 at best.
Paint Performance	Long term performance was not a yard consideration. Provided Paint Manufacturer would meet yard guarantee of 1 year, yard were generally satisfied.

APPLICATOR'S PERSPECTIVE

It was common practice in a number of shipbuilding yards to sub-contract the preparation and painting of Sea Water Ballast Tanks to specialist painting contractors. In some cases these painting contractors were linked formally (or informally) to paint manufacturers.

Considerations	Views & Influencing Factors
Type of Paint	No strong views held by the applicator – any type of paint could be applied. "Hard" types were preferred to "Soft" types, simply because they were easier to apply and inspect. Earlier "Hot applied" types of coating lost favour in the early 1970's due to rising concerns regarding fires and explosions in shipyards.
Paint Specification	The minimum number of coats coupled with fast drying/curing was preferred, so contractors could complete the project in the quickest possible time.
Surface Preparation	Whatever surface preparation was specified would be costed by the painting contractor, and carried out. However it was clearly in the shipyard interests to keep surface preparation costs to a minimum. This also suited the painting contractor for 3 reasons; 1. It reduced the need for equipment, such as mechanical tools. 2. It reduced the need for skilled workers. 3. It reduced the contract time.
Paint Performance	Invariably, performance guarantees were given by the paint manufacturer, particularly if the contract was "Supply & Apply". Eventually, and with some reluctance, painting contractors also became liable for their own work, whilst the paint companies retained the liability for re-supply of material only, in the event of a guarantee claim. Guarantee claims lead to the demise of a number of painting contractors.

CLASSIFICATION SOCIETY PERSPECTIVE

Traditionally, the Classification Societies have always considered that the shipowner should be responsible for the choice of coatings used to protect sea water ballast tanks. The vessel afterall belongs to the owner. Classification have had no mandate to become involved in corrosion prevention, although some of the majors have taken it upon themselves to give guidance on such matters.

In the last 10 years we have seen some major changes. IMO, SOLAS, and IACS have made some significant steps forward – we shall focus on these a little later in the chapter.

Considerations	Views & Influencing Factors
Type of Paint	Classification Societies made no distinction between generic types of paint. Virtually any paint could be "conditionally approved" for corrosion control, but would only achieve "Full Approval" following inspection by Class, after a period in service - usually 2 years. All kinds of coatings obtained approval - Hard, Soft, Semi-hard, single pack, and 2 pack.

Paint Specification	Single coat and multi-coat systems were approved. Dry Film Thickness for the complete system had to be above a minimum of 250 microns, although some multi-coat systems were approved at 200 microns.
Surface Preparation	Classification had no mandate to pronounce on surface preparation. The guidelines recommended that steel should be shotblasted and pre-primed, and then secondary preparation should take place to prepare the corroded areas to at least ST2. Intact shop primer was recommended to be cleaned. The guidelines preferred corrosion, burn marks, and welds to be gritblasted to Sa2.5, and the remaining shop primer to be "sweep blasted". This was considered by many yards and owners to be too expensive, and was seldom done.
Paint Performance	A number of Classification Societies clearly realised the importance of corrosion prevention in SWBT's – their guidelines are testament to this.! However, it was also still possible to move a "conditionally approved" coating to the "fully approved" status on the evidence of only two years corrosion control – hardly a long term policy!

In fairness to the Classification Societies, they were in a difficult position. They had to compete with each other for business (and still do!), so they had to differentiate themselves from each other. They also had to strike a balance between their mandatory and advisory roles. Too much advice, no matter how sensible it is, can deter some owners!

PAINT MANUFACTURERS PERSPECTIVE

At this point in the chapter I must declare that my background in the marine industry has been mainly with paint manufacturers, so you won't find it surprising that I have a considerable amount of empathy (and some sympathy!) with the paint companies. I spent about 12 years of my early working life designing and testing cargo and ballast tank coatings, and many years since then looking at some of the performance results.

In my early years at Camrex, I was involved in designing all types of ballast tank coatings - soft, hard, and semi-hard. Just like other companies, some of these approaches resulted in successful coatings, others not so successful. All the paint companies have had some painful experiences in ballast tanks.

PAIN and PAINT seem to go hand in hand - so I've been told on occasions!

Let's now consider the position of the paint manufacturers!

Considerations	Views & Influencing Factors
Type of Paint	All generic types of paints were available, and were promoted. BUT the drive for low cost/low price products pushed development towards the use of low technology cheap raw materials. High technology resins like epoxies and urethanes were diluted with cheaper extending resins. Products were designed "down to a low cost base", in order to meet the demands of yards and owners. (Not all yards and owners!)
Paint Specification	Again, in the interests of remaining competitive the number of coats was reduced to the bare minimum (one!), and dry film thickness was "cut to the bone".

Surface Preparation	Paints which required high steelwork and secondary preparation standards were uncompetitive due to high man/hour costs for preparation. Surface preparation requirements were gradually relaxed, and then we saw the influx of **"Surface Tolerant"** coatings.
Paint Performance	Paint Manufacturers in an effort to meet low price levels demanded by a very competitive market gradually moved the market downwards. Products were designed to meet the relatively short term guarantees of the shipyards – unfortunately, the owners wanted something better, but many (not all!) were not prepared to pay for it.

Clearly the needs and aspirations of all the parties involved, were incompatible.! On one hand we have the shipbuilder and shipowner asking for cheap products. The applicator asking for products easy to use, which can be applied to poorly prepared surfaces, in the minimum number of coats at low dry film thickness. On the other hand we have the shipowner still expecting long term performance, and the Paint Manufacturer stuck in the middle, trying to stretch science and technology beyond sensible limits to develop such coatings.

This demand for low cost, low specification, low surface preparation paints, coupled with high performance expectations lead to the appearance of unrealistic guarantees. It was perhaps the only way in which paint manufacturers could differentiate themselves from the competition, and maintain a competitive advantage.

A downward spiral if ever there was one!

THE CURRENT POSITION

Hopefully, the demand for low specification products is now behind us, although the search for that elusive low VOC, single pack, single coat, surface tolerant, non-toxic, light coloured, cheap, water ballast coating will still generate some weird and wonderful coatings in the future.

There is no doubt in my mind that the activities described earlier did little to provide effective corrosion control in SWBT's over the last 25 years. On the contrary they probably contributed to poor corrosion protection, and the disastrous pollution and loss consequences which occurred in subsequent years. All of these incidents have been well documented, and it is not my intention to go into further detail here. Suffice it to say, effective corrosion prevention or more precisely the lack of it, was seriously implicated as a major contributing factor.

This brings us to the current position, and in particular the Regulatory regime, which now exists for better corrosion prevention on the more susceptible of ship types. Figures generated by the Classification Societies, IACS, and IMO clearly demonstrate that the Tanker and Bulk Carrier sectors have suffered the most traumatic and the greatest number of incidents in past years. These ship types were the obvious first choice for regulatory changes. Accordingly, regulations have evolved , and have been adopted by IACS, SOLAS, and IMO in connection with corrosion prevention of SWBT's in Oil Tankers and Bulk Carriers.

REGULATION EVOLUTION – CORROSION PREVENTION IN SWBT's

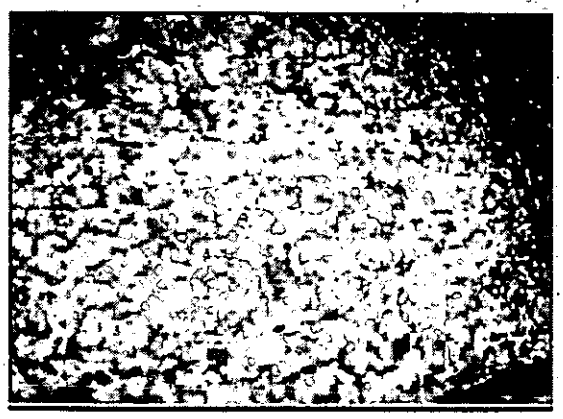
The major regulatory changes for ballast tank coatings can be summarised as follows;

Date	Regulation	Focus	Impact
1990	IACS UR Z7 "Hull Surveys"	Existing Ships	Introduction of surveys in SWBT's. Condition to be classified as "Good", "Fair", or "Poor". Existing ships in "Poor" condition, without coating, or coated with soft coating only, will be subject to annual surveys.
1990	IACS UR Z8 Corrosion Protection coating for SWB Spaces.	New Ships	IACS agree on unified requirements for protection of Salt Water Ballast Tanks from corrosion on newbuildings.
1993 (7)	Marpol 73/78 Annex 1 Regulation 13F	New Ships	Double Hull mandatory for all new Oil Tankers.
1993 (11)	IMO Resolution A744(18)	Existing Ships	Reinforces UR Z7. Gives greater effectiveness to surveys, discourages the use of "Soft" coatings, and encourages the use of "Hard" coatings.
1995	IMO Resolution A798(19) – Guidelines for the Selection, Application, and Maintenance of Corrosion Prevention systems for Dedicated SWBT's.	New Ships	Gives very clear guidance to Shipyard, Owner, and Paint Manufacturer on all aspects of Corrosion Prevention in SWBT's, and the involvement of the Administration before construction of the ship. There has to be an acceptable plan for corrosion control in SWBT's.
1996 (6)	Resolution MSC 47(66) approved by IMO, resulting in an amendment to Reg. 3 -2 Chapter II –1of SOLAS 1974.	New Ships	All dedicated SWBT's in Bulk Carriers and Oil Tankers to have an efficient corrosion prevention system. The corrosion prevention system to be approved by the Administration, and to be based on the IMO Guidelines in Resolution 798(19). This applies to all new ships (Tankers/Bulkers) built on or after 1st July 1998.
1998	IACS UI SC122 (Unified Interpretation of SOLAS Amendment Ch. II -1 Reg.3 -2	New Ships	Sets out the Guidelines for ensuring effective measures for corrosion prevention in SWBT's, and the scope of Class involvement in approval of those measures.

SUMMARISING THE MAIN POINTS

Existing Ships:

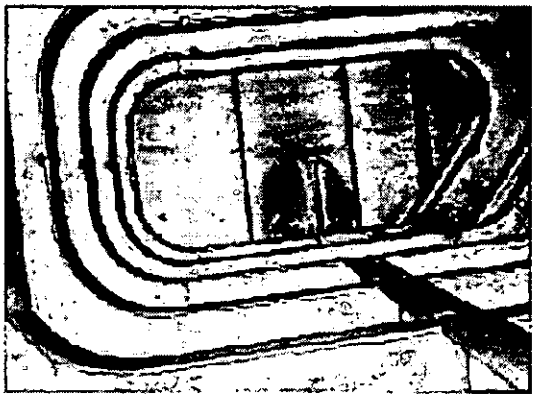
- Surveys must be carried out to establish true condition of coatings in SWBT's.
- Depending on condition and action taken, there may be a requirement for annual surveys.
- The use of "Soft" coatings is actively discouraged. In favour of "Hard" types.
- The threat of annual surveys and the associated cost implications is an incentive to owners to maintain coatings in SWBT's in "Good" or "Fair" condition, and to remove soft coatings.





Condition of "Soft" coating in SWBT in Double Hull Tanker

Photographs show condition after 5 years in service in SWBT's of Tanker, which carries cargoes up to 60 Degrees Centigrade. Exposure to temperature fluctuations and dirty ballast water has caused coating to "mud-crack" initially, followed by embrittlement, detachment, and then corrosion.





Condition of "Hard" coating in SWBT in Double Hull Tanker

Photographs show condition after 5 years in similar size double hull tanker carrying similar hot cargoes in the cargo oil tanks. Condition of hard coating is far superior than soft coating. Hard coating has the ability to withstand fluctuating operational temperatures, and mud crack propagation from silt in ballast water. The coating is covered with dirt only - beneath the dirt, the coating is in pristine condition.

N.B. Edges of plates, profiles and cut-outs are well protected.

Newbuildings:

Since July 1st 1998 all Oil Tanker and Bulker newbuildings must have a corrosion prevention system in compliance with UI SC122 of SOLAS Amendment Ch II –1 Reg. 3 –2

- The Selection, Application, and Maintenance of coatings for SWBT's must be addressed and agreed by all parties i.e. Shipbuilder, Owner, and Coating Manufacturer.
- The Classification Society must approve these measures.

- ❖ The selected coating must be hard, multi-coat with different colours for each coat, and the final colour must be light (distinguishable from rust!)
- ❖ The application process must consider, surface preparation (including steelwork and secondary preparation), Health & Safety, Environmental Control, Quality control procedures including "deviations", evidence of applicators experience, and details/suitability of any cathodic protection system to be used.
- ❖ The maintenance must consider, the coating manufacturer's documented procedures for maintaining the coating whilst the ship is in operation.

In essence the Shipbuilder and his applicator must provide sufficient evidence to the Owner and the Classification Society of their experience and capability in coating application. Similarly, the coating manufacturer must supply evidence of the quality and capability of the coating to the satisfaction of the Owner, and the Classification Society.

Clearly, the Classification Society now holds a very important and pivotal position.

THE FUTURE

In recent years we have seen a much welcomed change in attitudes towards corrosion in SWBT's. The decade of the 90's in regulatory terms has been particularly productive. Corrosion Prevention in SWBT's (and other areas on ships!) has been elevated to new levels of awareness, and of course expectations. It will be interesting to see how the relevant parties perform under this new regulatory regime. This new scenario raises a lot of questions!

Let's look at a few of them!

1. Classification Societies.

    1. Are they properly equipped to take on their new responsibilities?
    2. Are the Societies of equal competence?
    3. Do they have staff with adequate knowledge and experience of coatings and their application, to be able to approve/reject corrosion prevention measures?
    4. Will Class assess the coating capability of shipyards and applicators, and if so what evidence will be expected?
    5. Will Class assess the quality and suitability of coating systems, and if so what evidence will be expected? Will this extend to the companies themselves?
    6. Will Class monitor application in SWBT's? Do they have the experience?
    7. How will different Class Societies continue to differentiate themselves from each other?

2. Shipbuilders

    1. Are the existing facilities and methods of working in Shipyards capable of achieving the new standards expected?
    2. How can shipyards maintain (hopefully improve!) their present levels of steel productivity, whilst accommodating more stringent coating requirements into the build process? How can the two be integrated?
    3. Given the new importance now attached to Corrosion Prevention in SWBT's, is it likely that Shipyards may offer extended guarantees on these locations?

3. Applicators

1. How will applicators demonstrate their experience and capability to interested parties?
2. Will applicators need to have a recognised Quality Status?
3. What impact will higher standards of surface preparation and application have on applicators?
4. Will we see applicators taking on extended guarantees, and insure themselves accordingly?

4. Shipowners

1. Will owners expect longer term guarantees for the extra costs they will undoubtedly incur?
2. Do the owners have sufficient and properly qualified staff to monitor initial application in the shipyard?
3. Do they have staff capable of monitoring corrosion in SWBT's, and necessary maintenance therafter?

5. Paint Manufacturers

The addition of a steel envelop around the existing cargo space to create the double hull configuration also creates potential problems for the paint designers and manufacturers. Some of these are due to the design itself, but others are due to the operational characteristics of the ship.

1. How do coatings behave under the residues of mud left behind after de-ballasting?
2. How are coatings affected by microbes in mud, and how do they perform under conditions of Microbiologically Induced Corrosion (MIC). These conditions can be anticipated in a double hull configuration, where relatively warm conditions may accelerate the proliferation of Acid Producing, or Sulphate Reducing Bacteria?
3. How will coatings be influenced by new IMO recommendations relating to "Ballast Water Management Plans" {IMO Resolution A 868(20)}?
4. What impact will fluctuating temperature cycles have on the corrosion protection provided by coatings?
5. How will this be influenced by coating morpholgy and thickness.
6. Can coatings meet the long "Design Life" expectations of up to 25 years, now desired by shipowners?

Clearly, there are numerous challenges and opportunities facing all parties!

CONCLUSIONS

1. In the author's opinion, the answer to the last question posed above is "Yes – we can design paint systems to give 25 years life". However, in order to achieve such longevity, a "Back to Basics" *(David has asked if this could be defined in technical terms)* approach will need to be properly re-established and embedded into the working culture in shipbuilding yards.

2. We have seen the new requirements for Selection, Application, and Maintenance of coating systems for SWBT's. These are reinforced with good guidelines for corrosion prevention,

incorporating good working practices and recognised standards. All of this is based upon well established scientific foundation, sound technology, and some good experience.

Coating specifications are more increasingly being carefully considered and constructed, conditions of application and curing better controlled, with painting generally being elevated in the planning phase of the project, and better integrated into the building program itself. However, all of this will be of little value, if it is not properly controlled. This is where the biggest challenge exists – assuring appropriate quality control from the design stage, through manufacture and first application, and finally at the maintenance stage in service.

Paint needs to be given the same consideration as given to steel and the engine – after all the cost of paint and painting in terms of manhours accounts for a significant percentage of total man hours.

3. The new regulatory requirements are a considerable step forward in achieving long term corrosion prevention in SWBT's. However, there are still some obstacles and issues to be addressed, a couple of which I mention below.

4. Dry Film Thickness - Many specifications I have experienced recently do not specify a maximum dry film thickness, although a minimum is invariably specified. Many specifications also require multiple stripe coating operations to be carried out between each coat, on all welds, edges, and on areas difficult to access. This in my own personal experience has lead to the build up of excessively thick films in some locations in SWBT's. Thick films do not necessarily provide long term performance - Beware!

5. Surface Tolerance - Many coatings used in the past, and indeed still in use today are described as "Surface Tolerant", implying that they will tolerate a certain amount of surface contamination prior to application, and yet still give long term performance. That contamination could be rust, scale, previous coatings, moisture, oil , or salts.

   Internationally recognised standards have been in existence for many years relating to the removal of rust and scale from steel surfaces. They are well established standards. Standards are now being developed concerning levels of salts remaining on steel prior to painting, and some good guidance is given for their detection, measurement, and levels of acceptability. There are no recognised standards for the levels of acceptability of contaminants such as oil and water, nor are there any established methods for their measurement.

   On one thing the paint industry is fully agreed upon is; "Performance is inversely proportional to the degree of contamination - as surface contamination increases, performance decreases".

Once again, Beware!

Acknowledgement: I would like to thank my company - Milbros Shipping AS for allowing me the time to prepare this chapter.

Bill Woods
Milbros Shipping AS

Chapter 20

Strengthening and Repair of Structures Using Carbon Fibre Composites

Dr Paul S Hill

Strengthening and Repair of Structures using Carbon Fibre Composites

Dr Paul S Hill, MA MBA PhD MIM Ceng, Technical Manager, DML Composites,
PC1214 Devonport Royal Dockyard, Plymouth, PL1 4SG.
Tel 01752 553845, Fax 01752 552852, email paul.hill@devonport.co.uk

1 Introduction

The history of composite materials has been discussed widely in standard textbooks[1, 2, 3]. Glass fibre reinforced materials were first used in aircraft Radar covers at the end of the 1930's. Their use spread rapidly through marine craft to the point today where they are utilised in demanding services such as pressure vessels, pipes and blast panels on offshore oil and gas platforms. Carbon fibres were developed by the Royal Aircraft Establishment at the end of the 60's and were seized upon for the high strength and stiffness per unit mass they offered. They are now used in applications as diverse as sports goods, stealth aircraft and pipework repairs, Figure 1.

In all these applications, composites have been selected because they offer a performance or cost-benefit over traditional solutions – the saving can usually be traced back to the generic benefits of using composites, namely:

- Low density, and high mechanical properties, giving low mass components
- High durability, composite materials are extremely resistant to most common environments
- Ease of installation, derived from low mass and use of adhesive bonding techniques

Composites then, in the sense used here, are composed of fibres in a resin matrix. The fibres are very strong and stiff, and the matrix enables them to work together and be utilised in engineering components. There are a variety of materials and manufacturing methods, which all lead to final components with different mechanical properties. The selection of materials is therefore coupled with the selection of manufacturing process and these must be completed concurrently with the structural design of the part.

This paper gives a brief introduction to the constituents of composite materials and their design, and then reviews their application in repair and strengthening of offshore platforms, pipes, bridges, ships and their development for the repair of structures underwater.

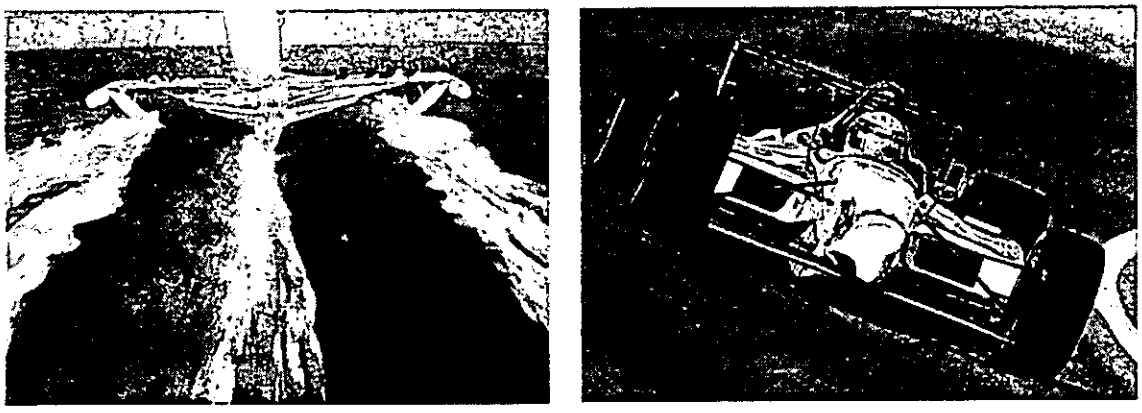


Figure 1 Typical examples of applications of composite materials

2 Materials

Engineering composites are commonly formed by the intimate mixing of two distinct phases, a fibrous reinforcement, and a continuous medium (resin) termed the matrix which encapsulates the reinforcement. The fibre reinforcement generally has high specific properties, i.e. high strength and stiffness at a relatively low density. The matrix in comparison has lower strength and stiffness.

In simple terms, the fibres and their arrangement define the material's mechanical properties and act to resist primary loads. The matrix acts to transmit the loads into the fibres, protects the surface of the fibres from damage and inhibits brittle fracture associated with the 'brittle' fibres.

2.1 Fibres

General properties of the different fibre types are shown in .Table 1.

Fibre	Tensile Strength (MPa)	Young's Modulus (GPa)	Density (kg/m^3)	Cost (£/kg)
Aramid	3150 – 3600	58 – 160	1390 - 1470	20
Carbon	2100 – 7100	220 – 900	1740 – 2200	10 – 200
Glass	3445 - 4890	72 - 87	2460 – 2580	2.5

Table 1. Typical properties of common reinforcing fibres

2.1.1 Aramid Fibres

Aramid fibres are produced in low and high modulus grades. The main characteristics of aramid fibres are their high strengths, moderate Young's moduli and low densities. Laminates formed from aramid fibres are known for their low compressive and shear strengths. The fibres themselves are susceptible to degradation from UV light and moisture. Aramid fibres are therefore used for structures requiring high tensile strength and impact resistance but not shear or compression strength and are often used in combination with other fibres (hybridised) to provide improved impact resistance.

2.1.2 Carbon Fibres

Carbon fibres are produced in many grades. The main characteristics of carbon fibres are their high strengths and Young's moduli, and their low densities and thermal expansivities. The wide range of fibres and properties that are available provide the maximum possibility for optimisation of the material to provide properties specifically matched to a particular application. Carbon fibres are used for structures that are weight sensitive, or which have high stiffness requirements.

2.1.3 Glass Fibres

Glass fibres are used for the majority of composite applications. The main forms are E-glass, most frequently used, and S2- or R-glass (trade names from different manufacturers), which is a more expensive high strength version. The main characteristics of glass fibres are their high strengths, moderate Young's moduli and density, and their low thermal conductivity. Glass fibres are used for structures that are not weight critical and which can be designed to accommodate their lower Young's moduli.

2.2 Resins

The main structural resins are unsaturated polyesters and epoxies, with phenolics used where there is a requirement for fire resistance. The main properties of these resins are summarised in Table 2 below.

	Tensile Strength (MPa)	Young's Modulus (GPa)	Strain at Failure (%)	Density (kg/m^3)	Cost (£/kg)
Polyester	50 - 75	3.1 – 4.6	1.0 – 2.5	1110 – 1250	~2.5
Epoxy	60 - 85	2.6 – 3.8	1.5 – 8.0	1110 - 1200	~5-10
Phenolic	60 - 80	3.0 – 4.0	1.0 – 1.8	1000 - 1250	~2.5

Table 2. Typical Properties of Common Resin Systems

2.2.1 Unsaturated Polyester Resins

Unsaturated polyester resins are used for the majority of composite structures. They consist of a relatively low molecular weight unsaturated polyester dissolved in styrene. Curing occurs by the polymerisation of the styrene which forms cross-links across unsaturated sites in the polyester.

Polyester resins are relatively inexpensive, easy to process, allow room temperature cure and have a good balance of mechanical properties and environmental/ chemical resistance.

The main issues relating to the use of polyester resins are:

- Moderate adhesive properties
- Styrene vapour release during cure
- Curing is strongly exothermic and can cause damage if processing rates are too high
- Shrinkage on cure of up to 8%

2.2.2 Epoxy Resins

Epoxy resins are used for the majority of high performance composite structures. They are generally two-part systems consisting of an epoxy resin and a hardener which is either an amine or anhydride. A wide variety of formulations are available giving a broad spectrum of properties. The higher performance epoxies require the application of heat during a controlled curing cycle to achieve the best properties.

Epoxies have excellent environmental and chemical resistance. Compared to polyesters, epoxies require more careful processing and are more expensive by a factor of 1.5 to 3. However, epoxies demonstrate better mechanical properties, give better performance at elevated temperature and exhibit a much lower degree of shrinkage (2 – 3%). Their use incurs less waste and permits faster production rates, they can therefore be competitive with polyester in terms of cost.

2.2.3 Phenolic Resins

Phenolic resins are of particular interest in structural applications owing to their flame-retardant properties, low smoke generation and high heat resistance (up to 316°C). Phenolic resins are produced by a condensation process from reacting phenol with formaldehyde.

Phenolics exhibit good dimensional stability and resistance to acids. Undesirable features of phenolics are their relatively low toughness and generation of water during curing. This latter point is important, as a phenolic that is not fully cured will give off water, in the form of steam, during a fire, which can cause failure of the laminate.

3 Manufacturing of Composite Materials

Apart from the raw materials, the way in which a composite material is manufactured will also affect its properties. This is because the manufacturing route dictates the proportion of fibres to resin, the amount of voids in the material, and the overall consistency.

3.1 Hand lay-up

This process is also commonly known as contact moulding and wet lay-up. The mould is wet out with resin, dry reinforcement is laid into the resin, and the ply is consolidated with a roller. The process is repeated until the desired thickness is achieved.

3.2 Vacuum Bag Moulding

This process is similar to hand-lay, but final laminate consolidation is achieved by covering the component with a plastic film (vacuum bag) and drawing a vacuum over the component. The pressure differential compresses the uncured composite, forcing out excess resin and drawing out entrapped air. This results in a laminate of higher fibre volume fraction and better consistency when compared to the hand lay-up process.

3.3 Resin Infusion under flexible tooling (RIFT)/Resin transfer moulding (RTM)

For RIFT, dry fabric reinforcement is first laid into a mould. The reinforcement is covered with a vacuum bag, the edges sealed and a vacuum drawn. The vacuum is used to draw resin into the reinforcement thus forming the composite component. This process results in a laminate of low void content and high volume fraction. The resin infusion process is well suited to larger components / structures and where a closed mould process is required to reduce emissions. It is ideal for producing low numbers of components.

Where large numbers of components are required RTM is a similar, and more suitable technique. A closed metal mould is normally used (which tend to be more expensive to make but are more durable than the cheaper tooling for RIFT), and the dry fibre preform is laid up within it. Resin is then injected under positive pressure (sometimes with vacuum assistance), to form the final component. The mould can also be heated to accelerate the cure of the resin and so reduce cycle times.

3.4 Pre-Preg

This method is used in both aerospace and Formula 1 type industries because it gives the most controlled form of component. Unidirectional fibres are pre-impregnated with a resin (usually an epoxy) and these sheets are laid up individual in whatever direction is desired to give fibres in the orientations required. The whole component is cured in an oven under vacuum or in an autoclave. High control over fibre alignment, fibre volume fraction and void content can be achieved.

3.5 Pultrusion

The above techniques are all labour driven. Pultrusion is an automated technique that was designed to reduce the end-cost of components. It is similar to extrusion in principle, in that the material is taken through a die to produce a component of constant cross-section. Fibres are arranged to feed into a resin bath, and then into a heated die, where they cure. The solid product emerges from the die and is pulled, driving the whole process and giving it its name. There is not the freedom to control the fibre alignment as with other methods (fibres must be aligned predominantly to the axis of the machine), or the volume fraction (the faster the running speed, the higher the pull force and the higher the volume fraction of the composite).

3.6 Filament winding

Filament winding is another automated technique used to produce objects with rotational symmetry. Pipes, tanks and pressure vessels are commonly produced in this way. The fibres are impregnated with resin on line and wound on to a rotating mandrel. The fibre placement is achieved using a computer controlled (CNC type) arm, which can move along the length of the mandrel as the mandrel rotates. The fibre angle can therefore be controlled to a certain extent, however geometry of the part most commonly dictates the angles that can be achieved (fibres naturally follow the high points on the surface profile).

4 Performance

4.1 Design

The fibres give the final composite its strength and stiffness, so the main objective of the design is to place the fibres in line with the loads to be carried. Fibres aligned in one direction produce highly anisotropic materials with very high stiffness and strength in the direction of the reinforcement. Away from this direction, properties tend to fall away rapidly until at the orientation perpendicular to the fibres they become similar to those of the matrix.

It is common for individual plies of unidirectional material to be combined to form a more complex construction. Such a laminate may contain many individual layers, each at different orientations with respect to one another, the sequence of plies being determined by design considerations.

Reinforcements are available where tows are stitched or woven together to form a fabric containing fibres at set orientations. Such reinforcements are characterised by the arrangement of the tows, common forms are:

- Unidirectional, (UD), At least 95% of fibres in the 0° direction
- Biaxial fabrics, (BX), Fibres in the 0° and 90° directions
- Bias fabrics, (XF), Fibres in the +45° and –45° directions
- Quadraxial fabrics, (QF), Fibres in the 0°, +45°, -45° and 90° directions

Reinforcements with fibres in different directions are usually balanced i.e. they have equal number of plies in the + and – angles. Unidirectional fabrics are the most highly anisotropic, whereas balanced, quadraxial reinforcements possess quasi-isotropic in-plane properties.

Typical properties of resin-infused laminated epoxy composites are shown in Table 3 (TS and CS are abbreviations for tensile strength and compressive strength respectively, HS and HM refer to high strength and high modulus).

		Longitudinal (0°)			Transverse (90°)				
Fibre	***Reinforcement***	***TS (MPa)***	***CS (MPa)***	***Modulus (GPa)***	***TS (MPa)***	***CS (MPa)***	***Modulus (GPa)***	ν_{12} -	ρ (kg/m^3)
Aramid	*Unidirectional*	1280	290	70	39	150	6	0.34	1370
E-glass	*Unidirectional*	700	580	39	72	85	9	0.26	1920
E-glass	*Quadraxial*	380	312	23	383	324	23	0.28	1920
HS-Carbon	*Unidirectional*	2003	797	112	50	85	7	0.26	1510
HS-Carbon	*Quadraxial*	596	420	48	632	404	49	0.31	1510
HM-Carbon	*Unidirectional*	1157	346	310	24	75	6	0.30	1660

Table 3. Typical Properties of Composite Materials

4.1.1 General Rules for Designing Laminates

- Align fibres in the direction of all loads
- Even if a design requires only 0° plies, include at least 10% of the laminate weight as 90° or 45° plies to accommodate unexpected loads.
- Alternate ply orientations to prevent large matrix cracks forming
- Where possible, keep the difference in angular orientation between adjacent plies to below 60°
- Balance the laminate about the mid-plane to prevent bending effects reducing in-plane properties
- Optimise the stacking sequence to maximise properties for a particular load case
- Taper thickness of laminates at edges to reduce peel stresses

4.1.2 Codes

There are few codes for design of composite components. Certain products are standardised, such as tanks, vessels and pipework (for example, BS 4994 for GRP tanks). Given the variety of materials which can be used it is hard to know what mechanical properties to use in design calculations. The aerospace industry has completed thousands of materials tests to qualify specific materials because of this – but this then prevents adoption of newer and better developments. Work is also underway in Europe to define a standard pultrusion that will have certain specified mechanical properties, but the end markets for these materials will be limited (though still significant).

MSL Engineering and DML Composites have produced an in-house design guidance note for composite materials. In the main, traditional hand-calculation methods will give a reasonable starting point, and more detailed analysis will then be required, perhaps using finite element type approaches. Most common FE packages now have composite modules, enabling more accurate modelling. It may be that for critical components the designs will then need to be validated by full scale testing.

4.2 Durability

Durability can be defined as the ability of the material to continue to meet the performance specification with time. The environments most commonly of interest are water/chemicals, dynamic loading and fire.

4.2.1 Chemical Resistance

In general composites are not greatly affected by common chemicals. Strong oxidising agents and bases are the common exceptions, but their effect varies with the resin matrix. Of the more common chemicals, water is usually the most aggressive, and the one that needs to be considered. Epoxies are the most resistant of the common matrices. Polyesters are usually adequate, as are the phenolics.

Typically, glass reinforced composites show a loss in strength on exposure to water (of up to 50% in some circumstances). The rate of degradation depends on the rate of moisture absorption, and so increases with temperature, concentration (relative humidity) and area of material exposed. Carbon and aramid reinforcements show excellent retention of properties during service (usually above 80% of short term strengths).

4.2.2 Fatigue Performance

Fibre reinforced composites in general are more resistant to dynamic loads than metals. The fatigue mechanism involves the accumulation of cracks within the material, which in themselves are not critical. As the general level of damage increases so the strength and stiffness of the material reduces (properties away from the fibre axes show a greater change). Carbon fibres show the greatest resistance to fatigue, glass and aramid show a greater reduction. Aramids in particular are susceptible to tension-compression loading. As a rough indication, if the loads in carbon reinforced composites are below half of the long-term strength then fatigue is unlikely to be a problem.

4.2.3 Fire Performance

Epoxy and polyester based materials do burn. However, glass-polyester composites are now commonly used in the offshore industry for fire protection. The degradation of the material actually occurs at the surface first, and then slowly proceeds through the thickness of the material. This gives excellent protection to the rear face of the composite.

Phenolic resins are used primarily because they do have good performance in fires. Whilst polyesters protect the substrate underneath, they emit noxious fumes. The smoke and toxicity of that smoke emitted by phenolics are much reduced compared to other resins. Further, the rate of flame spread is also better (slower). Therefore in fire critical applications phenolic resins are commonly selected, and it is possible to satisfy various standards, as set out in BS 476.

5 Adhesive bonding

Whilst there are a number of adhesive types available (epoxies, acrylics, polyurethanes, cyanoacyrlates etc.) the ones most suitable for constructing composite components are epoxies. There are a wide range of epoxies available, and selection must be made to suit the curing conditions. Room and low temperature curing systems are available, but those that require an elevated temperature cure usually have the best properties.

Adhesive bonds perform best in shear, and are not suitable for carrying tensile, peel or cleavage loads. Presuming this can be achieved the first step in making the bond is to ensure the surfaces to be joined are adequately prepared. The surfaces must be of a suitable cleanliness and surface roughness. Any contaminants left on the surface (oils from handling etc.) will reduce the bond strength, and the surfaces need to have a degree of roughness to ensure a good key is achieved. It is common to prepare substrates to painting standards (e.g. SA2½), and whilst this gives repeatability to the process it may not always guarantee the highest strength.

Once the surface is prepared the adhesive needs to be mixed. Manufacturers can provide pre-weighed packs and automatic dispensers, or adhesives and hardeners can be measured out as specified by the manufacturer. Careful mixing must be completed to ensure the adhesive will cure.

The adhesive must be applied to the bonding surfaces. It is not always necessary to apply to both surfaces, but the application must ensure no air is trapped when the surfaces are brought together. Some temporary support may be required, depending on the components being bonded.

The development of strength of the bond will depend on the specific adhesive and curing conditions. However, it is possible to get working strengths at ambient temperature within a matter of hours.

6 Structural Repairs using Carbon Fibre Reinforced Materials

The benefits of using composite materials were noted in section 1. The light weight of the materials combines with the adhesive technology inherent in their matrix formulation to present an unparalleled opportunity for simple repair techniques. The fibres can be oriented to carry loads in relevant directions and the composite either made in situ or a pre-formed section bonded in place. It is possible to complete a repair that is therefore simple to fit, requires no hot work (as welding does), and that is therefore cheaper than traditional solutions. In most cases the materials will be more expensive – it is hard to compete in cost terms with steel, but the installation is so much simpler that the overall cost is reduced.

6.1 Blast Walls

DML first installed composite repairs to a blast wall on Mobil Beryl Bravo in Autumn 1995, Figure 2. Two blast walls of size 8m deep by 40m long were strengthened to give a threefold increase in blast capacity. There were four competing repair solutions, but the composite was chosen as being lowest cost and lowest risk. In this particular case the costs included a series of validation tests, Figure 3, but given the installation time was less than 20% of any of the other systems it was still the most cost-effective solution, being less than half the cost of any other option.

The carbon strengthening was applied using the DML RIFT technique to the compression flange of the existing blast wall. This was sufficient to provide the increase in strength required. The repair utilised ultra high modulus and standard modulus carbon fibres. In Figure 2 the strengthened sections are the striped flanges along the walls. It was possible to install the carbon in very constricted areas, even when access was restricted to about 20mm around the flange. This flexibility makes the composite repair solutions very attractive.

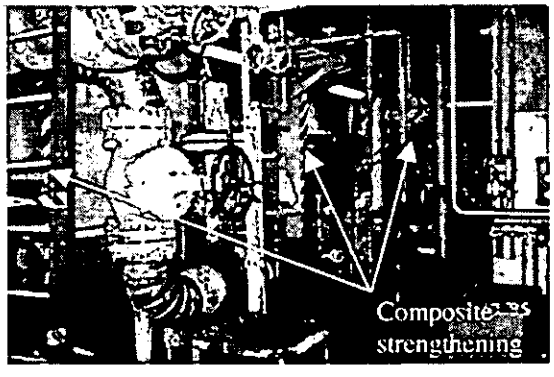


Figure 2. Blast Strengthening on Mobil Beryl Bravo

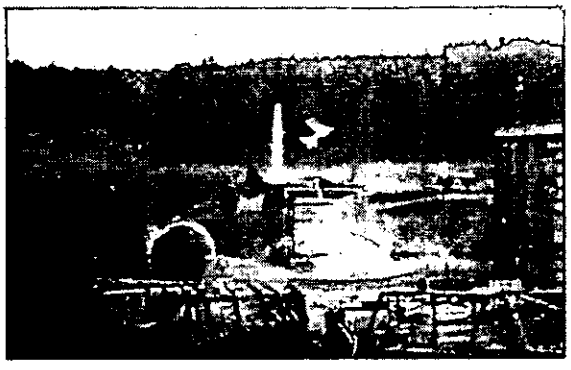


Figure 3. Blast Testing of Strengthening Solution

6.2 Bridges

Following the work on Beryl Bravo the first repair and strengthening solution for cast iron structures was applied in the London Underground network in 1995. London Underground Limited (LUL) are the third largest owner of bridges in the UK, behind the Highways Agency and Railtrack. Much of the network was constructed towards the end of the 19th Century. The materials of construction used were those popular at the time of construction, and many structures were built using cast iron. This has proven to be an excellent engineering material, but it does have some problems, including that it is brittle at failure, showing no ductility. LUL have completed extensive strengthening of the system, but on-going assessment identifies further work required. The traditional solutions required closing tracks

and interrupting the regular train service. Trains run for about 20 hours a day, and give a maintenance period of only about 3 working hours per night. Ideally, strengthening solutions should be able to be applied within this working window. Carbon fibre solutions have been developed that satisfy this, and they have enabled reduced cost strengthening to be achieved.

Carbon fibre reinforced materials have been proposed for strengthening structures since the mid-1980's. The first applications were to strengthen concrete bridges[4], where thin sections (less than 4mm thick, typically 150mm in width) of standard modulus carbon fibre can lead to sizeable improvements in load carrying capacity (i.e. in the order of 30% and above). The stiffness of the carbon fibre composite (typically 120GPa) matches that of the concrete structure, and so the composite is made to work effectively in the structure. However, for bridges constructed from cast iron or steel the benefit of the standard modulus carbon fibre is much reduced because the working strains of the metals is between 0.08 and 0.15%, and that of the carbon nearly 0.5%. This is compounded with steel in particular by the fact that the carbon material would have a stiffness about half that of the metal, and so not pick up any significant load at a given strain. DML Composites have developed a solution based on ultrahigh modulus carbon fibre materials, where the stiffness is about 3 times that of the standard modulus materials, and 50% greater than that of steel, Figure 4.

Further, the first carbon fibre strengthening solutions were produced by pultrusion. This is a good production route for thin materials as were originally required. However, for strengthening metallic structures the thickness of ultrahigh modulus (UHM) carbon composite required is usually in excess of 7mm – and pultrusion cannot produce this reliably. It is not considered good practice to produce unidirectional materials of this thickness without including some off-axis reinforcement. This is to improve handling strength (thick unidirectional materials can crack easily parallel to the fibre axis) and to carry 'operational loads', which may not have been considered in design (and which again could crack the laminate). Pultrusion produces composites with a high fibre volume fraction, typically 65% to 70%, and again this would not be compatible with the UHM fibres at the thicknesses required. Pultrusion also requires a die of fixed dimensions to define the profile of the product, and so plates cannot be tailored in width to specific requirements. Finally, the peel stresses at the ends of thick plates can be 6 times greater than the stresses in the middle if the plates are terminated squarely; ends should be tapered.

It was therefore decided to produce plates using the pre-preg route. This gave solutions to all the problems above, allowing glass fibres to be included at ±45°, controlling fibre volume fraction to below 55%, enabling plates of notionally any thickness, width and length to be manufactured, and giving the opportunity to incorporate a taper.

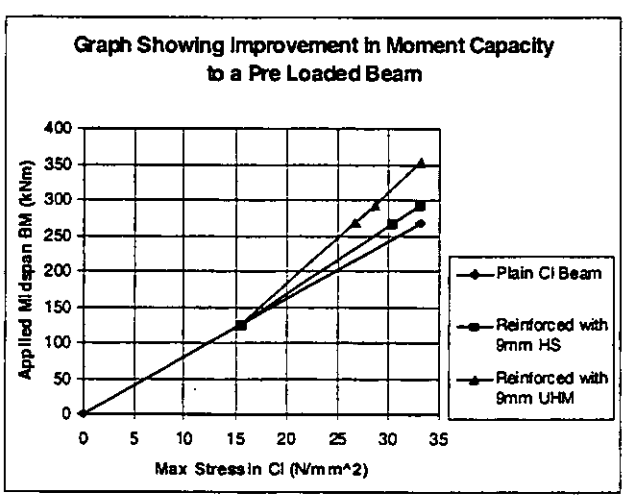


Figure 4. Comparison of strengthening achieved for a cast iron beam with equal thicknesses of standard and ultrahigh modulus carbon fibre materials

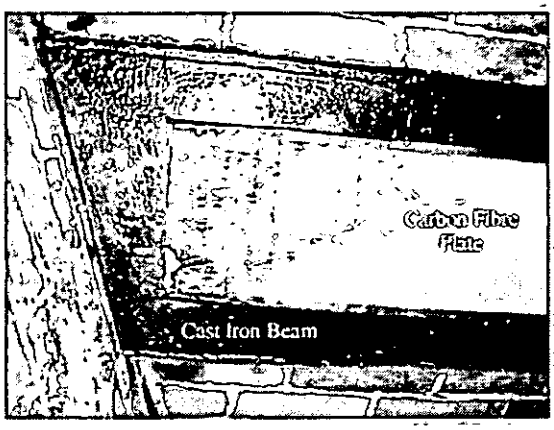


Figure 5. Taper on end of plate

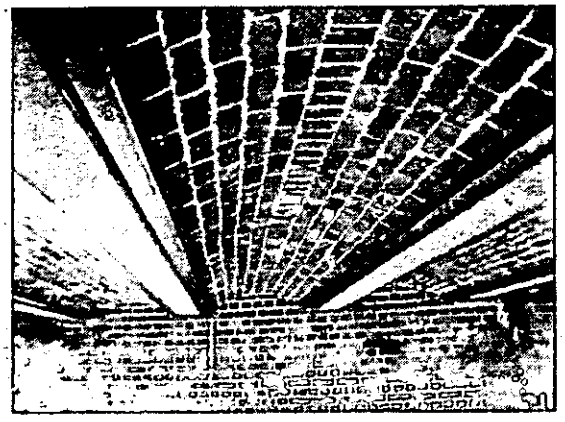


Figure 6. Prepreg carbon fibre plates installed on cast iron flanges

6.2.1 Validation

A large amount of test work has been undertaken to validate the carbon fibre strengthening solution. Design has been undertaken using standard composite beam theory (commonly applied for concrete-steel beams) and compared with FEA approaches. The predictions of both compare well with results measured on small scale and large scale tests completed in the laboratory, Figure 7. Validation testing has been completed in various projects, but the majority of the work has been completed as part of a LINK programme, where 50% of the funds were provided by DETR. Partners in the programme were DETR, DML Composites (lead partner), London Underground Ltd, DERA, MSL Engineering, University of Southampton and Structural Statics Ltd.

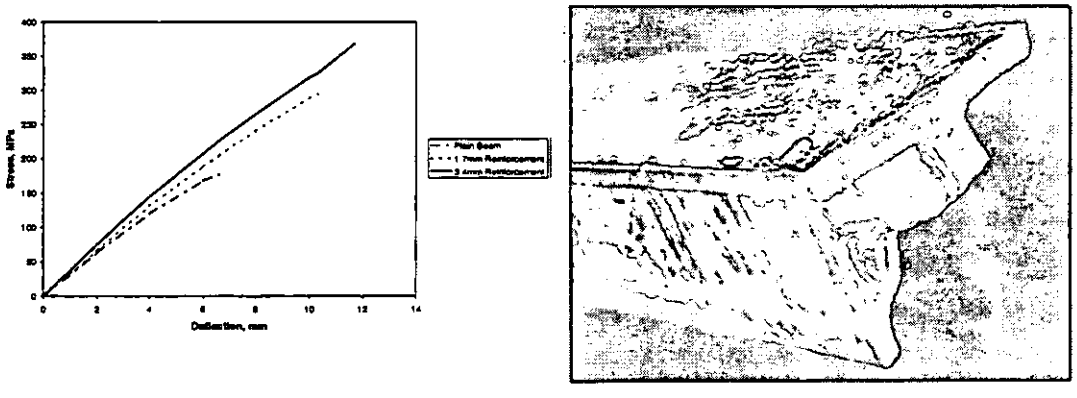


Figure 7. Laboratory tests to prove benefit of UHM carbon fibre plates

6.2.1.1 Acton Bridge

Whilst small scale tests were an important first step, it was also desirable to demonstrate the technique on a live structure. London Underground Ltd made the bridge over the entrance to Acton Works available for a trial, Figure 8. The bridge had no requirement for strengthening, and so was ideal to demonstrate theory in practice. Strain gauges were first applied to the bridge and a two week period allowed to record data of the performance in service. The carbon plates were then installed and a subsequent two week period of data recorded. The readings before and after were compared and demonstrated the 20% reduction in live load stress desired had been achieved, Figure 9.

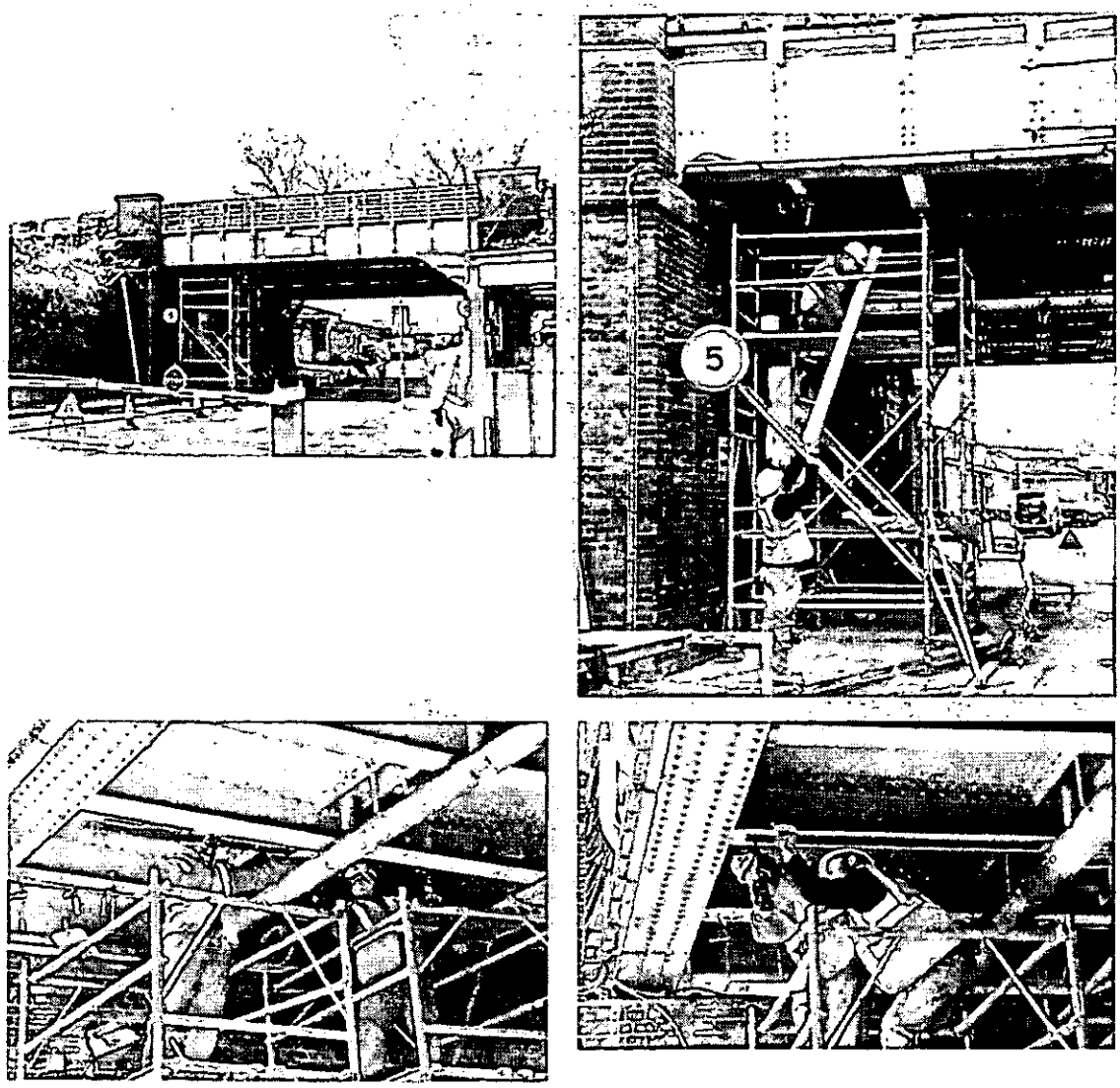


Figure 8. Installation of strengthening on London Underground Ltd Bridge D65A, Acton Town

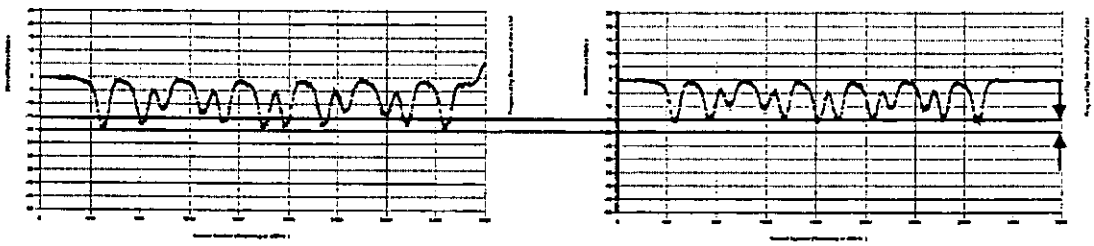


Figure 9. Measured Reduction in Live Load Stress

6.2.2 Installation

The great benefit of carbon fibre strengthening is the ease and speed of installation. Figure 8 shows some of the elements of installation. The steel plate that would be required to achieve the same degree of strengthening would weigh about 7 times more than the carbon plate, and so require mechanical handling equipment to enable installation.

The first step in the installation is the surface preparation. This step is perhaps the most critical – if it is not completed correctly then nothing can be done to rectify it later, short of starting again. Shot blasting of steel to SA2.5, or equivalent is recommended, although work is underway to see whether

grinding operations would be sufficient. Following degreasing of the metal, the adhesive (a low temperature curing epoxy) is applied to both the soffit of the beam and the carbon fibre plate. The plates are supplied with a peel ply surface – which is simply ripped off and leaves a surface which has both the required cleanliness and surface roughness for bonding.

The plates are then installed and held in place mechanically whilst the adhesive cures (typically four to eight hours – but may take up to seven days for full strength to be gained). On Acton Bridge no interruption to the traffic was allowed, and the adhesive saw live load during its cure. Laboratory tests are underway to quantify the effect of this on ultimate adhesive properties achieved, but the structural monitoring has demonstrated there are no short term problems.

The materials are highly durable and do not need painting unless they are likely to be exposed to direct sunlight, when they should be painted white to minimise any temperature rise.

6.2.3 Experience

DML Composites installed over 170 UHM carbon plates for London Underground in 1999. Other road and rail bridge have also been strengthened. Experience in service is about 18 months, and so the technique can still be considered to be in its infancy. The level of interest is however very high, and it is anticipated that the number of applications will rise in the near future. A guidance note on the strengthening of metallic structures using carbon fibre composites is being produced by the LINK programme, and the Concrete Society are producing a guidance note for the strengthening of concrete structures.

6.3 Strengthening using Resin Infusion

The use of pre-formed plates is ideal where the beams to be strengthened are flat and straight. However, given the structures in need of strengthening are usually over 100 years old this is not always the case. For structures with significant out-of-plane deviations it is possible to manufacture the composite on top of the structure. The carbon fibres themselves can be made into a fabric, and the fabrics can have good 'drape' – in that they conform to surface profiles. The fibres are then easily applied to the surface to be strengthened.

DML Composites have patented the RIFT manufacturing technique for the in-situ strengthening of structures. The carbon fibre fabric is first applied to the structure to be strengthened (the surface having been prepared as for plate bonding), and the consumables required to achieve impregnation fixed on top. Resin is then pulled into the laminate using a vacuum pump. The material that results bonds very strongly to the substrate and the composite produced has a low void content and fibre volume fraction similar to the pre-preg process.

The solution was used to strengthen the vent shaft at Shadwell Station on the East London Line in 1999, Figure 10. The vent shaft contains two levels of struts, 9 on each level, with cross bracings to support against buckling at ¼ points on the upper level and mid-points on the lower level. A failure at a similar structure in Rotherhithe station was thought to have been initiated by failure of one of the braces which doubled the effective length of the beam, and so the braces also required strengthening.

The idea of installing some additional steel struts and jacking them out to reduce the stress levels within the cast iron, and then strengthening the cast iron so that any additional loads could be carried was put forward as the best solution balancing cost, safety and convenience. The other main advantage of this particular solution was that the beams removed from Rotherhithe were still available. This gave the opportunity to validate the reinforcing technique at full scale prior to implementation and minimised the risk taken in using a novel technique. Given the large number of cast iron structures for which LUL have responsibility there was a future benefit in being able to prove a lower cost strengthening technique on such a job.

A linear length of beam of nearly 1km was strengthened, using about 1.5 tonnes of carbon fibre composite.

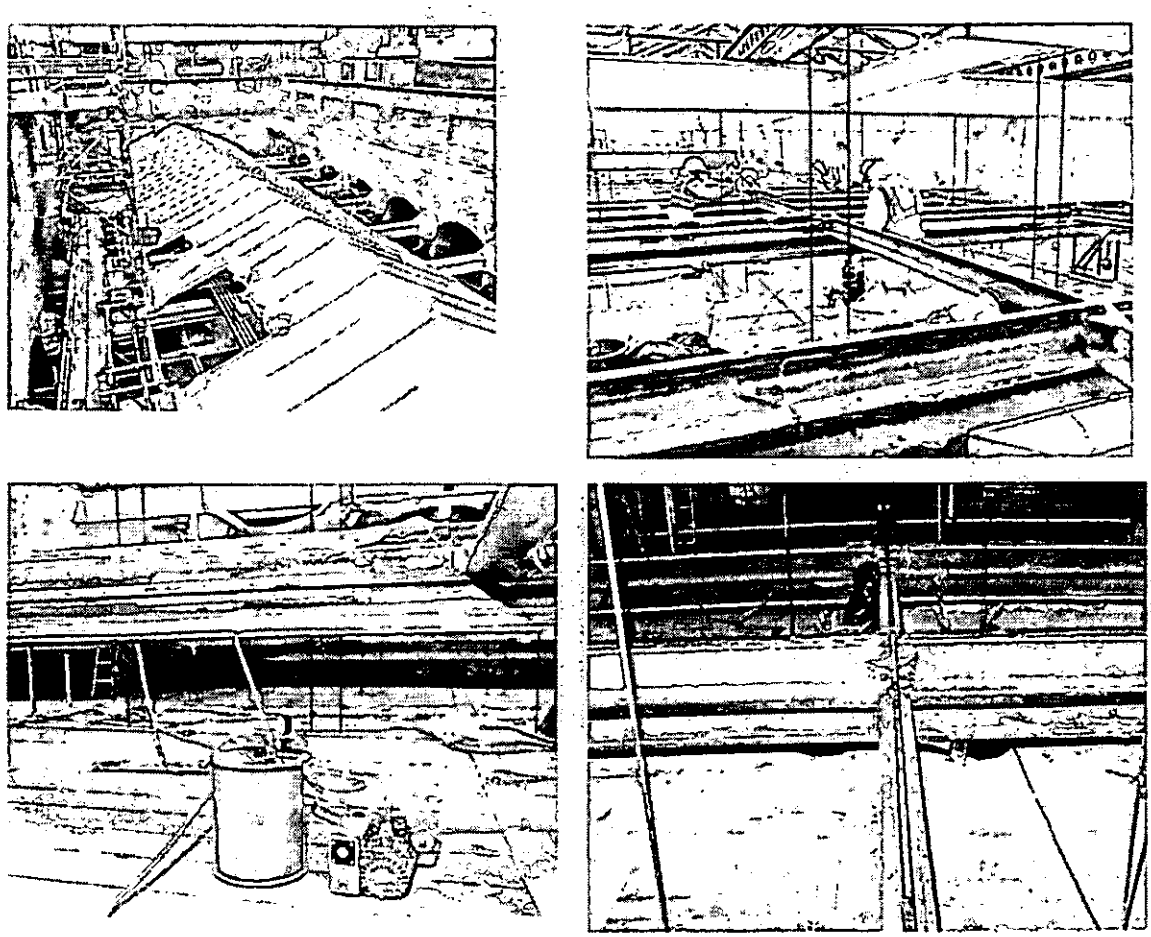


Figure 10. Strengthening of cast iron struts at Shadwell Station using RIFT technology

6.4 Type 42 Destroyer Bridge Screen Repair

Having developed the RIFT technique for structural repairs to bridges it was apparent there would be benefits of feeding it back into the main work at DML – repair and maintenance of Royal Navy ships, Figure 11. The first problem to receive attention was that of repairs between the bridge screen and deck on the Type 42 destroyers. This is a class defect, where misalignment between beams below this corner has been noted to lead to fatigue cracks. The original solution was to weld in place a customised forging – but this involved removing a large amount of the internal plant and equipment to gain access to the beams. The cost of this work made the simple application associated with composites highly attractive.

An initial design was undertaken using FE analysis, Figure 12, to size the repair. It was possible to reduce the stress concentration at the bridge screen by 60% through the application of a tailored repair. The application of the repair, Figure 13 to Figure 16, followed the same format as all the composite strengthening DML had undertaken previously using RIFT. The surface is prepared, the carbon fibre preform applied, the RIFT completed and the repair finished. It has now been in service on HMS Liverpool for two years with no reported problems with the repair itself.

Structural monitoring was used to demonstrate that the repair was forming as designed, and confirmatory data have now been recorded, and since then the repairs have been implemented on HMS Nottingham. Further similar repairs have also been completed.

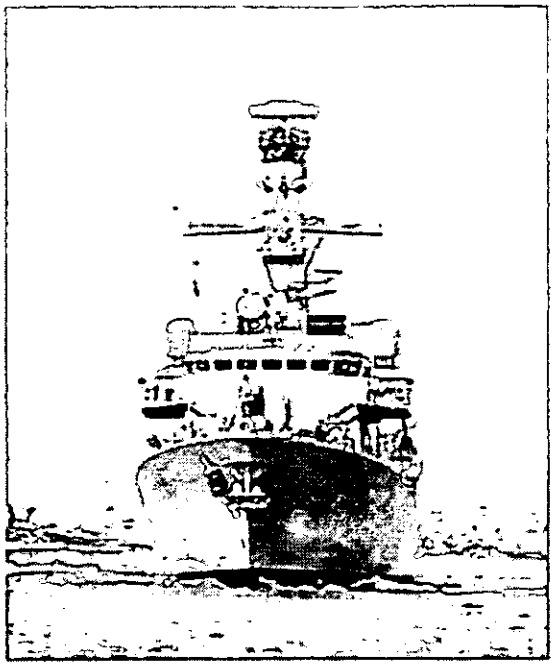


Figure 11. RN Ship

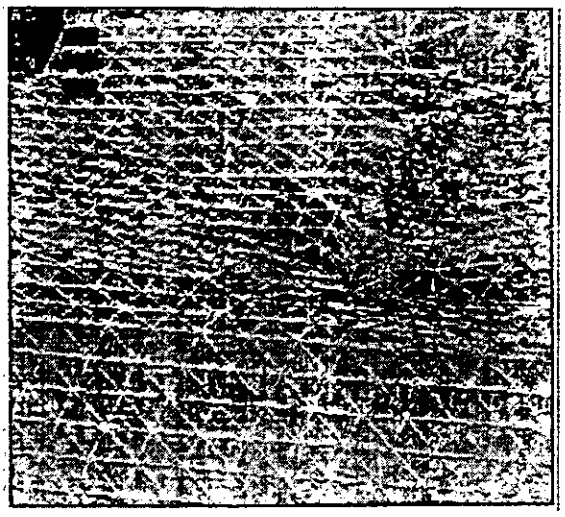


Figure 12. FE model of Type 42 Bridge Screen with Composite Repair

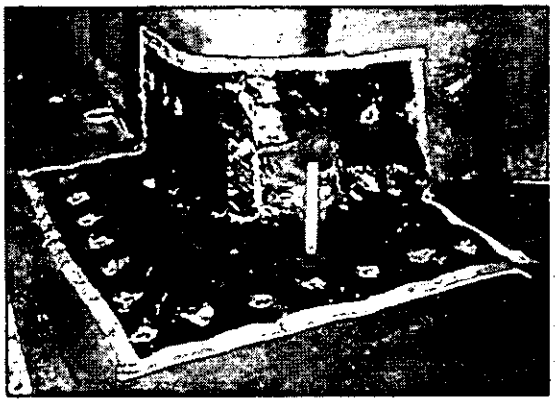


Figure 13. Carbon Fibre Preform

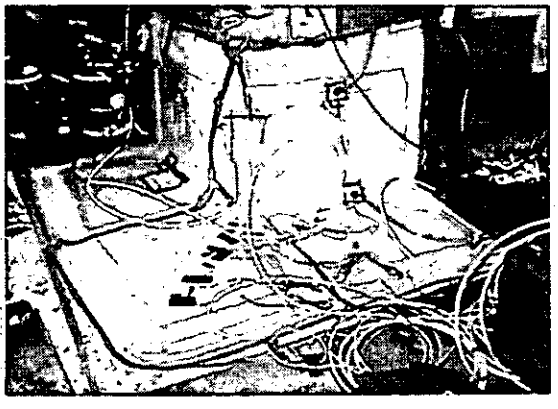


Figure 14. RIFT of Bridge Screen Repair

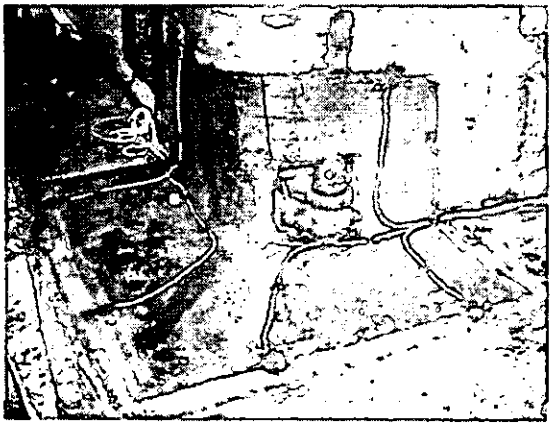


Figure 15. Completed Carbon Fibre Repair

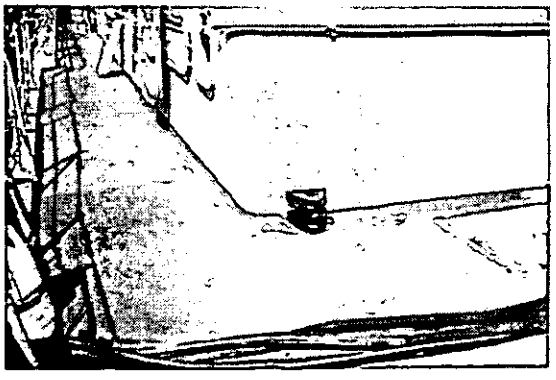


Figure 16. Repair after Painting

6.5 Other Ship Repairs

Carbon fibre has been used to repair other defects on ships. Work has been undertaken to look at the use of UHM carbon fibre to stop the growth of fatigue cracks. This work was first completed for use on aircraft, but has now been extended for ships. Typical defects are shown in Figure 17 to Figure 20.

Cracks at door corners are another common defect, Figure 17. They are usually repaired by cutting out the crack and welding in a new piece of plate. Carbon fibre repairs require the existing plate to be prepared, the crack filled, and the laminate applied on top. This is quicker and less intrusive than the weld repair and requires access from one side only.

Corrosion in decks has also been repaired, Figure 18 to Figure 20. Here again the cost savings stemming from easy installation were significant.

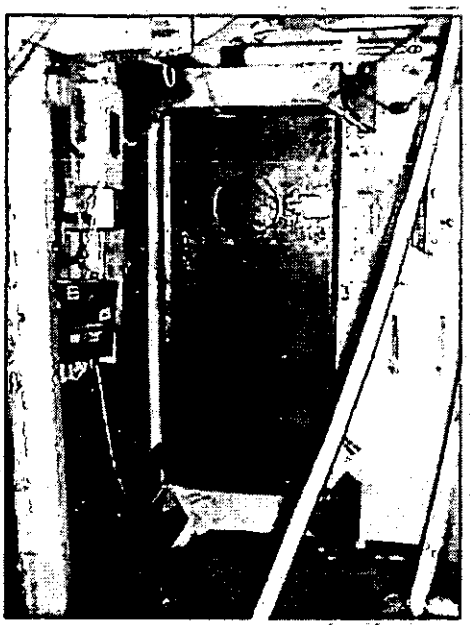


Figure 17. Repairs to cracks at door corners



Figure 18. Repair to corroded decks

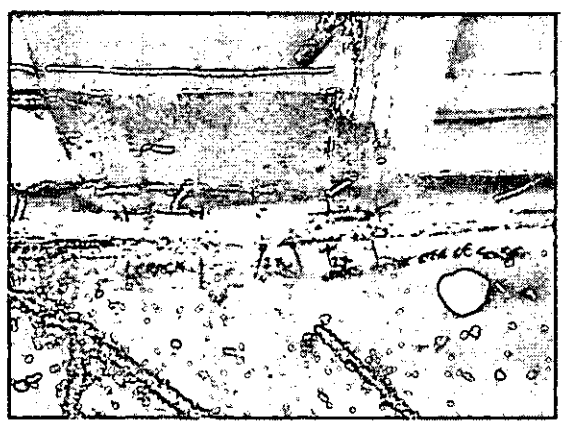


Figure 19. Corrosion defects marked on deck

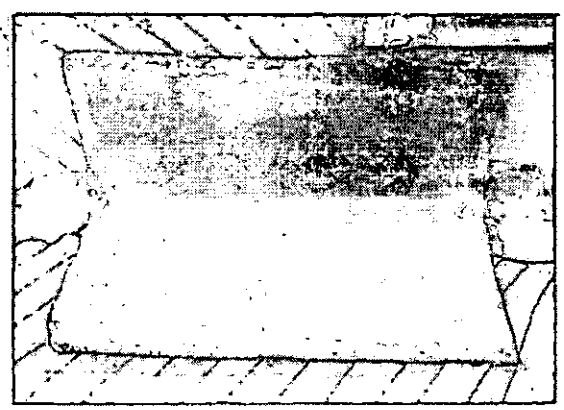


Figure 20. Completed repair

6.6 Composite Repairs for Metal Pipework

One further extension to the use of carbon fibre for the repair of metals has been in the development of a pipe repair system. Steel pipes in the process industry are particularly prone to corrosion. One of the most aggressive environments is offshore in the North Sea. DML Composites have been applying repairs to corroded metal pipes since 1995. The system is now designed and installed in line with an Industry standard prepared by AEA Technology for Shell Exploration and Production and BP-Amoco. Examples are shown below, Figure 21 to Figure 24.

Repairs have been applied on pipes designed to operate up to 50 bar. The general temperature limit is 100°C, but one specific set of repairs was designed to see excursions to 150°C. The size of defect repaired is important and must be considered at the design stage.

The benefits of the repair are still related to the simplicity of the system giving rise to cost-savings compared to traditional repair techniques. The systems work best when applied to a shot blasted

surface, but other than blasting there is no 'hot work' associated with the repair, minimising the hazard during application (a major consideration offshore). In many cases the repairs can be applied whilst the platform is still live, and have been used to extend the life of badly corroded pipes to the next scheduled shutdown – preventing the need to interrupt production (which would equate to lost revenue, and be very expensive). Composite pipe repairs are the fastest growing composite repair at present, and are likely to see rapid further expansion as experience in the North Sea grows.

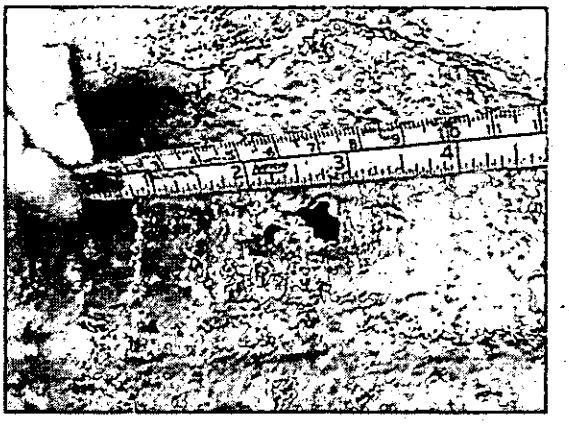


Figure 21. Defect prior to repair



Figure 22. Repaired pipe

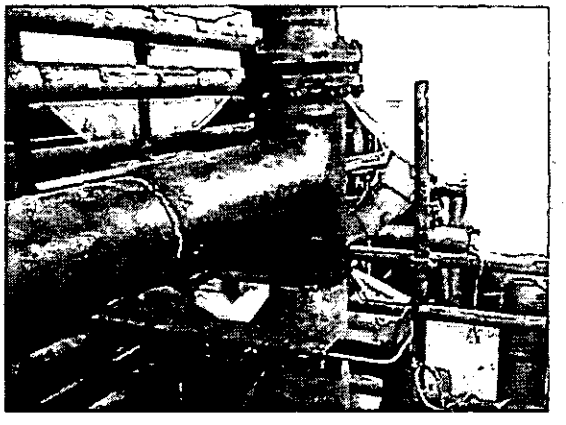


Figure 23. Repaired tee

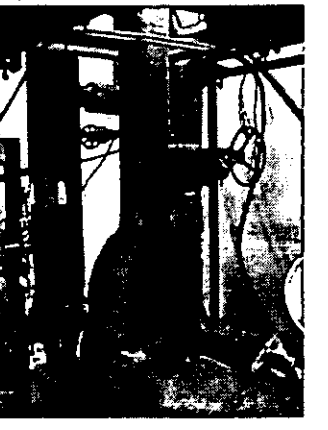


Figure 24. Repaired reducer

7 Underwater Repair

All the repair techniques mentioned so far require the work piece to be dry. In most cases this is not difficult to achieve, with local tenting being all that is required. However in humid environments and underwater it is not possible to provide a dry surface. DML have therefore been working to develop a system that can be applied in wet conditions and still be used to give a permanent repair. This work has been undertaken as part of two joint industry programmes. Sponsors of the work were BP-Amoco, Elf Exploration, Enterprise Oil, Health and Safety Executive, Marathon Oil, Rockwater Ltd, Shell UK Exploration and Production, DERA, BG plc, MOD and Mobil North Sea Ltd.

The initial solution was to adapt the RIFT technique. The sealed vacuum bag gives the opportunity to provide an enclosed environment around the carbon fibre, which can then be dried out prior to the resin being drawn in. Trials were successful, but the view was taken that the technique should be adapted to become ROV friendly, and the dexterity required for RIFT made this challenge more complicated than desired. Further work was therefore undertaken to simplify the repair process. A modified resin system was formulated by DERA, and an application system developed by DML. The resin cures in the presence of water, simplifying the repair concept. Two full scale demonstrators were repaired underwater following laboratory trials, Figure 25 to Figure 30. The first demonstrator was a 12" diameter pipe with a defect machined equivalent to a fully circumferential girth weld defect. Once repaired this was subject to an axial load and the failure load measured. The second demonstrator was a 24" diameter pipe with a 20mm diameter hole machined in. After repair this was subject to an

internal pressure test, and the failure pressure recorded. Results are shown in Table 4 and Table 5. The benefit of the approach is the increased speed of response that can be achieved using the composite repair compared to traditional metal clamp solutions, resulting in a cost-benefit to the owner of the damaged structure.



Figure 25. Test spool in diver tank



Figure 26. Sealing of leak

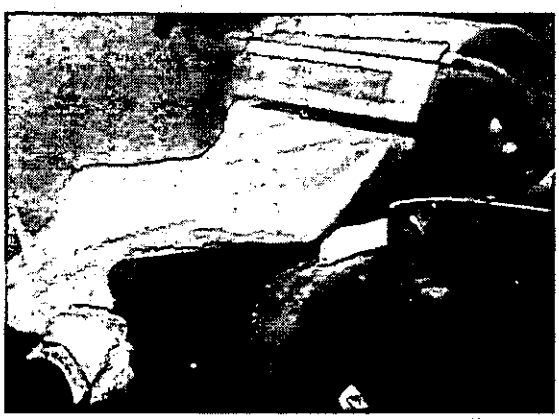


Figure 27. Application of first layer of glass fibre

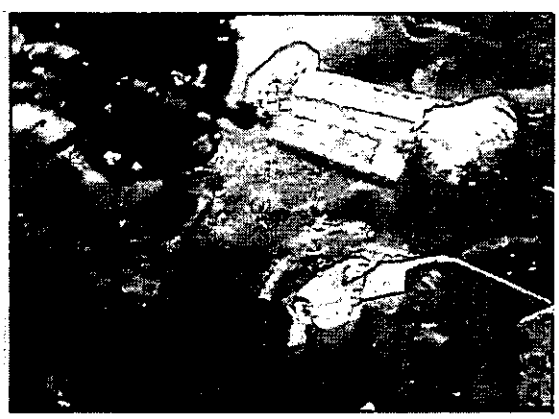


Figure 28. Application of carbon fibre

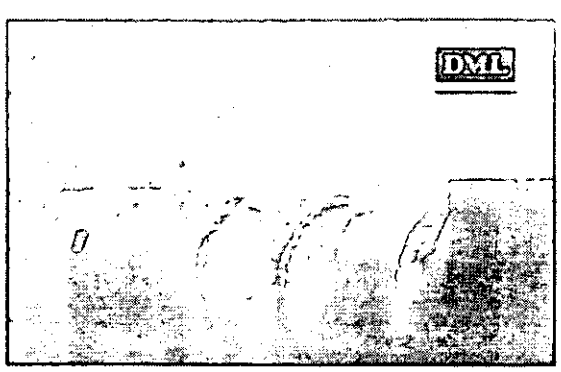


Figure 29. Curing underwater, heat supplied by hot water



Figure 30. Pipe prior to testing, with strain gauges attached

	Demonstrated	*Predicted*
Pressure	57.4	100 bar
Diameter	24"	Independent of diameter
Defect size	20mm	2.0mm
Repair thickness	8mm	15mm

Table 4. Internal pressure capability of repair applied underwater

	Demonstrated	*Predicted (service)*
Tubular diameter	0.3m	2m
Repair thickness	10mm	5mm
Repair overlap	0.1475m	0.1475m
Axial Load	692kN	4254kN

Table 5. Axial load capability of repair applied underwater

7.1 Application

The application of the underwater repairs follows the outline of that for the current repairs being completed topside. However, to simplify the handling of the materials for the divers a specific tool was designed and manufactured to apply the composite, Figure 27 and Figure 28. The surface preparation is achieved by shot blasting underwater. A primer is then applied to the shot blasted surface to protect and preserve it, however the oxygen content of the water is low, particularly at greater depths, and the prepared surface can degrade more slowly than a pipe in the air.

For the weld defect a filled layer was applied to the defect to provide a firm surface over which to laminate. The pipe with the 'hole' defect was subject to an internal water pressure of about 1 bar during the repair, which resulted in water leaking through the hole; a mechanism to seal the leak prior to application of the composite was therefore required, see Figure 26.

Once the pipe is prepared for repair the application of the composite is very quick, taking about 10 to 15 minutes. After the composite has been applied the resin will cure at temperatures down to 5°C. However, at this temperature it will take about two weeks to cure, therefore local heating is desirable. With any diver support system hot water is always available, and so it was decided to use this to cure the resin. A leaking hose in an insulated jacket was used to flood the surface of the repair with water at about 60°C. The repair cured in just over a day.

The results from the tests are shown in Table 4 and Table 5, along with predicted capability of the repairs as demonstrated. The figures are indicative, and specific solutions for each repair scenario need to be developed. The capability of the system to repair structures is high (based on the axial load test), but its internal pressure capability is modest in comparison. Further work is underway to improve the performance of the system, and the first applications are now being considered.

8 Summary

This paper has given a brief introduction to composite materials, their manufacture and performance. Experience in the use of carbon fibre composites for the repair of various structures onshore, offshore and subsea has been summarised. Composite materials present the opportunity to undertake repairs to a wide variety of load bearing structures in a more cost-effective manner than traditional solution. The main cost-benefit is derived from the simple installation procedures associated with the light weight of the materials, their high mechanical performance and the use of adhesive bonding.

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Chapter 21

Fire Retarding Coatings

Dr Murray Orpin

Fire Retarding Coatings

Dr. M R Orpin

Pyro Technologies

E-mail: murray@pyrotechnologies.co.uk

Abstract

This chapter describes the various types of fire retardant coating that exist within the marine industry in terms of the mechanism by which they resist fire, their primary fire properties and their application to different substrates. Particular emphasis is placed on the distinction between coatings that are required to be active when exposed to fire, such as intumescents, and those that provide truly passive fire insulation, such as syntactics and polymer composites.

1. Introduction

Coatings employed within the marine industry are required primarily to resist the marine environment. Hence, they will protect their substrate from corrosion, erosion, biofouling, etc. as well as often being decorative to some degree. One unique class of coating exists, however, which must resist fire as well as complying with the above protective requirements.

The marine industry has until recently, with the introduction of the new IMO High Speed Craft Code, required much of it's primary structures to be non-combustible with obvious exception of the leisure market where polyester, vinylester and epoxy GRP have been used extensively along with wood. Fire retardant coatings have a small part to play in this area where they are primarily required to prevent ignition or flame spread. These will not be considered here but rather the scenario of protecting critical primary elements in large floating or fixed marine vessels and structures. Here, a fire retardant coating is required to resist not only the fire in itself but also the potentially catastrophic effect of the heat, or thermal flux, generated by it.

Non fire retardant coatings can themselves represent a substantial fire risk, even when applied to a non-combustible substrate such as steel. PVC coating, marine grade epoxies or polyurethanes as well as melamine-based laminate have all been used historically. All of these have also been responsible for significant loss of life in tragic ferry fires such as those of the Scandinavian Star and Moby Prince. Not all fire retardant coatings are themselves safe for use in applications where smoke and toxic fumes would present direct risk to personnel, as will be considered.

2. The Requirements

Obviously, there is no real merit or true integrity in a marine structure if it fails catastrophically as soon as an on-board fire takes hold. Even traditional "non-combustible" materials such as steel may be subject to severe warpage and deformation at fire temperatures. Further to this, steel has a thermal conductivity 200 times higher than polymer composite material and aluminium 750 times higher. This must inevitably lead to rapid heat transfer throughout a structural component as well as to other components or zones in the

overall structure, i.e., the ship. In the case of aluminium alloys, high temperatures can be potentially disastrous because even the more heat resistant alloys begin to lose their properties above 100°C, reducing to 50 - 70% of initial strength by 200°C and to 20 - 30% of initial strength by 300°C. Since aluminium also has a very high thermal conductivity, exposure to temperature is felt very quickly throughout a structure. This rapid fall-off in properties can obviously lead to catastrophic failure of a ship's superstructure where many of the loads will be compressive. Fire temperatures will be 3 or 4 times higher than these critical temperatures and it therefore follows that there is a grave risk of sudden structural collapse in the affected area and within those in thermal contact which could cause failure of, or damage to, the surrounding structural elements before there has been any elapsed time for extinguishing of the fire source or for escape of personnel.

Ultimately, in a real fire, aluminium alloys will melt between 600 - 700°C and can contribute to the fire with fierce burning and high heat release as was demonstrated in the fires on board the "Sir Galahad" in the Falklands War. Although steels are more heat resistant, they lose their structural properties rapidly above ca. 400°C and are also capable of catastrophic collapse, as illustrated by the Piper Alpha disaster.

The true fire retarding coatings of the marine industry are therefore required to provide thermal insulation during a period appropriate to either extinguishing the fire, for personnel to escape or for some other process, such as the venting of highly flammable vessel contents. Secondary to this might come the issue of smoke and toxicity in fire.

Apart from the above key requisites, other important criteria of a fire retardant marine coating are:

- Ability to bond to any relevant substrate
- Substrate bond integrity vs. time, temperature, weathering
- Application and cure in the marine environment, where necessary
- Resistance to the marine environment (salt, UV, water, etc.)
- Durability (abrasion, impact, fatigue)
- Blast resistance (petroleum industry)

Each of the main classes of fire retardant coating outlined below address most, if not all of these criteria.

3. The solutions

There are two primary classes of fire retardant marine coating that address the above requirements and that are correspondingly specified and used, namely:

1. Intumescents
2. Insulative Coatings (syntactic foams, polymer composites, elastomers)

Both classes are commonly described as offering 'passive fire protection'. However, the intumescents are essentially active in a fire as the basis of their performance and must rely on being able to maintain this ability throughout their lifetime. Insulative coatings resist fire via

a combination of thermal insulation, thermal stability and heat quenching endothermic reactions within their matrix.

3.1 Intumescent Coatings

The term '*intumescent*' defines a material that is stable under normal conditions but which, during fire conditions, undergoes a chemical reaction that results in expansion to several times it's initial volume leaving a fire stable and insulating carbonaceous char, as illustrated in the diagram opposite. Most common intumescent reactions are based on the thermal degradation of inorganic or organic pyrophosphates. A coating would contain such a material, which acts as the 'spumifier' or gas producer in the intumescent process, bound in an appropriate resin matrix along with other synergistic additives. The higher the yield of carbon and phosphorous from the thermal degradation process, the more stable is the final char.

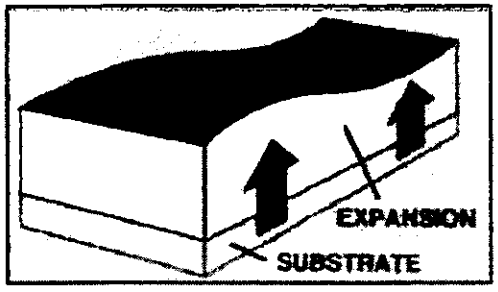


Fig.1. *Expansion of an intumescent coating*

Many non-marine intumescent coatings are capable of expansion up to 50-100 times their initial thickness. However, such coatings produce very weak chars that are rapidly eroded away in a turbulent fire as might be typically experienced in the oil and gas industry. Moreover, they are not capable of resisting the extremes of the marine environment.

Marine intumescents are typically based on two-pack epoxy systems and are available in both solvent-based and solvent-free formulations, although the latter are rapidly becoming the preferred option. These coatings produce a lower volumetric expansion in fire but result in a much stronger char and, as a result, are able to offer protection times of up to 4 hours. Much greater coating thicknesses than normal must be employed, typically 4–20mm. The intumescent process does not commence until above 200°C and so these coatings are only really applicable to a steel substrate whose critical temperature lies in the 300-400°C region. Aluminium would not normally be an appropriate substrate.

For medium to thick intumescent layers, reinforcement must normally be incorporated into the coating in order to support the char as it is produced. This is normally steel, glass or carbon mesh. Appendix A and B show the reinforcement detail for the application of two different types of mesh in the coating of a square hollow section.

Marine intumescents are normally spray applied but they may also be trowelled, cast in situ or even pre-cast. For optimum corrosion protection and longevity, most manufacturers would recommend their application over a cured, high quality epoxy primer rather than to freshly blasted steel. Similarly, although the coatings are resistant to weathering, optimum performance would be obtained through top-coating with a high performance polyurethane or acrylic system.

3.1.1 Typical Intumescent Properties

The table below lists the physical and mechanical properties of a cured intumescent coating, in this case 'System E' from Carboline Europe Ltd.

Fig. 2. Physical & Mechanical Properties of a Typical Marine Intumescent Coating

Property & Test Method	Value
Tensile Strength to ASTM D638	12.7 MPa
Tensile Modulus to ASTM D638	1.8 GPa
Compressive Strength to ASTM D695	28.3 MPa
Compressive Modulus to ASTM D695	1.1 GPa
Flexural Strength to ASTM D790	18.0 MPa
Flexural Modulus to ASTM D790	2.5 GPa
Impact Strength to ASTM D256	9.0 J/m
Lap Shear Strength to ASTM D1002	9.9 MPa
Hardness (Shore D)	75
Nominal Density	1100 kg/m^3
Thermal Expansion to ASTM D696#	16.8 x 10^{-6}/cm°K
Thermal Conductivity to ASTM C177	0.246 W/m°K
Specific Heat Capacity @ 20°C	1.33 J/g
Oxygen Index to ASTM D2832#	26.4%
Water Vapour Transmission to ASTM E96-90(B)	0.023 $g/h.m^2$
Flash Point for separate and mixed components (closed cup)	>100°C
Pot Life @ 20°C	40 minutes
Substrate Service Temperature (Maximum)	66°C

In addition to the above, coatings such as System E have also undergone blast tests in the region of 1.5 bar overpressure without sustaining any damage.

Most manufacturers of marine grade epoxy intumescents have fully tested and certified their coatings for up to 3 hours hydrocarbon pool or jet fire exposure, during which time they must be capable of keeping the temperature of the steel substrate below a mean temperature of 300-400°C. Accordingly, this level of performance in invariably approved by the offshore regulators, Lloyds Register and Det Norske Veritas. Cellulosic fire resistance is obviously more readily achieved, for which the manufacturers carry independent certification for up to 3 hours protection. Appendix C summarises the fire approvals obtained by Carboline's System E.

The individual coating manufacturers will recommend specific coating thicknesses in order to achieve a desired level of fire protection. Normally, up to 10mm of epoxy intumescent may be applied in a single coat.

3.1.2 Suppliers

Epoxy intumescents have been supplied to the offshore oil and gas industry for over 20 years as fire protective coatings to structural steel-work, sometimes incorporating several hundred tonnes of material in a single project. Over this period, the dominant products have been:

- Chartek series from Textron (currently Chartek VII)
- Pitt-Char from PPG Industries

More recent products are those such as System E from Carboline and M90 from Leighs Paints.

3.2 Syntactic Foams

As can be seen from the data presented above, although intumescent coatings have been used widely in the marine industry as a cost-effective means of fire protection for structures, they nevertheless have certain technical limitation, such as:

- Low upper service temperature (typically 60-70°C)
- Relatively poor thermal insulation
- Inactive until above 200°C
- Non appropriate for a continuously wet environment (e.g., splash zones)
- Will release smoke and toxic fumes in a fire
- Not appropriate for aluminium protection

Some or all of these issues are addressed by the second class of fire retarding coatings referred to earlier, namely insulative coatings. Syntactic foam based coatings, specifically phenolic resin based syntactic coatings, have become firmly established over a short period in the offshore oil and gas industry. The phenolic systems produced under the ContraTherm name by Alderley Materials Ltd. have been applied to most of the major North Sea projects in the past 3 years equating to around 10,000m^2 of coating area.

ContraTherm systems address all the above areas by offering a fully bonded, insulative layer (35-50mm typically) that can tolerate substrates up to 250°C. They are 3-7 times less thermally conductive than intumescent or composite materials and so offer instant protection to any substrate in a fire situation. Phenolic composite top-skins protect the systems in the harshest environments, including splash zones or sub-sea. Finally, the phenolic matrix produces virtually no smoke or fumes in fire making ContraTherm systems appropriate for use in areas critical to personnel survival.

A syntactic foam or material possesses a microcellular structure that is, by definition, introduced through the use of lightweight additives rather than through the direct foaming of the resin matrix with a volatile blowing agent. Figure 3 illustrates the typical microstructure of a syntactic foam that, in this case, also includes reinforcing fibres. The resin in the case of

a syntactic system is performing the same function as it would in a fibre reinforced composite. However, it is difficult to achieve a high fibre loading in conventional syntactics due to rheological constraints in processing and application. As a result, most systems are optimised in their content of inorganic microspheres and achieve densities between 500-700kg/m^3. Most common resin matrices are proven and established although, until approximately five years ago, relatively few commercial examples of phenolic syntactic foam existed.

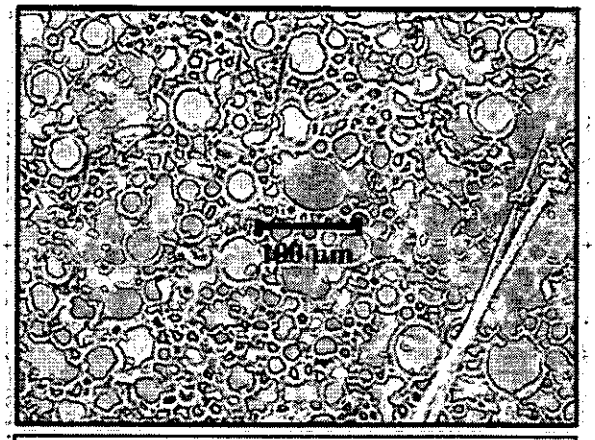


Fig.3. *Microstructure of a syntactic foam*

Phenolic composites have themselves become well recognised as a material of choice for construction in many industries where composites have been preferred as the best design solution in conjunction with a requirement for maximum fire safety and low density (1-8).

ContraTherm products are typically supplied as complete systems which would include all the materials required to fully protect a substrate, typically in carbon steel, for anything up to 2 hours of hydrocarbon jet fire or pool fire conditions. Specific thicknesses of primary components would be tailored to meet the exact fire resistance or insulation demands. All materials are site-appliable and are cured under 'ambient' conditions to be fully handleable within 24-48 hours and with full active service being possible from one week after application. At any point in it's service, a ContraTherm system is removable and/or repairable without compromise to it's performance.

Two phenolic syntactic foams are commercially produced by Alderley Materials for coating applications, namely C50 and C60, which have cured densities of 500kg/m^3 and 125kg/m^3 respectively. C50 was originally developed to meet a recognised need for an elevated temperature insulation material with fire resistance which could be applied underneath conventional epoxy intumescent coatings where the substrate was operating at temperatures above ca. 70°C. The move to more marginal and deep water oil and gas fields has lead to both ever hotter process temperatures and lighter weight materials are also increasingly in demand. C50 is unique in that it is phenolic resin based having mechanical properties and thermal conductivity which are broadly a function of it's density. In fire, however, C50 is designed to have negligible thermal movement and to fuse in the presence of a high carbon and phosphorous yield so that a highly stable, rigid char is formed which results in excellent levels of protection.

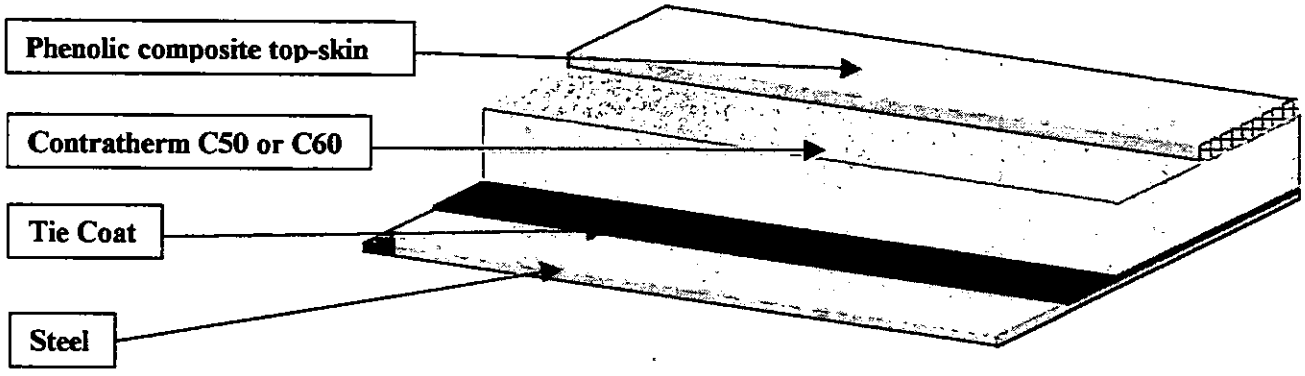
ContraTherm systems are tolerant of operating temperatures in the range –180°C to 250°C; temperatures up to 400°C are under examination. They also retain full integrity of bond and performance after severe thermal shocks such as crash cooling due to, for example, an LNG vessel blow-down (+120°C to –190°C in 10 minutes).

ContraTherm systems are also fully removable through mechanical techniques or with the use of ultra high-pressure water jet equipment. This allows inspection on demand. Full reinstatement of the system is then possible even at running temperature around 150°C. Repaired sections have been incorporated in all certified Jet Fire tests in order to show that there is no loss of performance after repair work.

The phenolic composite skins, which are integral to ContraTherm systems, are currently wet applied by contact moulding and ambient curing, although they could be readily adapted to other approaches such as resin infusion moulding or even spray deposition. Typical application is illustrated in Figure 4 below. AML's phenolic composite skins are modified from what is considered to be conventional phenolic GRP such that they offer the benefits of phenolic composites without the risk of structural instability in fire due to delamination. This modification is both chemical and physical resulting in laminates that degrade in fire to effectively a carbon-ceramic-glass plate which can protect the underlying syntactic foam for extremely long periods in fire allowing the foam to continue to provide insulation.

A full ContraTherm system consists of:

1. Shot-blasted steel primed with a high performance primer to NORSOK System 7 (where thermally sprayed aluminium (TSA) is used, a ContraTherm phenolic primer is specified).
2. ContraTherm Tie Coat (provides a tacky interlayer to hold the syntactic foam and give good bond integrity).
3. ContraTherm phenolic syntactic foam, either C50 or C60 (see below).
4. ContraTherm phenolic composite top-skin (typically 1-5mm thick).
5. Decorative finish (e.g., single pack acrylic)



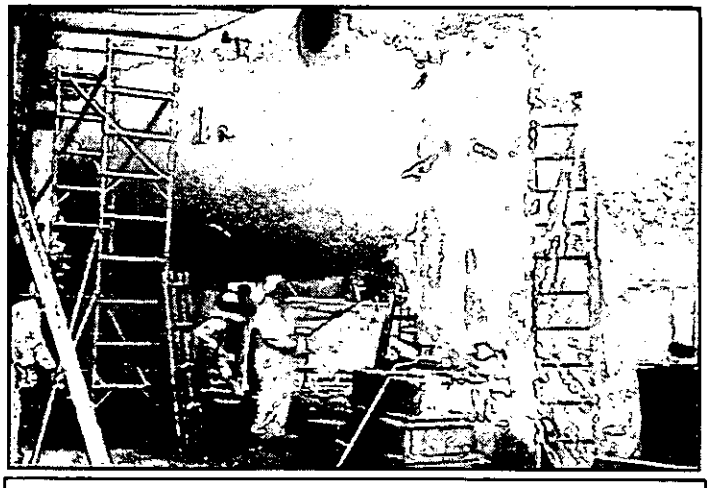


Fig. 4. *Coating a process vessel with ContraTherm JF211*

Fig.5. 90 minute jet fire test of JF211 coating system on a tubular substrate



All ContraTherm materials are designed with fire in mind. With a background in the oil and gas industry, they are stable to fire and temperature extremes as a pre-requisite. Both full scale and indicative testing have proven that ContraTherm phenolic composite structures can both survive and offer protection in the most severe hydrocarbon jet and pool fires for up to 2 hours. Figure 5 illustrates one of Alderley Materials' certified jet fire tests taking place. After 90 minutes of this test, only a small portion of the composite top-skin had been eroded by the flame pressure. The rest of the system had charred but remained intact, protecting the steel substrate that it coated.

The very low density syntactic phenolic foam, C60, is an entirely novel and unique material having a cured density of 125kg/m^3 and a thermal conductivity of 0.035 W/m.K. C60 is supplied as a user-friendly two or three pack system that cures to an extremely tough insulative coating with a degree of resiliency and is capable of being put into extreme temperature service (-180°C to 250°C) within a very short time. Likewise, C60 is fully fire resistant as soon as it is cured.

As with C50, ContraTherm C60 may be chemically bonded to primed carbon steel via the ContraTherm Tie Coat and an approved primer, as shown above. Once coated with an appropriate phenolic composite top-skin, a C60-based system provides an integrally bonded corrosion protection, thermal insulation equivalent to mineral wool or foamed glass and fire protection up to the most severe conditions of J120 or H120. C60 also exhibits the normal excellent low smoke and fume characteristics of the ContraTherm product range, meeting the most stringent of standards. The graph opposite illustrates the indicative Jet Fire performance of C60 systems of differing thicknesses when bonded to 6mm carbon steel. On this scale, the middle 20mm line roughly equates to the performance of the current JF211 system with a 30mm C50 syntactic core.

Due to it's semi-resilient nature, a ContraTherm C60 based coating is extremely

impact resistant and will withstand very high impact forces without damage. The foam alone is rigid and will withstand being walked on but is also capable of full recovery after being crushed to 50% of it's original thickness under a sustained high load.

Both ContraTherm C50 and C60 based coating have been indicatively blast tested against a 1.5 bar overpressure without sustaining damage.

Further details on ContraTherm systems may be found in references 9-12.

Some attempt has been made to offer epoxy resin based syntactic coating systems to the marine industry. However, these have failed to match the benefits of the phenolic systems described above and have made little impact.

3.2 Polymer Composites

Polymer matrix composites have been used within the marine industry in some form for over 40 years, primarily as self-supporting structures. Within the past 10 years however, composites have been also used in a new role as passive fire protection coatings. The majority of the work in this area has been carried out by Vosper Thorneycroft, the specialist GRP shipbuilder, who have taken their skill in the production of large composite structures and applied it to the direct coating of alternate structures.

Vosper Thorneycroft have typically worked in resin systems that would not be expected to perform well as fire retardant coatings, such as vinyl ester and modified acrylic. However, it has been well demonstrated that when thick coatings of glass reinforced composites based on these resins are used, exceptional fire resistance is achievable. The fire performance of thick section composites in the 10-30mm range has been studied and modelled by the Centre for Composites Engineering at the University of Newcastle (13, 14). The conclusions of this ongoing study are that resistance to extreme heat flux and ablative effects are achieved with sufficiently thick composite coatings via a process of endothermic decomposition combined with the relatively low thermal conductivity and non-combustible reinforcement. An accurate predictive model has also been established and proven based on extensive testing.

Polymer composite coatings are normally applied direct to a blast cleaned metallic substrate, invariably steel. Common structures that have been protected in this way are production risers, jackets and legs from offshore oil and gas installations. Vosper Thorneycroft have carried out certified testing up to a two hour jet fire rating in order to gain regulatory approval for this type of work.

Added benefits of this type of fire retardant coating are an extremely robust corrosion barrier that can withstand almost and level of blast or impact. However, the system is relatively slow and labour-intensive to apply and can prove costly. It will not tolerate temperatures above ca. 120°C and is also 2-5 times more dense than a syntactic coating system.

On-site manual application under controlled conditions is normal and system repair or reinstatement is readily carried, as with the syntactic systems described above.

Historically, other companies have offered competitive composite fire protection coatings to the marine industry. For example, SP Offshore Systems have tested a similar coating to Vosper Thorneycroft based on epoxy.

3.4 Elastomers

The final material in the insulative coating class is that of the specially modified elastomer. This approach is less commonly used since factory application is mandatory because of the curing conditions.

The only significant coating here is a highly fire retarded vulcanised polychloroprene rubber system produced by Trelleborg under the name Viking Firestop. Heat and pressure are needed to cure the rubber onto a freshly blasted substrate, normally pipe-work. The finished product resists fire in a similar manner to polymer composite coatings with additional heat quenching performance form additives within the rubber. Again such a system represents a very tough corrosion barrier.

This type of coating has been more commonly used in the Norwegian sector.

4. Coating Selection

The forgoing sections have described the basic fire retardant coating options available to the marine industry based on the premise given at the start, that the most significant function of fire retardant marine coatings is the protection of primary structures. This has been a very common requirement within the offshore oil and gas sector for many years and is becoming increasingly vital to commercial and passenger shipping.

Figure 6 below illustrates in table form the comparative performance of the various types of coating described above.

Fig.6.

Property	Intumescents	Phenolic Syntactic	Polymer Composite	Modified Elastomer
Relative cost	Low	Medium	High	High
Thicknesses	5-20mm	35-50mm	10-30mm	10-30mm
Thermal Conductivity (W/m.K)	0.250	0.035-0.08	0.250	0.20
Application	Spray/trowel	Manual	Manual	Specialist
Primer required	Optional	Norsok System 7	None	None
Repairability	Yes	Yes	Yes	No
Weather resistance	Excellent with top coat	Excellent	Excellent	Excellent
Salt water resistance	Poor	Excellent	Excellent	Excellent
Service temperature	Up to 70°C	Up to 250°C	Up to 120°C	Up to 120°C
Smoke & fume emission	High	Negligible	High	High
Impact resistance	Medium	High	Very high	Very high
Suitability for aluminium	No	Yes	With care	With care

5. Conclusion

The issue of fire protection is becoming an increasingly important issue within the marine industry with changes in legislation brought about by such as the Cullen Report and the High Speed Craft Code.

The coatings described here mainly relate to the petroleum element of the industry with the stress being on the protection of structures from the thermal effects of a fire and resistance to an aggressive marine environment. It must also be recognised that the shipping industry that the shipping industry utilises thin film intumescent paints and fire retardant veneers for the purposes of interior decoration and prevention of fire propagation. This area requires different treatment since most materials struggle to meet the latest codes of practice in terms of heat release; the prime aim of interior fire legislation is to prevent flashover conditions in a cabin or room. An excellent treatment of the problems associated with this area can be found in reference 15.

It is clear from the above that fire retardant coatings exist that can protect critical structures for several hours in the event of the most severe fires possible. Where low density, thermal efficiency and personnel safety/comfort are desirable factors, phenolic syntactic coatings are an obvious choice. If cost is the primary driver, and the above criteria can be compromised on, then intumescent coatings will invariably be considered first. The key with all fire protective coating is compliance with legislation and the safety case of the relevant operators and industry regulators.

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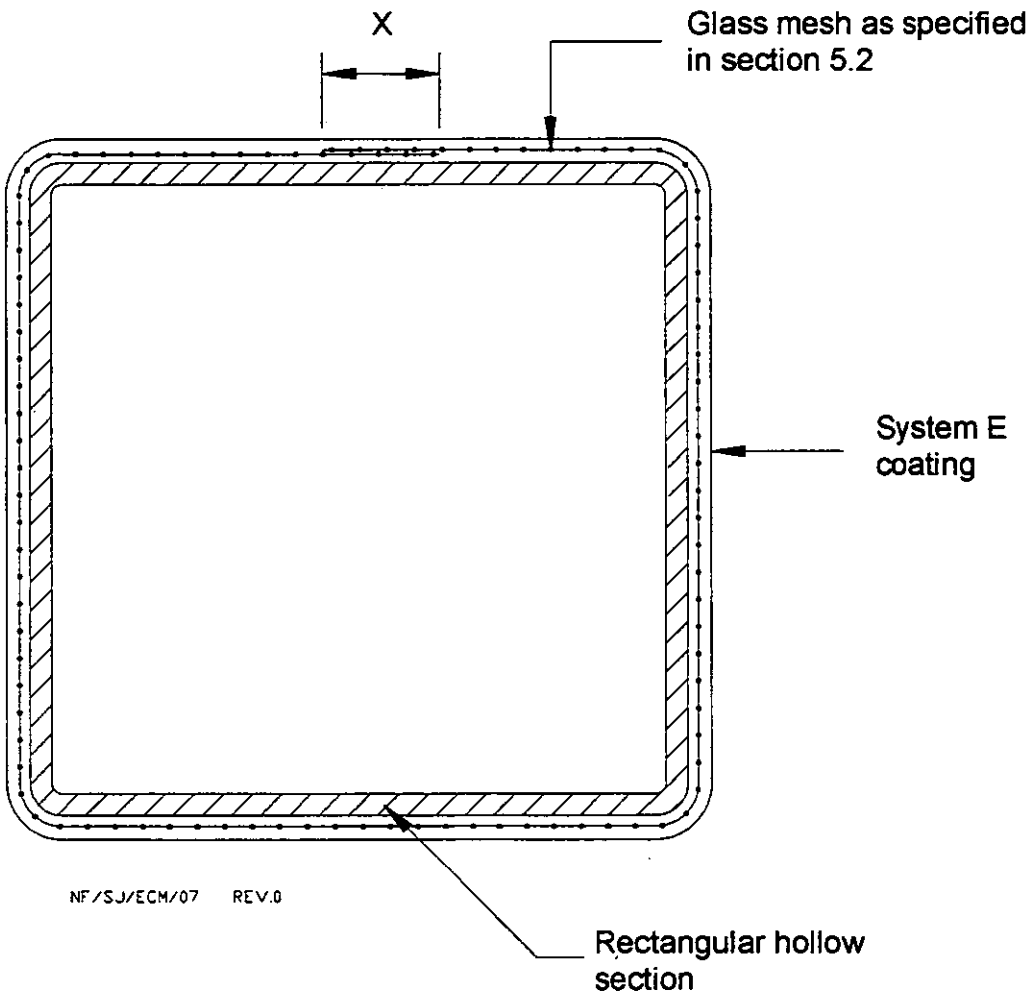
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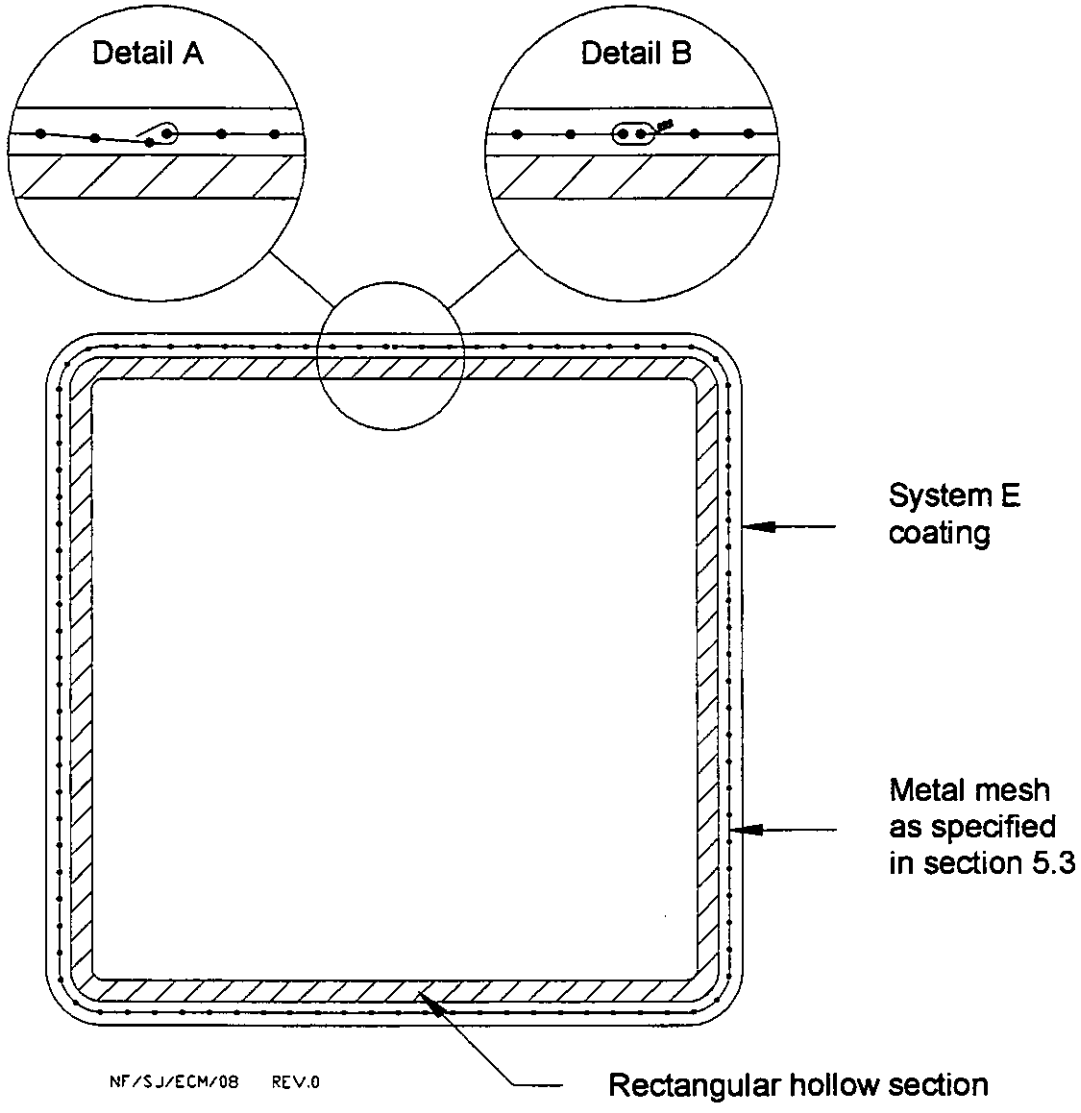
Appendix A: Rectangular hollow section, System E protection reinforced with glass mesh



Important: The amount by which the mesh overlaps itself (distance X) must be at least 50 mm.

Fire type	Coating depth	Mesh position
Cellulosic	Up to 4 mm	No mesh required
	4 mm and above	Coating mid-depth
Hydrocarbon	Between 4 and 12 mm	Coating mid-depth
	12 mm and above	6 mm from outer surface of the coating

Appendix B: Rectangular hollow section, System E protection reinforced with metal mesh



Important: The edges of the mesh shall abut and be tied together, either as shown in Detail A or as shown in Detail B. Full details are given in section 5.3.1 (Hollows, p13).

Fire type	Coating depth	Mesh position
Cellulosic	Between 4 and 8 mm	A minimum of 2 mm away from the surface of the steel
	Greater than 8 mm	Within the middle third of the coating thickness
Hydrocarbon	Up to 13 mm	At the surface of the steel
	Above 13 mm	Nominally 6 mm from the surface of the steel

Appendix C

Summary of System E Approvals

(Carboline Europe Ltd.)

1. **Structural steel, I-section**
   Steel weld-mesh reinforcement
   UK Department of Energy hydrocarbon time/temperature relationship
   Approvals from Lloyds Register of Shipping
   Up to 3 hours protection

2. **Structural steel, I-section**
   E-glass fabric reinforcement
   Fire-tested to BS476: Part 20 : 1987, Appendix D Hydrocarbon Curve
   Approvals from Lloyds Register of Shipping
   Up to 4 hours protection

3. **Structural steel, hollow sections**
   Steel weld-mesh or E-glass fabric reinforcement
   Fire-tested to BS476: Part 20 : 1987, Appendix D Hydrocarbon Curve
   Approvals from Lloyds Register of Shipping
   Up to 4 hours protection

4. **Jet Fire Test**
   Steel weld-mesh and Carbon Fibre fabric reinforcement
   Fire-tested to HSE/NPD interim test method at SINTEF NBL, Norway
   Approvals from Lloyds Register of Shipping
   Up to 2 hours protection

5. **H0, H60 and H120 Decks**
   Steel weld-mesh reinforcement retained with pins
   UK Department of Energy hydrocarbon time/temperature relationship
   Approvals from Lloyds Register of Shipping
   Up to 2 hours protection

6. **H0, H60 and H120 Bulkheads**
   Steel weld-mesh reinforcement retained with pins
   UK Department of Energy hydrocarbon time/temperature relationship
   Approvals from Lloyds Register of Shipping
   Up to 2 hours protection

7. **UL1709 listing**
   Approval from Underwriters Laboratories Inc. (USA)

8. **Blast Resistance**
   Flat Steel Plate, Universal Columns and Square Hollow Sections tested
   Steel weld-mesh reinforced and un-reinforced specimens tested
   Building Research Establishment, Cardington
   Letter of compliance from Lloyds Register of Shipping

9. **Structural Steel (cellulosic fire)**
   I-sections, hollow sections and solid rods.
   Steel weld-mesh or glass scrim reinforced
   Warrington Fire Research Centre Assessment

Chapter 22

Painting Marine Composites

Nigel Clegg

Painting Marine Composites

Nigel Clegg, Consultant

Abstract

This lecture will consider the practical benefits and limitations of painting marine composite materials, examining the physical and chemical behaviour of a range of coating types, in relation to both technical requirements and owners expectations.

There will also be discussion about the use of coatings for the prevention and treatment of 'Osmosis', the use of fire retarding materials, selectively strippable camouflage coatings and the practical difficulties of preventing antifouling detachment.

Introduction

It's a sad fact of life, but even brand new boats only keep their shine for just a few short seasons, and without some form of protection they quickly start to look tired, faded and distinctly second-hand. Known technically as 'ultra violet degradation', this effect is caused primarily by ultra violet energy radiated by the sun, although water, oxygen and general wear and tear also play their part.

Regular waxing with a good quality wax polish can help to delay the inevitable, and may also help to restore slightly dulled finishes, but eventually there comes a time where there is no option but to sand down and paint.

Of course, owners of timber and metal yachts are well used to the idea of regular re-painting, and most would never dream of letting their pride and joy fall into a state of dilapidation. But owners of glassfibre boats have always looked upon painting as a last resort, with many believing that it will devalue their craft, rather like a back street car re-spray. Others are not even aware that glassfibre can be painted, or perhaps have never given it any thought, so it's little wonder that there are so many yachts around in dire need of some love and attention.

This negative approach to boat maintenance would seem to be very much out of character with the spirit of yacht ownership, as most owners are usually only too keen to preserve their investments. One reason may be that glassfibre is still considered by many to be 'maintenance free', although it is more likely that dull and faded gelcoats are seen for what they are - unsightly but comparatively harmless.

One result of this attitude, and the domination of glassfibre boats generally, is that UK sales of yacht paints have fallen significantly over the past thirty years or so, from about 1.2 million litres in 1972, to around 620,000 litres in 1999. European markets have seen similar trends.

But whilst volumes of paint sold may have fallen significantly, the total ***value*** of paint sold has actually increased, perhaps reflecting the higher cost, and higher performance materials now used to protect and re-finish composite materials.

But with many glassfibre yachts now fifteen or twenty years old, there are probably upwards of 50,000 craft around the country in dire need of painting - a fact which has not been lost on the major paint manufacturers. Faced with ever declining sales to owners of traditional craft, Messrs Awlgrip, Blakes, International ***et al*** have tried hard to overcome these old prejudices by marketing topsides painting as an accepted and affordable part of glassfibre boat maintenance.

Perhaps the most inspired idea was the launch of International's chain of Interspray Centres during the early 1980's. The plan was to establish a network of selected boatyards around Europe, all capable of spraying the firms Perfection 709 finish in controlled conditions and to high standards. In return for their investment, participating boatyards received free promotional material, were listed in advertisements promoting the Interspray network, and received technical training and support.

However, the real purpose of this exercise was not just to sell Internationals spray finishes, but to make boat owners more aware of the benefits of painting their craft, and so promote sales of topsides paints generally. In reality, only a limited number of owners would ever contemplate paying the £2,000 or so that it costs to have a boat sprayed; but many more would be motivated to have a go themselves armed with a paintbrush and roller, even if the results were not quite as impressive.

The idea of spray painting pleasure yachts was quite revolutionary twenty years ago, and provided a number of benefits; but environmental concern and health and safety are the watchwords now. Spray painting is rapid and provides superb finishes, but it can also be polluting and hazardous.

Indeed, environmental legislation is now so onerous in countries like the Netherlands that some boat builders have been forced to return to more traditional methods of painting. This may be bad news for professional painters, but it has led to the development of some of the best new brushing paints that we have seen for years.

Underwater Protection

But its not just the topsides of glassfibre yachts which can benefit from painting.

One of the most widely publicised problems associated with glassfibre boats is that of 'Osmosis'; in which moisture absorbed by the laminate hydrolyses elements of the polyester lay-up resin, to liberate a series of (hygroscopic) breakdown products. These breakdown products encourage and accelerate further moisture absorption to such an extent that they can ultimately cause severe blistering in the protective gelcoat.

Osmosis can easily be prevented by coating the underwater area with an effective moisture barrier; preferably when the hull is new, and before it is first put into service; although older vessels can still benefit provided certain checks are made first.

However, once the lay-up resin has started to hydrolyse, it is essential to completely remove the gelcoat, together with any breakdown products before the hull is re-coated.

Other applications

The use of coatings for topsides refinishing and underwater protection are obvious enough, but there are many other applications for coatings on marine composites.

We should also consider that not all marine composites are comprised of standard glass reinforced polyester.

The use of carbon fibre and Kevlar reinforcements in conjunction with epoxy structural resins is now very well established; but there is also increasing interest in the construction of timber composites, using either lightweight Cedar or Balsa cores, or more traditional marine timbers such as teak or mahogany encapsulated with epoxy glassfibre sheathing.

The epoxy resins used in these composites have excellent mechanical properties, allied with excellent resistance to moisture absorption; but they must be well protected if the resins structural integrity is not to be damaged prematurely by ultra violet light.

There is also the practical necessity of keeping the yachts bottom clean of fouling growth, usually by applying an antifouling coating. Thankfully, composite materials are compatible with just about all antifouling biocides, (unlike aluminium hulls for instance), although maintaining good adhesion to the yachts underside is often easier said than done.

Clearly, the potential uses for coatings on marine composites is many and diverse, but can be summarised as follows:.

- Cosmetic finishing and re-finishing;
- Protection against marine fouling growth (i.e. antifoulings);
- Protection against moisture absorption and 'osmosis';
- Protection against aggressive chemicals (i.e. in processing tanks and sewage holding tanks);
- Fire protection;
- Protection against ultra violet degradation (primarily where epoxy structural resins have been used).
- There are also many 'specific' applications such as camouflage and matched infra red reflectance coatings for the defence industry; radar reflective coatings; and conductive coatings to shield against radio frequency (RF) interference.

Having identified a variety of uses for coatings, we will now consider the requirements of each application, and the suitability of various coating types.

Yacht Topsides and Superstructures

Gelcoat finishes usually last for around ten to fifteen years, although this varies widely depending on the gelcoat colour, and the environmental conditions to which the vessel or structure is exposed.

However, a large percentage of glassfibre pleasure boats around Europe are now at least thirty years old, and are clearly beginning to show their age.

Prolonged exposure to sunlight results in clearly visible 'ultra violet degradation', where the gelcoat finish becomes noticeably dull and 'chalky', and in some cases, looses its colour altogether.

In severe cases, the gelcoat can become weakened and friable, exposing the structural laminate beneath to damage from ultra violet energy and moisture ingress. Some gelcoats also take on a 'crazed' appearance, similar to that of antique porcelain.

However, whilst gelcoats are comparatively easy to paint, the choice of materials raises a number of issues such as abrasion and abrasion resistance, and overall adhesion.

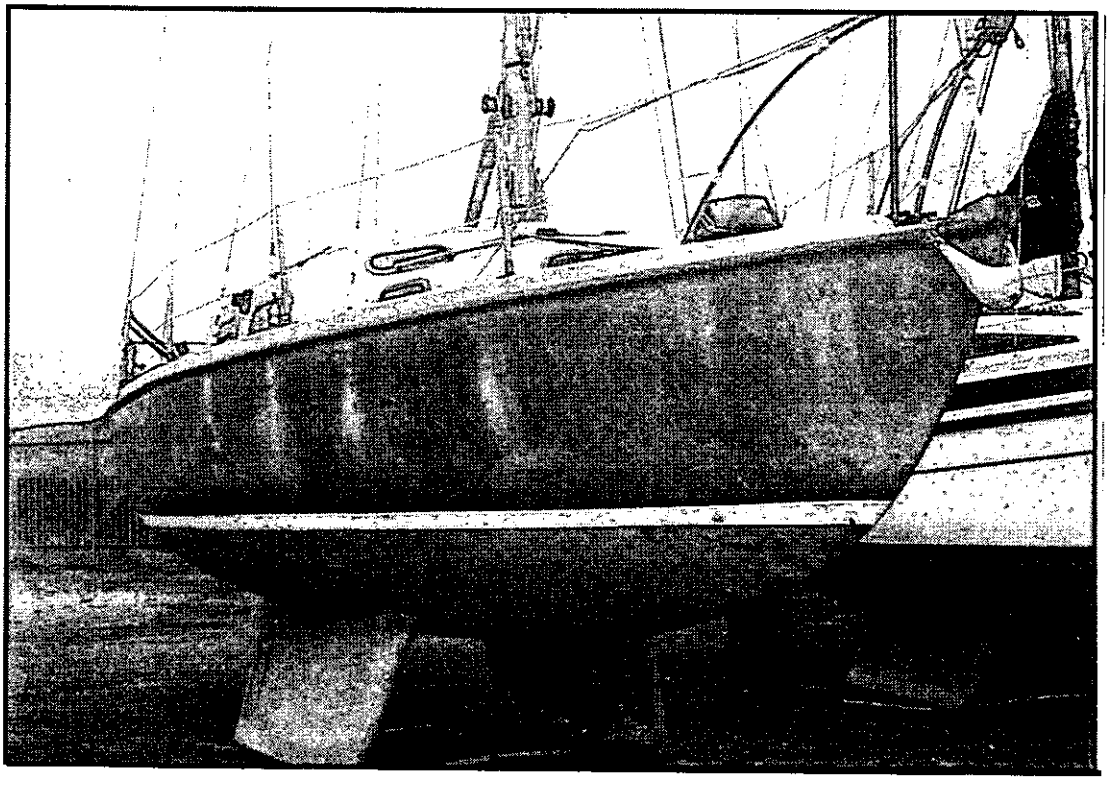


Fig 1. A badly faded gelcoat on a glassfibre sailing yacht. Red and blue gelcoats are especially prone to this problem, which can only be remedied by painting.

Abrasion Resistance, Gloss and Adhesion

Polyester gelcoats are remarkably hard and tough materials, which can withstand a lot of knocks and scrapes before they sustain noticeable damage. Most gelcoats are also comparatively thick at around 500 ~ 600 μM (20 ~ 23.6 Thou); compared with a dry film thickness of just 30 ~ 40 μM (1.2 ~ 1.6 Thou) per coat for a typical gloss finishing paint.

Some boat manufacturers, most notably Westerly Yachts, also lay up the first layer(s) of reinforcement with structural resins pigmented to the same colour as the outer gelcoat, so that even deep scratches and gouges are not easily noticeable.

Polyester gelcoats also provide very good gloss levels, (85% is typical), although they don't offer the extreme gloss, and 'distinction of image' qualities of two pack polyurethane yacht finishes, such as those manufactured by Awlgrip, Blakes, International and Jotun.

In most applications this is a positive advantage, as the slightly 'soft' gloss helps to mask any minor irregularities and imperfections in the moulding, and also general signs of wear and tear.

The combination of good gloss, high film thickness and excellent abrasion resistance means that gelcoats provide very good durability in a variety of environments, with little need for periodic maintenance or re-painting. Any coating scheme designed to replace, or refinish a gelcoat surface will be expected to offer durability at least as good as the gelcoat which it is covering, although in practice, this is often easier said than done.

Coatings for Topsides Finishing

Given the durability of gelcoat systems, the most obvious choice for re-finishing a glassfibre yacht would be yet a further application of gelcoat. However, despite their many positive attributes, polyester gelcoats are really only suitable for application inside a female mould, as they are reluctant to cure properly when exposed to the atmosphere (owing to an effect known as oxygen inhibition); which apart from reducing their resistance to abrasion and moisture absorption, also results in dull and sticky finishes.

This can be overcome to some extent by using wax inhibited gelcoat resins; but these must be heavily polished to provide an acceptable cosmetic finish, which in turn significantly increases application costs. The very hard, and often brittle nature of gelcoats also makes them prone to shatter and flake off when subject to impact.

Gelcoats are occasionally used for re-finishing, but it is generally accepted that wet paint finishes provide a better standard of finish; are easier to apply; and are more cost effective in use.

Two Component Polyurethanes

For most purposes, two pack polyurethane finishes (cured with aliphatic isocyanates) offer the best overall balance of cost, ease of application and durability. Polyurethanes also have the

added benefit of excellent chemical adhesion to well prepared gelcoat surfaces; owing to reaction between their isocyanate curing agents, and redundant OH (hydroxyl) groups in the polyester resin.

Well cured polyurethanes also have excellent abrasion resistance, and can provide gloss and colour retention at least as good as that of the original gelcoat; and usually very much better.

However, it is essential that sufficient coats are applied to ensure adequate film thickness, especially in areas subject fender wear and to repeated abrasion.

Most two pack polyurethanes have traditionally been applied by spray; indeed, the poor brush application properties of many older polyurethane products has meant that there was little practical alternative. However, recent concerns about health and safety, and more particularly the inhalation of isocyanate droplets, have forced manufacturers to make significant improvements in brush application properties, to the point that many professional painters can achieve better results by brush than by spray; and at lower cost.

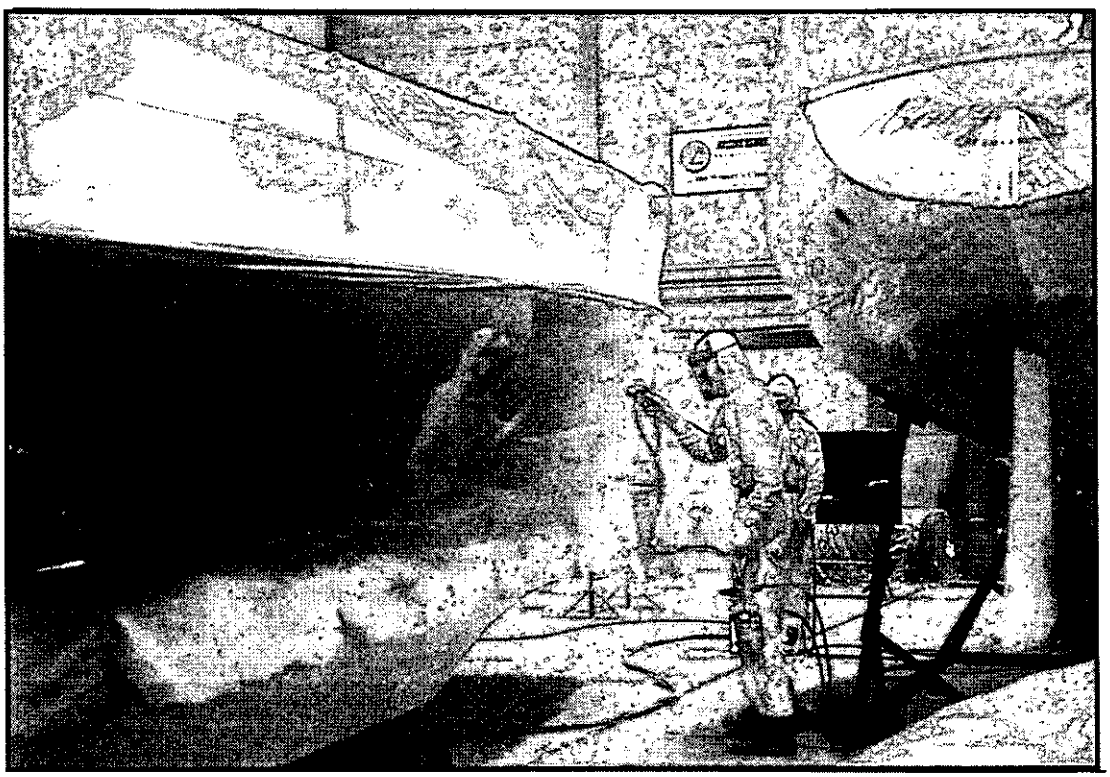


Fig 2. A 15 metre catamaran hull being spray painted with Awlgrip Awlcraft 2000 Acrylated Polyurethane. Note the air fed breathing apparatus worn by the two spray hands. This is essential when spray applying all two pack polyurethanes.

Acrylated Polyurethanes

Acrylated Polyurethanes such as Awlcraft 2000 and International Interspray 800 have also been used extensively for topsides painting, but they have somewhat lower abrasion resistance

than standard two pack polyurethanes, especially when cured under what could be termed 'ideal' conditions. The reason for this apparent anomaly is that 'properly' cured acrylated polyurethanes form comparatively soft films, whereas the urea formed by reacting isocyanate curing agents with atmospheric moisture (as would happen in cold or damp conditions) is much harder.

Experience has shown that the hardness of acrylated polyurethanes can be improved somewhat by deliberately 'over-curing' them with the addition of 15 ~ 20 % too much curing agent; although this tends to result in brittle films, and reduces their long term gloss retention.

A further problem is that the superb application properties and 'off the gun finishes' provided by acrylated polyurethanes can tempt painters into using only one or two coats, whilst their excellent flow and application properties often result in film thickness of just 20 or 25 μM per coat.

Nevertheless, acrylated polyurethanes offer significantly better long term gloss retention than normal aliphatic cured polyurethanes, and are an ideal choice where abrasion and chemical resistance is not pre-requisite. They are not, however, suitable for brush or roller application, except to very limited areas.

(Note: Acrylated Polyurethanes are known technically as Hydroxyl Branched Acrylics).

Conventional Enamel Coatings

Conventional enamels can be used for re-finishing glassfibre, however, their lack of durability and poor adhesion to even well prepared gelcoats severely limits their usefulness in this application.

Most enamels also have comparatively dull gloss (relative to gelcoats and polyurethanes), which would fall below the expectations of most owners of glassfibre vessels.

Silicone modified alkyd enamels, such as Epifanes Nautiforte and International Toplac have much better gloss, and long term gloss retention, but their abrasion resistance is no better than that of a normal enamel.

Furthermore, like most conventional alkyds, silicone alkyds continue to cure slowly throughout their lives, gradually becoming harder and more brittle with age. In a normal alkyd, this activity is curtailed when the coating is overcoated after two or three years.

However, with silicone alkyds retaining their high gloss for much longer periods (up to ten years is typical), there is often no apparent need to re-paint, and the coating continues to cure until it becomes so brittle that it eventually crazes.

This crazing effect is commonly reported as a product or application defect, whereas it would be more accurately described as a 'product characteristic'.

Urethane modified alkyds, and urethane oil coatings provide better gloss and abrasion resistance than alkyds, but their long term gloss retention is often poor, especially in marine

environments. These coatings also tend to have better cohesive than adhesive strength, especially to gelcoat surfaces, and require very good preparation if they are not to suffer flaking and large scale detachment.



Fig 3. Strict Health and Safety legislation in some parts of Europe has forced paint manufacturers to significantly improve the brushing qualities of their two pack polyurethanes. With practice, experienced brush hands can achieve results as good as, or even better than spray applied finishes, and at lower cost..

However, whilst 'conventional' finishes have their limitations, they are significantly more permeable to moisture than epoxies and polyurethanes, which can be beneficial on older laminates where there is evidence of 'osmotic' activity.

Epoxies are not suitable for use as cosmetic finish except in enclosed environments (such as Engine Rooms and Machine Rooms) as they have very poor resistance to ultra violet light, and will quickly loose their gloss.

The coating schemes discussed here are just as applicable to laminates where epoxy structural resins have been used, although considerations overall cost, durability and adhesion to the substrate will usually dictate the use of a high performance epoxy and or polyurethane finishing scheme, rather than conventional coatings.

Two pack polyurethane varnishes can also be used on epoxy/timber composites (appearance permitting), and will provide adequate ultraviolet protection for the structural epoxy resin.

Priming Topsides and Superstructures

Different manufacturers approach the subject of priming in different ways, all of which have their merits and disadvantages.

Where two pack polyurethane or acrylated polyurethanes are to be applied, the usual procedure is to prime with either an epoxy or polyurethane primer/undercoat system.

Polyurethane undercoats (such as International Polyurethane Basecoat) have the advantage of better (natural) adhesion to gelcoat surfaces than epoxies, and can be 'accelerated' to some extent by adding small quantities of tin compounds. Nevertheless, polyurethane undercoats tend to be comparatively 'low build' coatings, which can be difficult to sand when cured, and are sensitive to atmospheric moisture whilst curing.

Epoxy primers (such as Awlgrip 545 and Blakes Epoxy Primer Undercoat) usually have better moisture barrier properties than polyurethanes, and also lend themselves better to high build applications, after which they can be sanded smooth in preparation for finishing. Epoxy primers are also perfectly compatible with epoxy filling and fairing compounds used on Superyacht topsides.

However, there can be problems of poor adhesion between the epoxy primer/undercoat and polyurethane finishing schemes, even where the undercoat has been well sanded. (It is usually necessary to sand with fine grades of sandpaper, thereby reducing adhesion).

Furthermore, any residual solvent present in the epoxy undercoat (either due to over application or premature overcoating) can promote undercure in the polyurethane finishing scheme; as the alcoholic solvents used in epoxies will readily react with isocyanate curing agents, and in severe cases, will result in CO_2 gas bubbling.

Historically, there have been a number of problems associated with both epoxy and especially polyurethane priming and undercoating systems on glassfibre, including many instances of 'splitting' (or cohesive failure); usually as a result of excessive application and consequent solvent entrapment. Some fast drying polyurethane formulations have been especially prone to this problem.

As a result, many boatyards prefer to apply an additional two or three coats of polyurethane finish directly to the prepared gelcoat (instead of using an undercoat), thereby improving the overall strength and abrasion resistance of the scheme.

Conventional finishes can be applied over either epoxy or polyurethane undercoating systems, although adhesion is usually poor, (especially where epoxy primers have been used).

Also, if an epoxy or polyurethane priming and undercoating scheme has already been applied, (with associated cost and preparation requirements), there would seem to be little point in overcoating it with a lower performance finishing scheme, unless re-coatability is important.

Selectively Strippable Camouflage Finishes

One notable variation from these precepts is where selectively strippable camouflage finishes are required for defence applications.

In these applications, there is a need to be able to rapidly, and often repeatedly change camouflage colours to match the local environment; preferably without significant increases in weight or overall thickness of the coating scheme. Weight considerations are especially important for aviation coatings.

To fulfil this requirement, a selectively strippable coating scheme can be used; comprised of an epoxy primer and undercoat, with a 'lacquer drying' acrylic finish. The acrylic coating is resoluble in its own solvent, and so can be selectively removed with a solvent based stripper, without damaging the epoxy priming scheme beneath.

Underwater Coating Schemes

Polyester gelcoats and laminates have good water resistance, but they are, nonetheless, prone to damage caused by long term moisture absorption, which can ultimately result in severe blistering and disruption to the gelcoat layer. These defects are commonly known as 'Osmosis'.

Current polyester resin formulations such as isophthalics and vinyl esters have much better moisture absorption characteristics than earlier orthophthalic types; but it is nonetheless extremely desirable to protect marine composites from unnecessary moisture absorption.

Glassfibre hulls are known to transmit small, but significant quantities of moisture from the sea, which is dispersed into the bilges as water vapour. To be beneficial, the coating scheme must provide a better moisture barrier than the gelcoat which is being coated; and should preferably be less permeable than the laminate as a whole.

This will protect the laminate against potentially damaging moisture accumulations, and possible hydrolysation of the polyester lay-up resin.

In the early 1980's, two pack polyurethane coatings (such as Internationals Perfection 709) became very popular for protecting underwater laminates; partly owing to their good adhesion

to polyesters, but probably more because they were being heavily marketed at that time as 'universal' coatings for use both above and below the waterline.

If properly applied, polyurethanes provided quite adequate protection against moisture ingress, but the film thickness applied were in most instances inadequate, as were the specifications at the time.

Polyurethanes are also sensitive to moisture during cure, which can easily result in severe undercure in boatyard conditions, and will significantly increase moisture permeability.

Developments in two pack epoxies meant that they became the preferred choice form the late 1980's onwards, with solvent free types such as Blakes SFE200 and International Gelshield gaining particular popularity.

However, marketing and cosmetic appearance were equally important factors in this change, as there were many other coatings, such as epoxy tars, vinyl tars and also solvented epoxies, which offered better moisture barrier properties than solvent free epoxies and were easier to apply; but were never promoted. (Note: The use of coal tars in paint coatings has since been banned in many countries owing to carcinogenic risks).

The relative moisture permeabilities of various coating types can be seen in the graph (Fig 4) on page 11.

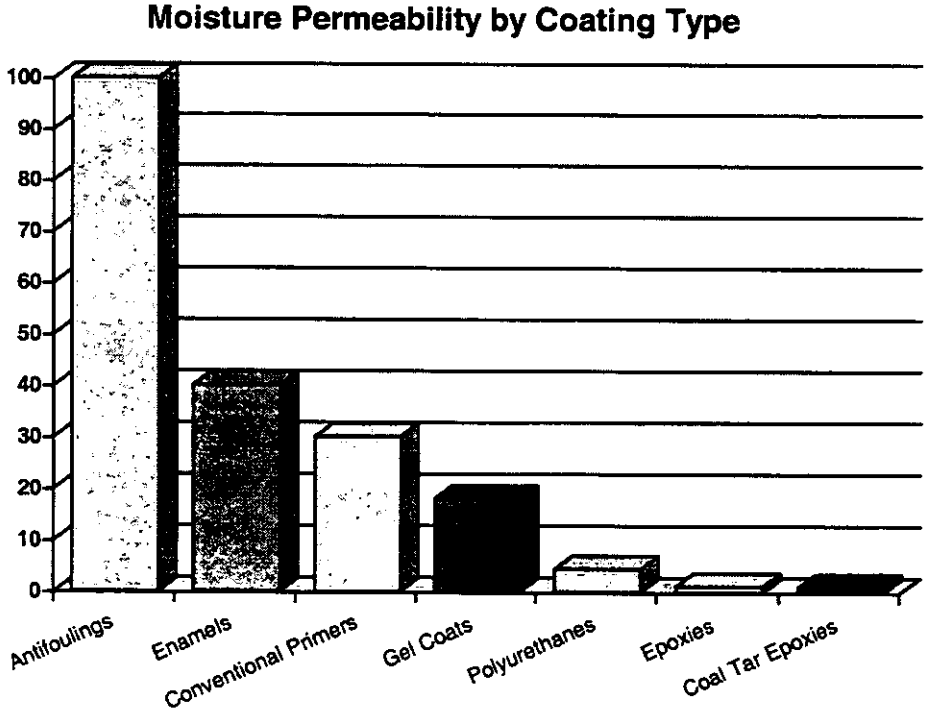


Fig 4. Graph showing Relative Moisture Permeability by Coating Type.

For most practical purposes, solvented epoxies offer (marginally) better moisture barrier properties than equivalent solvent free types; but they are much more tolerant to cold and damp application conditions, and are also more flexible in terms of maximum overcoating intervals. Their disadvantage is the risk of solvent entrapment resulting from premature overcoating and/or excessive application, and unpleasant solvent vapours when painting indoors.

These limitations are not usually problematic for DIY application, as these are typically carried out outdoors, with overcoating intervals extended from one weekend to the next; but professional applicators are normally under rather more pressure.

There is also a common misconception that only solvent free epoxies can be used for osmosis protection, probably as a result of marketing in the 1980's. In practice, either type of epoxy will provide satisfactory protection, but practical limitations such as workshop conditions must be borne in mind when deciding which material to use.

Whichever type of coating scheme is used, an absolute minimum dry film thickness (DFT) of 300 μM is recommended, with 500 μM being preferred. Also note that antifouling coatings provide no worthwhile protection against moisture ingress.

Coatings for Osmosis Treatment

If an osmosis prevention coating scheme is applied early enough, there should be no need to carry out an osmosis treatment; but sadly, osmosis prevention is not usually considered until it is far too late.

Osmosis in glassfibre is characterised by visible blisters or swellings in the gelcoat, which contain liquid when pierced.

The causes and cures of osmosis are discussed much more fully elsewhere, (see **Useful References** on page 19), but suffice to say it is caused by moisture ingress, which results in breakdown of the polyester laminating and gelcoat resins. These in turn liberate a series of (hygroscopic) breakdown products, which encourage further moisture absorption, and ultimately result in blistering of the gelcoat, and in a few severe cases, structural delamination.

Successful treatment requires complete removal of these hygroscopic substances, which is often difficult, as they have boiling points of around 200 °C, and are involatile at ambient temperatures.

Treatment therefore requires complete removal of the protective gelcoat, so that the breakdown products can be washed out with hot, fresh water, and the laminate dried; after which the gelcoat can be replaced with a suitable coating scheme.

In most early osmosis treatments (from the 1970's), prepared laminates were re-coated using solvented epoxies; although many of these failed owing to solvent being absorbed and trapped within the porous substrate.

To avoid this, the paint manufacturers developed a variety of solvent free coatings specifically for application directly to bare laminates.

These have mostly been very successful, but like many solvent free epoxies, they are prone to 'amine sweating' if applied in cold or damp conditions, and also tend to suffer from poor intercoat adhesion unless overcoating intervals are kept to an absolute minimum. It should also be stressed that only the first coat needs to be solvent free, as once this is applied, it effectively 'seals' the laminate, and prevents solvent absorption.

However, for marketing and commercial reasons, the paint manufacturers have always tended to specify solvent free coatings throughout, whereas solvented coatings are often more suitable (and practical) once the initial (solvent free) priming coat has been applied.

Whichever type of coating scheme is used, an absolute minimum dry film thickness (DFT) of 500 μM is recommended, with 600 μM + being preferred (not including fillers).

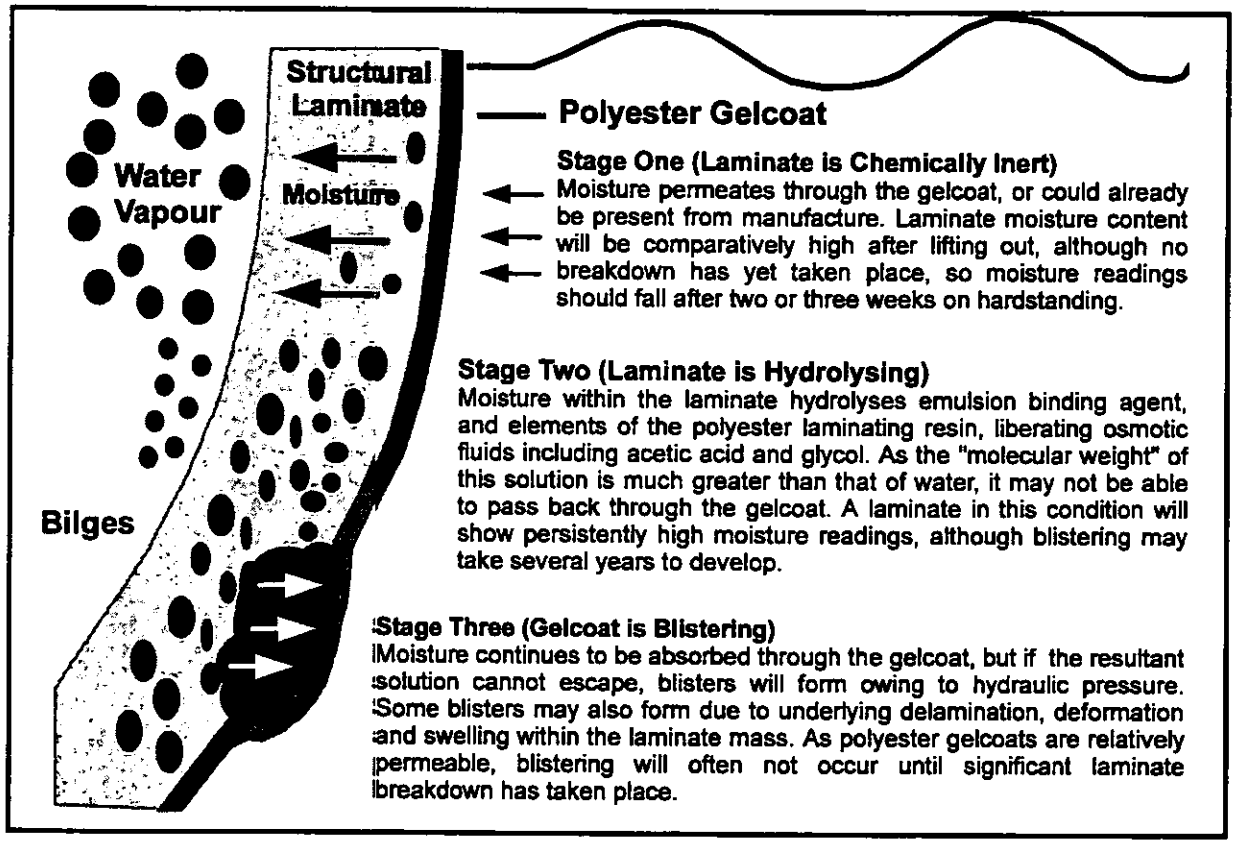


Fig 5 Diagram Showing the Osmotic Process in Fibreglass Hulls

Osmosis treatment schemes usually incorporate some kind of profiling filler to restore the original hull profile. Solvent free epoxy fillers are ideal for this application, but for protection, they should always be applied ***between*** coats of epoxy primer. However, polyester fillers should never be used underwater, as they are prone to rapid moisture absorption and swelling, and will quickly fail.

Painting Bilges

Contrary to popular belief, bilges in glassfibre boats are better not painted, as a highly impermeable coating such as a two pack epoxy or polyurethane would prevent incoming moisture from dispersing into the bilges, increasing the risks of osmosis (even where an osmosis prevention scheme has been applied externally).

If a cosmetic coating is required, it is best to use a comparatively permeable coating such as a conventional alkyd. If an epoxy or polyurethane is used, only one or two coats should be applied, and the total film thickness must be lower than that of the external protective coating scheme.

Antifoulings

When glassfibre boats were introduced in the early 1960's, it was widely believed that gelcoat finishes were so hard, and so shiny that no marine fouling organism would ever be able to colonise on them. However, these predictions overlooked the fact that marine fouling has been constantly evolving over millions of years, and has survived by clinging to a variety of surfaces in hostile and widely varying conditions around our coasts.

In practice, glassfibre is just as prone to fouling as any other boat-building material, although it does have the advantage of not being subject to corrosion, or the dreaded marine borers *Limnoria Lignorum* (Gribble) and *Teredo Navilis*; which attack timber.

As with other marine vessels, marine growth is most easily controlled by application of an antifouling paint, which repels fouling by releasing soluble biocides such as copper into the sea at a controlled rate.

To achieve this, antifouling paints are mostly comprised of biocidal material such as cuprous oxide and organic boosting biocides, loosely bound by a sparingly soluble resin system, which is designed to dissolve slowly throughout its life..

Antifoulings are also extremely permeable to moisture, and provide no protection against moisture ingress or osmosis in GRP, or corrosion in metals. Indeed, the formulation of modern antifoulings actually encourages sea water to diffuse through the antifouling system, as this provides more consistent biocide leaching rates.

However, the overriding requirements for good fouling control mean that antifouling coatings tend to be comparatively weak and friable materials, with poor abrasion resistance and adhesive qualities. This is even more critical towards the end of the antifoulings service life, when most of the biocide has been depleted.

As a result, antifouling systems are notoriously prone to failure owing to detachment and mechanical damage, and usually need to be removed altogether every six to eight years or so.

Priming Schemes for Antifoulings

Many of these problems can be avoided by using a suitable antifouling primer or 'tie coat', and by following the manufacturers recommended overcoating intervals.

Most current antifouling primers are based on chlorinated rubber (Blakes) or vinyl (International Paint) resin systems, which are softened slightly by the solvents in the antifouling system, hence improving intercoat adhesion.

These priming systems can be applied in widely varying conditions, and have wide 'overcoating windows'; but they are prone to 'mud cracking' if overcoated prematurely, or if the antifouling is applied too thickly. They also provide only limited protection for the substrate.

An alternative approach is to use an epoxy primer, pigmented with mica flake, as in the International Paint Interprotect and Gelshield 200 products. This encourages adhesion by producing a slightly rough surface, whilst also providing excellent moisture barrier properties; although the first coat of antifouling must be applied within a strictly specified 'overcoating window' if satisfactory adhesion is to be achieved.

However, once the first coat of antifouling has been applied to the primer, subsequent coats can usually be applied over a much longer period; although some antifoulings must be immersed in water within a certain period.

Potable Water and Sewage Holding Tanks

Many glassfibre vessel have integral drinking water and sewage holding tanks moulded into the hull structure.

A few vessels also have integral fuel tanks, although thankfully, safety concerns have meant that most builders now fit metal tanks.

Water and sewage tanks are even more prone to osmotic problems than the hull itself, as the water is predominantly fresh (rather than salt), and is usually warmer than seawater. Moisture condensing on the tank deck head also tends to be aggressive (often more so than the tank contents themselves), and can be problematic even when the tank has been drained.

Furthermore, the contents of sewage holding tanks tend to be quite strongly alkaline (owing to the presence of soap solutions and suchlike), whilst potable water tanks are customarily sterilised with sodium hyperchlorite (bleach) solutions, which are also strongly alkaline.

Polyester resins have good resistance to moderately strong acids (i.e. battery acid) and many other mild chemicals; but they have poor resistance to strong alkali, which tend to break ester linkages apart.

Where tanks are moulded integrally, there is the double problem of moisture absorption from both inside and outside of the hull, which further increases the risk of laminate breakdown and blistering.

Sadly, most glassfibre tanks are put into service unpainted, partly because of the cost of painting them, and also because of poor access. Ideally though, tanks should be coated internally with a suitable epoxy coating to protect both the laminate, and (in the case of potable water), the tanks contents.

Sewage tanks are best coated with an epoxy, such as those customarily used for osmosis treatment and protection. Solvent free coatings are especially useful in this situation owing to the lack of ventilation inside tanks, and the risk of 'pooling' and excessive film thickness in the tank bottom.

However, drinking water tanks must only be painted with epoxies specifically certified for use in 'potable water tanks'. Other epoxies will leach phenol and other noxious substances into the water, making it unpleasant or harmful to drink. Forced ventilation will also be required to ensure that the coating dries and cures properly, without entrapped solvent which could not only cause failure, but may also taint the water supply

Chemical Tanks

Where very strong or corrosive chemicals must be carried in composite tanks, specialist coatings should be used to protect both the tank and its contents.

Aggressive chemicals such as strong acids and alkali can be contained using glass flake epoxies, usually applied at dry film thicknesses of 750 μM or more. These also provide an excellent moisture barrier, but are very expensive.

Foodstuffs are usually contained with specialist solvent free epoxy or polyurethane coatings, which apart from protecting the tank, are easy to clean, and do not require good ventilation. Many of these are applied by heated airless spray for rapid drying and cure.

However, it is essential that the polyester resin is well cured before coating, as styrene monomer evolving from uncured polyesters tends to inhibit cure of epoxies. This is especially important where the polyester resin or gelcoat has been exposed to oxygen during cure, (i.e. where no mould was used), as this too inhibits cure.

Fire Retarding Coatings

Where there is a requirement for fire protection, laminates can be constructed using specially formulated fire retardant polyester resins, which may contain aluminium hydroxide, compounds of antimony and chloro-paraffins. These protect the laminate by releasing a mixture of non flammable gasses and steam to keep the flame front a few vital millimetres away from the exposed surface.

Limitations are that the protective gasses are toxic, and fire retardant laminates are very prone to osmosis (owing to the use of hygroscopic salts). Furthermore, a fire retardant laminate must be specified at newbuilding, whereas in practice, most fire retarding systems are only specified later in the vessels life; usually owing to a change in use, or changes in legislation.

Fire retarding coating systems come into two different categories; those which control the surface spread of flame, and 'intumescent' coatings, which expand when heated, so providing a protective thermal insulating layer.

Coatings which control the surface spread of flame are readily available, and are widely used in ships accommodation and engine rooms to prevent local burn damage (such as a dropped match or weld damage) from spreading elsewhere via the paint scheme.

However, the effectiveness of these coatings (and their certification) is substrate specific, so the data sheet must be checked before use. There are also limitations on minimum and maximum coating thickness, so thick accumulations of paint must be removed periodically.

Intumescent coating systems protect the substrate against fire, whilst also preserving structural integrity for a limited period until passengers can be evacuated safely, and if possible, the fire extinguished.

Limitations are that intumescent coatings require a very high temperature to intumesce, which is much higher than the glass transition temperature (TG) of the composite (which is usually less than 70 °C), and may even be higher than its self ignition temperature. Additionally, intumescent coatings rely on the substrate to dissipate much of the heat which passes through the intumesced material, whereas composites usually have very poor thermal conductivity.

Nevertheless, an increasing number of intumescent coatings and gelcoats are being developed for composites to meet the requirements of recent legislation.

Preparing Glassfibre for Painting

New gelcoat has a very hard, glossy appearance, and will usually be contaminated with some mould release wax from manufacture. This wax is used to prevent the gelcoat from sticking to the mould, and likewise it will reduce adhesion of paint coatings.

As with all surface preparation, the first step is to remove any oil, grease or wax with a good degreaser. However, note that acetone and strongly alkaline degreasers (i.e. caustic soda) must not be used on composites, as they will damage the resin system.

When degreasing has been completed, surfaces should thoroughly sanded with 'wet or dry' abrasive paper, used wet, to provide a good mechanical key. If protective coatings are to be applied, (i.e. underwater), surfaces should be sanded with 80 or 120 grit paper to ensure good adhesion. However, where finish coatings are to be applied (i.e. on topsides and superstructures), 180 or 220 grit paper should be used initially, followed by finer grades of up to 400 grit to prevent sanding marks from showing through.

In all cases, surfaces must be sanded with a firm, circular action until they are uniformly dull, with no glossy areas remaining; simply scratching the surface is of little benefit, and will not provide an adequate key for good coating adhesion.

Special fibreglass 'wash' primers are available, which react chemically with the gelcoat to avoid the need for sanding, but they are very sensitive to moisture, and can be unreliable, so it is generally better to stick to thorough mechanical preparation.

Any star crazing will need to be repaired at this stage, preferably by grinding out and then filling the affected area. Some painters prefer to deepen and widen each crack individually with a sharp tool, so that it forms a 'vee', but this is slow work, and is only practical when repairing localised damage. When doing this work, make sure that the crazed gelcoat is well attached to the laminate, and is not loose, as it could quickly spoil the new finish.

Pin holing can be even more difficult to overcome, and is often not visible until after the first coat of paint has been applied. Large pinholes are best filled individually with a fine filler, which should be pressed well into the holes with a filling knife, although the filler can sometimes pop out again if any air is trapped. Smaller pinholes are virtually impossible to pack with filler, but they can usually be filled by brush applying two or three coats of undercoat, working each coat well into the surface. Spray application is not recommended, as the changing air pressure usually makes the paint pop out of the holes shortly after painting.

Underwater preparation is rather more straightforward, although we should always be aware of physical defects which can allow ready moisture ingress. Antifoulings must first be removed by wet sanding, or with a proprietary antifouling remover. Do not remove antifoulings by dry sanding or by burning as they contain toxic materials.

In practice it will often be found difficult to remove the colour staining from antifoulings, but this does not pose a problem as long as the antifoulings themselves have been completely removed. Any antifouling remaining in deep scratch marks can be removed with an antifouling remover, or with cloths soaked in a strong solvent (such as a polyurethane thinner).

Checking Moisture Content

Finally, composite materials should always be checked for moisture content with an electronic moisture meter before painting.

Persistently high moisture readings in a glassfibre structure may indicate an 'osmotic' condition as discussed previously. Osmotic laminates can be coated, but there is a risk that the new coating scheme will blister owing the osmotic activity, which is clearly undesirable.

Where this condition is identified in topsides and superstructures, it is usually best to specify a comparatively permeable coating, such as an alkyd or silicone alkyd, as these will be much less prone to blister. Alternatively, a 'thick' priming scheme can be used, (i.e. several coats of epoxy or polyurethane primer/undercoat) to minimise moisture absorption through the coating scheme, and to increase overall mechanical strength.

For underwater areas, it will be necessary to take a decision on whether to leave the hull uncoated, (save for an antifouling primer and antifouling), or whether to carry out a full osmosis treatment.

Given the high costs of osmosis treatment, and the usually long timescale before blistering becomes visible, it is often most practical to leave the hull untreated until such time as it shows clearly visible symptoms of osmosis, rather than just high moisture meter readings.

Useful References

Title	Author	Publisher	ISBN Ref
How to Paint Your Boat	Nigel Clegg	Adlard Coles Nautical	ISBN 0-7136-4097-9
Metal Corrosion in Boats	Nigel Warren	Adlard Coles Nautical	ISBN 0-7136-4869-4
Osmosis and The Care and Repair of Glassfibre Yachts	Staton-Bevan	Adlard Coles Nautical	ISBN 0-7136-3513-4
Blakes Osmosis Manual	Nigel Clegg	Blakes Paints Southampton	N/A
The Osmosis Manual	Nigel Clegg	Nigel Clegg	N/A

Glossary of Painting Terms

Nigel Clegg

Glossary of Painting Terms

There are a number of specialist technical terms used in relation to paints and painting, many of which are not encountered outside of the industry. Some terms may be interpreted in different ways, and many will not conform strictly to dictionary definitions.
Where appropriate, chemical terms are also included, as these will often help the reader to a better understanding of the products that they are using.
The following is a glossary of over 300 of the terms used in this book, and in the coatings industry generally:-

Abbreviations

µ or µM
Abbreviations commonly used to denote microns when measuring or specifying paint film thickness. There are one thousand microns in a millimetre, and one million microns in a metre. To convert microns into thousandths of an inch (Mil), divide the figure by 25.4.

BSB4 (Viscosity Cup)
Abbreviation for British Standard Viscosity Cup, type B4. Viscosity is expressed as the number of seconds taken for the sample to flow through the orifice in the bottom of the cup, hence it is sometimes be referred to as a **Flow Cup**.

DFT
Abbreviation for **Dry Film Thickness**, usually expressed in **Microns** or **µM**.

F.P.
Abbreviation for **Flash Point**.

HVLP Spray
Abbreviation for High Volume Low Pressure. HVLP sprayguns are a modern development of Conventional spray, and as their name implies, utilise large volumes of low pressure compressed air to **Atomise** the liquid paint. The **Transfer Efficiency** of **HVLP** sprayguns is much higher than that of conventional guns, which are gradually being phased out.

LEL
Abbreviation for **Lower Explosive Limit.**

Mil
Abbreviation for one thousandth of an inch, or "one **Thou**" (engineering term). The use of this imperial measurement has now generally been superseded by the metric Micron in the coatings industry. To convert Mils to Microns, multiply the figure by 25.4

OEL
Abbreviation for **Occupational Exposure Limit**, sometimes referred to as the **Occupational Exposure Standard** or **OES**.

PPA Code
A Personal Protection Advice system, used by some manufacturers to indicate the safety precautions recommended when using a particular product, (e.g. PPA 2/3).

RH
Abbreviation for **Relative Humidity**

RAQ
Abbreviation for **Required Air Quantity**, a measure of the amount of ventilation required to maintain a safe working atmosphere when painting. The RAQ is usually expressed as the volume of fresh air required for each litre of paint applied.

S.G.
Abbreviation for Specific Gravity, usually expressed in grams per cubic centimetre, or kilograms per litre measured at 20 °C. Pure water has an S.G. of 1.0 (See also **Relative Density).**

TWA
Abbreviation for **Time Weighted Average**, frequently used to define **Occupational Exposure Limits**.

VOC and VOC Compliancy
VOC is an abbreviation for a **Volatile Organic Compound,** such as a paint solvent. Emission of VOC's into the atmosphere is a matter of considerable environmental concern, and is driving the trend towards "Low VOC" and water borne coatings, as well as more efficient application methods such as **HVLP** spray. Many coatings are now formulated to meet internationally agreed limits on volatile organic content, and are said to be "VOC Compliant".

WFT
Abbreviation for **Wet Film Thickness,** usually expressed in **Microns** or **µM**.

Alphabetical Listing

A

Abrasion
Damage or wear due to contact with moving abrasive surfaces (such as fenders). Also see **Mechanical Damage.**

Abrasion
Deliberate scoring or roughening of a surface (i.e. sanding), to promote good mechanical adhesion of applied paint coatings.

Absorption
Process whereby one substance is soaked up by a another. Examples are the absorption of paint by porous surfaces, and the absorption of moisture by hygroscopic substances (as in osmotic laminates).

Accelerator
An Accelerator is sometimes used to speed the rate of cure of an applied paint film (usually a polyurethane). Accelerators need to be used with caution, as coatings cured too quickly will not release solvent adequately, and may suffer from **Solvent Entrapment.** The term accelerator is often used incorrectly to describe a curing agent.

Acetic Acid
An organic acid, most commonly found in vinegar. It is also found in some osmotic laminates, and will be evident by it's characteristic vinegary odour. Acetic acid is a key component in acetates (such as butyl acetate), and in many silicone rubber sealants.

Acetone
A Ketone solvent used in nail polish remover and sometimes as an equipment cleaner, which is very aggressive to paint coatings and polyester gelcoats. Acetone is very volatile, and highly inflammable.

Acid
A chemical compound which gives off ions in solution. Common acids include battery (sulphuric) acid, and rust removers (normally based on Phosphoric and Hydrochloric Acids).

Acid Number
A number quoted to indicate the quantity of free acid present in an **Oil** or **Resin**.

Activator
Synonymous with **Curing Agent.**

Adduct
A curing agent which has been partly cross linked with a base resin. This technique is often used with epoxies to improve film build properties, and to render the curing agent less irritant to the user.

Adhesion
Bonding strength of a coating to it's substrate, or to the previous coat of paint.

Air Assisted Airless Spray
See **Airmix Spray**

Air Cap
The part of a conventional spraygun which directs jets of compressed air at a stream of paint to achieve **Atomisation**, and to control fan width.

Air Drying Resins
Binders which dry and harden by solvent evaporation, by reaction with atmospheric oxygen, or by a combination of both. These resins are typically used in the manufacture of **Conventional** enamels and varnishes.

Air Entrapment
Inclusion of air bubbles into a paint film, usually caused by poor application technique.

Airless Spray
Application method where the paint is forced through a Fluid Tip under great hydraulic pressure to achieve **Atomisation.** Airless Spray is a very rapid method of paint application, but the quality of finish achieved is generally poor. Airless is ideally suited for painting commercial vessels, and for application of antifoulings and high build anticorrosives.

Airmix Spray
Airmix is a hybrid of conventional and airless spray systems, where the paint is atomised by hydraulic pressure (as in Airless Spray), but is also assisted by a small volume of compressed air in a similar manner to conventional spray. Airmix is a Trade Mark of Kremlin SA, the French Company that developed this system in the 1970's. Many other manufacturers now supply similar equipment, generally titled as **Air Assisted Airless Spray**.

Alcohols
A range of compounds containing the **Hydroxyl (OH) Group**, i.e. Methanol, Ethanol, etc. Alcohols are often used as solvents in paints, and most are highly flammable.

Aliphatic
Organic compounds in which the carbon atoms are arranged in open-ended chains. Examples include White Spirit and some paint resins.

Alkalis
Compounds which are soluble **Hydroxides** of a metal, i.e. Sodium Hydroxide (Caustic Soda)

Alkyd Resins
Synthetic Polyesters formed from polycarboxylic acid or it's anhydride (phthalic anhydride), a polyhydric alcohol (i.e. glycerol or pantaerythritol), and a vegetable oil. Alkyd resins are widely used in the manufacture of conventional type varnishes and enamels, and cure by reaction with atmospheric oxygen. The term alkyd is derived from the words Alcohol and Acid.

Alloy
A mixture of different base metals, blended to optimise characteristics for a particular end use. Examples include Brass, Stainless Steel and Solder.

Aluminium
A metallic element which in flake form may be incorporated into primers as a barrier pigment, thereby reducing permeability to moisture and oxygen. Aluminium is a highly reactive metal, and will rapidly corrode in a marine environment. It is widely used for boat building and in the manufacture outboard motors etc., but needs to be very well protected.

Aluminium Spraying
Similar to Zinc Spraying, molten aluminium is sprayed onto prepared steel using a special heated spraygun. Aluminium sprayed surfaces are difficult to paint satisfactorily, and severely limit the choice of antifouling.

Substrate Temperature
The temperature of a surface being painted, rather than the **Ambient** temperature. Substrate temperature has a significant effect on application characteristics and curing of paint films. The temperature of lead and cast iron keels can take many days to equalise to ambient temperature.

Ambient (Conditions)
Temperature and Relative Humidity of the air in a workshop, sprayshop, or otherwise surrounding the surface being painted.

Amides
Organic compounds formed by replacing hydrogen atoms in ammonia with organic acid radicals. Used widely in the manufacture of epoxy resins, i.e. Polyamides.

Amine
Amines are **Organic** derivatives of Ammonia, containing atoms of Carbon, Nitrogen and Hydrogen, and are the backbone of **Epoxy** curing agents. They are hygroscopic, and are strongly alkaline in aqueous solution.

Amine Adduct
Amine based epoxy curing agent which has been partially reacted with a base resin to improve application properties, and/or to render it less irritant to the user.

Amine Sweating
A condition where a thin, sticky film of amine carbomate forms on the surface of an epoxy coating or filler, generally caused by inadequate curing temperatures and/or high humidity. Amine Sweat must be removed by washing with fresh water before overcoating.

Anchor Pattern
Term for Surface Profile, used to define the roughness of a surface, and the standard of surface preparation for painting.

Anode
Positive electrode, as in a battery or a Corrosion Cell. Also used by convention to describe the sacrificial electrodes used to prevent corrosion, although these are electrochemicaly negative. Sacrificial Anodes are usually manufactured from Zinc or Magnesium alloy, and are fitted to prevent or reduce **Corrosion** of unprotected metal, (i.e. propellers), and underwater areas where the coating scheme has been damaged.
See also **Electrolysis**.

Anticorrosive Pigments
Used in paints to enhance protection of metal substrates from corrosion. Examples include aluminium and zinc pigments, which provide local **Sacrificial Protection** to substrates when the coating scheme suffers **Mechanical Damage**. Inert pigments such as mica flake can also be used to minimise the moisture and oxygen permeability of paint films.

Antifouling
Paint coating containing a water soluble biocide, and applied to the underwater area of marine vessels. These coatings are formulated to discourage the collection of water-borne plant and animal growth.

Aromatic (Solvents)
Organic compounds where the carbon atoms are arranged in a closed, six sided ring, (known as the Benzene Ring). Examples include Xylene, Toluene and Benzene itself.

Atomisation
Conversion of a coherent liquid (such as paint), into tiny droplets of the same, as in spray application. A well atomised paint droplet has a typical diameter of 15 ~ 25 μM when using a Conventional Spraygun.

Auto - Ignition Temperature
The temperature at which a substance will catch fire without the application of an external source of ignition. Also known as the Spontaneous Ignition Temperature.

B

Bar
A unit of pressure, relative to normal atmospheric pressure. This unit is widely used when measuring hydraulic and compressed air pressures, and is equivalent to 1 kilogram/M² or 14.2 Pounds per Square Inch.

Barrier Coat
Barrier Coats are used to allow application of a paints which are incompatible with existing coating schemes. This is normally achieved by incorporating flake type pigments to minimise solvent absorption by the underlying coatings. Barrier coats are often specified when applying antifoulings over a scheme of unknown history. They may also be used to retard discoloration caused by tar containing primers.

Barrier Pigments
These are incorporated into anticorrosive paints to minimise moisture and oxygen permeability. They are also used in Barrier Coats (above) to minimise permeability to solvents, coal tar, etc.

Base (Component)
One part of a two component product, to which the curing agent is added shortly before application. Any Pigments and Extenders are usually dispersed into the base component because it is more stable, and is safer to handle.

Binder
The **Resin, Vehicle** or **Polymer** used to bind pigments and extenders into a cohesive paint film. The function of the binder is to change from a liquid to solid phase after application of the paint coating. The binder usually lends it's name to the coating as a generic type, i.e. **Epoxy, Polyurethane, Alkyd**, etc.

Biocide
Active ingredient used in **Antifoulings** to discourage marine growth..

Bitumen
A tar like mixture of **Hydrocarbons**

Blast Cleaning
Surface preparation method using abrasive grit propelled by compressed air. Note that the use of sand as an abrasive when open blasting is considered dangerous due to liberation of free silica, and is indeed illegal in many countries.

Blebs
Soft, unbroken **Blisters,** caused by entrapment of air or solvent vapour within a coating scheme.

Bleeding
Discoloration of coatings caused by migration of soluble pigments or binders from underlying coats into finish coats. Primers containing Coal Tar, and red antifoulings are particularly prone to bleeding.

Blistering
Localised swelling in a paint film caused by gas or fluid pressure within the coating scheme, or within the underlying substrate.

Blooming
Defect in which a cloudy or milky film appears on a newly painted surface. Blooming is usually caused by surface moisture, particularly in cold or damp conditions. Blooming may also occur due to excessive use of thinners when spraying.

Blushing
Whitening and loss of gloss in a newly applied finish due to surface moisture. Blushing is usually a more severe version of **Blooming** above.

Body
The apparent viscosity of a paint or varnish.

Bonding (Electrical)
Connection of heavy cables between (for example) sacrificial anodes and stern gear, to minimise any difference in electrical potential. Effective bonding is essential to prevent corrosion.

Bounce Back
Effect where paint droplets are prevented from being deposited on a surface due to excessive atomising air pressure.

Boxing
Method of mixing two liquids by pouring them repeatedly between two containers. This method is only suitable for mixing low viscosity materials.

Bridging
Defect where a paint film is applied over surface depression or crack, and subsequently dries to form a skin.

Bright Work
Varnished wooden surfaces on a boats exterior.

Brittleness
Tendency of a paint to crack when stretched or bent, usually due to ageing, but sometimes due to the nature of formulation (as in polyester gelcoats).

Brush Marks
Imperfections in a paint film due to use of a paint with poor flow properties, or poor technique. Adverse application conditions will also promote brush marks.

Brush Wash
See **Equipment Cleaner** and **Reclaimed Solvent.**

Brushability
Ease of brushing out, or ease of brush application. A good brush paint should be easy to apply, and will "flow out" to provide a smooth finish without any brush marks.

Bubbling
The appearance of bubbles in a newly applied finish, generally due to poor application technique. A similar defect can occur in two pack polyurethanes contaminated with water, due to release of carbon dioxide gas.

Build
A measure of paint thickness on a substrate. The term "High Build" is often used for coatings applied with a **Wet Film Thickness** of over 100 μM per coat.

Bulkhead
A solid partition between compartments of a vessel. Bulkheads are usually an essential part of a vessels design, providing strength, and sometimes designed to contain water in the event of collision damage.

Burnishing
Polishing of a paint or varnish to improve surface smoothness. Burnishing is sometimes used to repair localised damage to paint films.

Butanol or **Butyl Alcohol**
An organic alcohol used as a solvent for epoxies in conjunction with an aromatic solvent, such as **Xylene**. Butanol is also used in the manufacture of **Butyl Acetate** below.

Butyl Acetate
A solvent used in polyurethanes in conjunction with aromatic solvents such as **Xylene** and **Toluene**. Butyl Acetate is an **Ester** of Butanol and Acetic Acid, and has the distinctive odour of "pear drops".

C

Carvel
A form of construction where wooden planks are laid side by side, and only fastened to the frames and inner structure.

Catalyst
A substance used to speed up a chemical reaction, but which (strictly speaking) is not actually consumed. The term catalyst is often used incorrectly to describe a **Curing Agent** or **Activator.**

Cathode
Negative electrode, as in a battery or a corrosion cell.

Cathodic Protection
A method of protecting metals from corrosion in a marine environment, where an expendable Cathode (usually a zinc alloy) is used to create a more powerful cell than the natural corrosion cell. See also **Electrolysis**

Caulk
A flexible material inserted between the wooden planks in yachts of Carvel Construction to prevent the ingress of moisture.

Chalking
Severe surface breakdown of a paint film caused by Ultra Violet light, and resulting in a powdery deposit. Epoxies are particularly prone to this type of breakdown and will chalk within a few months of exposure to the elements.

Chipping (Mechanical Damage)
Paint scheme failure where fragments of the film detach due to mechanical impact.

Chipping (Method of Preparation)
Method of preparing steel for painting by using special hammers. The preparation standard achieved is poor, and is only suitable for on board maintenance of commercial vessels.

Chromates
Salts of chromic acid sometimes used as pigments in etch primers and anticorrosive coatings. The use of Chromates is declining due to the carcinogenic risks associated with these compounds.

Cissing
A paint defect caused by poor surface wetting, generally caused by silicone contamination. Ciss marks are often referred to as "fish eyes" due to their characteristic circular pattern.

Clinker
A form of construction where each plank overlays the plank below it, and is riveted or otherwise directly fastened directly to it.

Coal Tar Epoxy
Paint coating in which Coal Tar and Epoxy Resin are combined to form the Binder. Coal Tar Epoxies have excellent moisture barrier and anticorrosive properties, however, their use is now declining due to the carcinogenic risk associated with Coal Tar products.

Cobbwebbing
Premature drying of paint during spray application, resulting in a characteristic "spiders web" type effect. Cobbwebbing usually occurs due to the use of solvents which are too fast evaporating for the application conditions.

Cofferdam
Watertight enclosures or compartments built into larger yachts and ships to provide buoyancy in the event of collision damage. Access to Cofferdams is often very poor, causing great difficulty when painting.

Cohesive Strength
A measure of the internal strength of a paint film, as opposed to it's adhesive strength. Paint films with low cohesive strength (such as those which are undercured or solvent entrapped) are particularly prone to failure by **Splitting**.

Cold Moulded
A construction method where several veneers are moulded to the desired shape by fastening each veneer in place until a cold setting glue has cured.

Colour Fast
Resistance to loss of colour or fading on exposure to Ultra Violet light.

Compound
A substance which is the reaction product of two or more chemical elements.

Conventional (Coatings)
Conventional coatings rely on reaction with atmospheric oxygen to form hard films. This description would exclude coatings such as two component epoxies and polyurethanes, as their curing mechanism is entirely self contained within the base and curing agent materials.

Conventional Spray
Application system where the liquid paint is **Atomised** by jets of compressed air. Conventional Spray is by far the most popular method of spray application, but is gradually being phased out in favour of **HVLP** systems due to it's poor **Transfer Efficiency.**

Non Convertible Resin
A binder which dries solely by solvent evaporation, and does not undergo any permanent chemical change. Non Convertible Resins are resoluble in their own solvents, and most have poor resistance to fuels and oils.

Convertible Resins
Binders which change chemically on drying, and are not re-soluble in their original solvent. This description would include enamels and varnishes, but excludes most antifoulings.

Copolymer
A type of **Antifouling** where the primary **Biocide** (usually an organo tin) forms part of the binder.

Corrosion
Degradation of a metal substrate by electrochemical action, ultimately resulting in loss of mechanical strength.

Coverage
Measure of the area covered by a given volume of paint at it's recommended film thickness. To calculate coverage, divide the volume of paint (in millilitres) by the Wet Film Thickness applied (in Microns). The answer will be given in M^3/litre. Conversely, multiply the area to be painted by the specified Wet Film Thickness to calculate the quantity of paint required (in millilitres).

Cracking
See **Brittleness**

Cratering
Formation of holes or deep depressions in paint films. This term is sometimes used to describe **Cissing** or **Fish Eyes**.

Cross Hatching
Spraying in an overlapping fashion, firstly horizontally and then vertically, or vice versa.

Cross Link Density (or XLD)
Cross Link Density is a measure of the degree of cure achieved within a paint film. Most high performance coatings are formulated to achieve 85 ~ 90% Cross Linking. Coatings with XLD's below about 70% are generally regarded as **Undercured**, and will often remain soft with a poor gloss.

Cross Linking
Effect where molecules in a polymer link together due to chemical reaction to give a rigid, three dimensional structure. This effect is also known as **Curing**. The degree of cure is referred to as the **Cross Link Density** (sometimes abbreviated to XLD).

Cure
Cross Linking or **Polymerisation** within a resin system.

Curing Agent
One part of a two component product, which reacts with the Base to achieve **Cure, Cross Linking**, or **Polymerisation.**

Curtaining
See **Sags**.

Curvetta Line
Style line often used on yachts, just below the Gunwale.

D

Degreaser
A material used to remove surface dirt and contamination from a surface prior to painting. Water soluble detergents are generally the most effective degreasers for preparing yachts for painting.

Delamination
Separation of layers in a **Laminate**, resulting in loss of mechanical strength, particularly in **GRP** structures and in Plywood.

Dermatitis
Chronic inflammation and irritation of the skin, usually caused by repeated contact with a skin **Sensitiser** or an irritating material. Exposure to Epoxy Resins and used engine oil are common causes of Dermatitis, but it can also be caused by repeated contact with paper and wood shavings. The use of solvents and harsh detergents for hand cleaning significantly increases the risk of Dermatitis.

Dew Point
Surface temperature below which atmospheric moisture will condense, making painting impossible. The actual Dew Point is determined by Relative Humidity. To avoid the risk of condensation, the substrate temperature must always be at least 4 °C above the Dew Point temperature.

Diffusion Type (Antifoulings)
A type of Antifouling in which the Biocide is physically added to the Binder, and slowly diffuses through the coating once it is immersed in water.

Dispersion
Process of grinding Pigments and Extenders to reduce their particle size, and to separate the particles from one another. This process also ensures that the surface of the **Pigment** particles is thoroughly "wetted" with **Resin**.

Grind Size
The particle size diameter of dispersed pigments or extenders, measured in **µM** using a Grind Gauge

Relative Humidity (RH)
Measure of the volume of moisture present in the atmosphere, relative to temperature. Warm air will take up relatively high volumes of moisture, whereas cold air will absorb very little. When the air becomes saturated with moisture, (i.e. 100% RH) mist or fog occurs, and moisture condenses on any surfaces at or below ambient temperature.

Driers
Paint additives which speed up the rate of reaction with atmospheric moisture in **Conventional** paints and varnishes. Traditionally, tiny quantities of Lead Napthenate were used for this purpose, but this has now been replaced by Zinc, Cobalt and Zirconium compounds.

Dry Film Thickness (DFT)
Thickness of a paint film after curing when all solvent has evaporated. Dry Film Thickness is generally measured in µM or Microns, but may also be expressed in Mil or Thou. See also **Wet Film Thickness.**

Dry Film Thickness Gauge
An electronic or magnetic gauge used to determine the thickness of a dry paint film or scheme. Determination of DFT's on timber or plastic substrates is not possible without removing a sample for measurement with a micrometer, or inspection under a microscope.

Dry Spray
Dull, grainy finish caused by spray mist settling on a partially dry paint coating. Dry Spray is commonly caused by excessive Atomising Air Pressure, but may also be due to the use of unsuitable thinners, high ambient temperatures, or poor application technique.

Dulling
Loss of **Gloss** or **Sheen**

E

Efflorescence
Liberation and migration of soluble alkaline salts from cement or concrete, due to the presence of moisture. This effect is similar to osmosis in GRP, and causes blistering of paint coatings. Any blister fluid will be strongly alkaline, and can burn sensitive skin.

Electrochemical Reaction
An electric current caused by dissimilar metals sharing a common electrolyte, usually resulting in **Corrosion**.

Electrochemical Series
Relative voltages of different metals if suspended in a common electrolyte. Any two of these metals would form a corrosive **Cell** if connected together.

Electrolysis
Corrosion due to electric current flowing through dissimilar metals immersed in a common electrolyte. The metals in the electrolyte are termed electrodes, and are called the **Anode** (positive), and the **Cathode** (negative). See also **Galvanic Corrosion**.

Emulsions
These are paints made from Synthetic Resins suspended in water as extremely small droplets, which fuse together on drying to form a **Film**

Epoxy Adduct
See **Amine Adduct.**

Epoxy Ester
Epoxy esters are effectively single component epoxies, and dry by reaction with atmospheric oxygen. Whilst these coatings generally form tough films, their properties are nearer to those of conventional coatings than epoxies.

Epoxy Resins
These are tough, chemical and water resistant resins formed by Polymerisation of epichlorohydrin and bis phenol. These Resins remain in a liquid state until they are Cross Linked with a Curing Agent. Epoxies have very poor resistance to Ultra Violet Light, and will discolour and chalk on outdoor exposure.

Equipment Cleaner
A blend of solvents formulated specifically for equipment cleaning, rather than for application. Many equipment cleaners contain reclaimed or poor quality solvents, and should not be used for thinning.

Esters
Organic compounds obtained reacting an alcohol with an Organic Acid, as in **Butyl Acetate,** and in Poly***ester*** resins.

Extenders
Powders (other than colouring pigments) used in paints to achieve film build, strength, opacity, and ease of sanding. These ingredients are sometimes referred to as **Fillers**.

F

Fading
A loss of colour density in a paint film, usually due to the use of Pigments which are not **Colourfast**.

False Body
See **Thixotropy.**

Fan Width
The width of the **Fan Pattern** achieved when a spraygun is held at a specified distance (usually 30 cm) from a surface. The Fan Width may be altered by the choice of Aircap, and by adjustment of the Fan Width control (Conventional Sprayguns). The Fan Width of Airless spray is selected by changing the **Fluid Tip**

Fillers
Materials used to fill irregularities in a surface, to achieve a good surface profile. Most fillers used in yacht painting are based on Epoxy resins, as other types generally absorb too much moisture for satisfactory use in a marine environment.

Film
Any single coat or layer of paint applied to a surface, rather than multiple coats or a **Paint Scheme**.

Paint Scheme
Define

Film Integrity
The continuity or soundness of a paint film.

Film Thickness
Usually refers to **Dry Film Thickness**

Fingering
A broken or uneven spray pattern, commonly caused by a blocked **Air Cap** (Conventional spray) or a dirty **Fluid Tip** (Airless spray).

Fire Retarding Paint
Generally means a paint which retards the "Surface Spread of Flame", but provides limited protection for the substrate. These coatings are often specified in areas with a high fire risk such as galleys and engine rooms.
See also **Intumescent** Paints.

Fish Eyes
A paint defect caused by poor surface wetting, often associated with silicone contamination. Ciss marks are sometimes referred to as "fish eyes" due to their characteristic circular pattern.

Flaking
Disintegration of a dry paint film into small pieces, generally due to ageing or other film breakdown.

Flammability
Measure of the ease of catching fire.

Flash Point
The temperature at which a Flammable liquid will produce sufficient vapour to allow ignition by a small external flame or spark.
See also **Auto Ignition Temperature**

Floating (Floatation)
Separation of pigment, dyestuffs or other paint components to the surface of a paint film, often giving a "milky" appearance

Flooding
See **Floating**.

Flow Cup
A special cup used for measuring the viscosity of paint and other fluids.

Fluid Tip
Orifice in a **Spray Gun** through which the paint emerges. The size of the orifice controls the rate of paint delivery (and application).

Foaming
An effect where many small bubbles are formed whilst a **Paint** or **Varnish** is being mixed or applied, usually due to poor technique or chemical reaction.

Fogging
Misty, cloudy or "milky" appearance.

Freeboard
The height of a vessel's side above the waterline.

Fungicide
See Biocide. A Biocide directed specifically against fungal infestation.

Fungus
A simple life form which causes infestation of various substances, especially wood, where Wet Rot and Dry Rot can cause destruction.

G

Galvanic Corrosion
An Electrochemical effect caused when dissimilar metals (which act as a Cathode and Anode) are in contact with a common Electrolyte. Electrolysis occurs which causes breakdown of one of the metals resulting in loss of mechanical strength. e.g. Dezincification of brasses.

Galvanising
A process by where steel is coated with zinc to form a rust proof barrier. Galvanised surfaces are difficult to paint, and severely limit the choice of antifouling.

Gelcoat
Protective outer resin layer on Glass Reinforced Polyester Laminates. Gelcoats are usually coloured, but some builders use unpigmented gelcoat for underwater areas.

Glass Fibre
See Glass Reinforced Polyester.

Glass Reinforced Polyester or GRP

A structural material formed by impregnation of glass fibres with a polyester resin. A considerable volume of the GRP is glass.

Gloss
A measure of how reflective a dry paint film is.

Gloss Retention
The ability of a Gloss finish to maintain its reflective nature with time and outdoor exposure.

Glycols
These are syrupy, high molecular weight **alcohols**, each molecule having two **Hydroxyl (OH) Groups**. Glycols are hygroscopic, do not evaporate, and usually have boiling points of around 200 °C. They are used in the manufacture of Anti Freeze, hydraulic brake fluids and polyester boatbuilding resins, and are often found (as breakdown products) in osmotic laminates. Being highly polar, Glycols are water soluble, and conduct electricity.

Grit
Abrasive used in preparation of a Substrate for painting. Grit sizes are scaled with low numbers (course) and high numbers (fine). Blasting grit should be selected according to the Profile required and the nature of the surface to be blasted.

Grit Blasting
See Blast Cleaning.

H

Knots
Hard, often highly resinous inclusion in timber. Must be sealed by the application of knotting before painting with Conventional coatings.

Hardener
See Curing Agent.

Hardness
The degree to which a surface will withstand mechanical pressure without deformation or damage.

Hiding Power
See Opacity.

High Build Coatings
A term used to describe paint coatings which have relatively high **Wet Film Thicknesses**, (usually in excess of 100μ).

Holding Primer
A thin primer applied directly to freshly prepared metal surfaces, and used to "Hold Back" corrosion until a full coating scheme can be applied. Holding primers are usually formulated to allow overcoating intervals of three months or more, and provide good protection during newbuilding or refitting. It is important that holding primers are not applied too thickly, or more than a single coat applied, as this may result in failure due to **Splitting.**

Holiday
See Pin Holes.

Horn Holes
Jets in projections on a conventional spraygun Aircap, through which compressed air flows to aid **Atomisation,** and to control **Fan Width**. If these holes become blocked, the spray pattern will be seriously distorted.

Horning
Irregular spray pattern, usually in airless spraying. Sometimes referred to as Tram Lines.

Hot Moulding
A method of moulding wood Veneers using heat and pressure to hold the laminates while the glue sets.

Hydrocarbons
A range of Organic Compounds which contain only the Elements carbon and hydrogen.

Hydroxides
A chemical group usually encountered in the form of metal hydroxides such as sodium hydroxide, (Caustic Soda).

Hydroxyl Group (OH Group)
An ionic group consisting of a hydrogen coupled with an oxygen atom.

Hygroscopic
Compounds which attract and absorb moisture from any available source. Examples include Epoxy and Polyurethane Curing Agents, which must be kept in sealed containers. Some osmotic breakdown products are also hygroscopic, and must be completely removed before the laminate can be dried satisfactorily.

I - J

Impact Resistance
Ability of a film to withstand hard knocks.

Incompatible (or Incompatibility)
Used to describe a situation where two products are not suitable for direct contact or mixing.

Inert Pigments
A pigment which does not change its composition under the conditions under which the paint would normally be used.

Infra Red (Light)
Electromagnetic energy having a wavelength of between 0.7 to 500 μM. Light of these wavelengths provides radiant heat, and is invisible to the human eye.

Inhibitive Pigments
See Anticorrosive Pigments.

Insoluble
Term used to describe a substance which will not dissolve in a specific Solvent. The same substance may well be soluble in other solvents (including water).

Intercoat Adhesion
A measure of the degree of force required to detach one coat of paint from another. Usually determined by an Adhesion Test

Adhesion Test
Method of testing the integrity of a paint scheme. The usual test involves cutting the scheme in a prescribed pattern with a sharp instrument, and then attempting to remove it with an adhesive tape.

Intumescent (Paint)
Fire retarding paints which expand rapidly on exposure to heat, to such a degree that they protect the **Substrate** by insulation, and do not themselves burn.

Ions
Atoms are normally electrically neutral. If an atom gains an overall positive charge it is called a positive ion. If an atom gains a negative charge it is called a negative ion.

Iron
A metallic Chemical Element (Fe) obtained from natural ores. Generally used in the form of its Alloy, Steel. Some oxides of iron are also used as pigments.

Isocyanates
See Polyurethanes.

Isopropanol
An Organic Alcohol. Used as a solvent for rapid drying primers. Also used as a de icing solvent for car windscreens etc. Has a very distinctive odour, and is highly flammable.

K

Ketones
Organic Compounds such as Acetone (nail varnish remover). Ketone solvents are commonly used in paint manufacture. Most Ketones are very aggressive solvents, and are highly flammable.

Key
Mechanical bond between any **Substrate** and a paint film

Laminate
A structural material consisting of layers bonded together to achieve an optimum strength to weight ratio.

Laying Off
The technique of lightly dragging a brush over a freshly painted or varnished surface to even out Brush Marks.

Leaching
The slow, controlled removal of a slightly soluble substance by water. Usually applicable to Antifoulings.

Leafing
Orientation of pigment flakes parallel to the substrate as the film forms, to provide a more impermeable barrier. These are sometimes referred to as lamellar films.

LEL or Lower Explosive Limit
The minimum percentage of solvent which, when mixed with air forms a potentially explosive mixture. Note that there is also an upper explosive limit, beyond which there is insufficient air (oxygen) to permit an explosion.

Lifting
Softening and raising of an existing coating when overcoated. This effect is normally due to incompatibility or premature overcoating.

M

Mandrel Test
A physical test method where a soft aluminium panel is coated with a paint scheme, and then deliberately bent to test for **Adhesion** and flexibility. The diameter of bend, and the temperature at which the test is carried out will usually be specified.

Mechanical Damage
Mechanical damage
Define

Metamerism
An effect where two paints appear to have the same colour under one lighting condition, but are noticeably different when lighting conditions change. This is a complex problem, caused by the use of different pigments to achieve the same colour. A "Non Metameric" colour match will appear the same under all lighting conditions, but is difficult to achieve unless using identical pigments to those in the original paint.

Methyl Ethyl Ketone
A Ketone solvent commonly used in paint manufacture. Most Ketones are very aggressive solvents, and are highly flammable.

Methylene Chloride
A very aggressive solvent used in paint-strippers. Methylene Chloride is non-flammable, but is very toxic and produces dangerous decomposition products (including phosgene) if heated. Also known as Dichloromethane.

Micron (Abbreviation µ or µM)
A micron is one millionth of a metre. It is the modern-day unit used to measure Film Thickness. To convert to Thou or Mil, divide measurement by 25.4

Mill Scale
A very hard oxide layer formed on the surface of steel plate whilst at very high temperature, (i.e. during manufacture or welding). Mill Scale must be completely removed before painting, preferably by Blast Cleaning, as it will promote rapid corrosion if allowed to remain.

Miscible
Capable of mixing or blending uniformly.

Mist Coat
A technique where a thin coat of finishing paint is spray applied to a surface shortly before applying a full wet coat. The Mist Coat is normally overcoated within an hour and whilst it is still soft. This method is used to enhance appearance, and to achieve greater film thickness per coat.

Monomers
These are the chemical "building bricks" of Polymers.

Mud Cracking
Irregular cracking of a paint film which results in an effect similar to a dried up river bed. This is normally due to application of an incompatible coating or very excessive film thickness.

N

Newtonian
A type of Rheology where the application of a force (e.g. Stirring, brushing, spraying) has an effect on viscosity directly proportional to the force applied. See also Thixotropy.

Non Volatile or Involatile
Non-evaporating, but not necessarily solid component of a paint or varnish.

O

Occupational Exposure Limit or OEL
The maximum concentration of any dust, gas, or vapour to which workers may be continuously subjected in their place of work, without detriment to health during a normal working lifetime. These limits are set by The World Health Organisation based on current knowledge, and are reviewed annually. Where exposure may exceed these limits for only short periods, Time Weighted Average limits may be set.

Potential Difference
The difference in electric charge between two points, expressed as a Voltage.

Threshold Limit Value or TLV
This expression has generally been superseded by the term **"Occupational Exposure Limit".**

Oleoresinous
Paints or varnishes based solely on drying or semi drying vegetable oils such as tung, puerilla, linseed and soya bean. Truly oleoresinous coatings are rarely used nowadays because of their slow drying and poor durability, and have generally been superseded by **Alkyds**.

Opacity
Obliterating power of a paint.

Orange Peel
Spray painting defect where the applied film has a textured appearance similar to an orange skin, usually owing to poor atomisation.

Organic
Chemical compounds of carbon and other elements, but excluding carbon itself. Carbon has the unique ability to form chemical chains of almost infinite length, playing a vital part in long chain polymers.

Osmosis (Classical Definition)
Usually the transfer of water through a semi-permeable membrane from a less concentrated solution to a more highly concentrated solution. This often occurs where pockets containing osmotic solutions are present within a GRP laminate.

Osmosis (in GRP)
Chemical breakdown within a glassfibre laminate due to moisture ingress, which ultimately causes blistering of the gelcoat.

Overcure
A condition caused by excessive addition of curing agent to a two component paint. Overcure tends to cause brittleness in polyurethanes and Amine Sweating in epoxies, but ***does not*** accelerate the rate of cure.

Overspray
Atomised paint which "over shoots" the surface being painted.

Oxidation
The addition of oxygen to an element or compound. The conversion of iron or steel to rust is an example of oxidation.

Oxides
Chemical Compounds of oxygen and any another element.

P - Q

Paint
Any pigmented surface coating, whether used for protective, cosmetic or specialist purposes.

Paint Pads
Flat or slightly curved pad using very short hairs, or a special foam. Generally used for the application of finishes.

Pass
Motion of a Spray Gun over the surface to be painted, in one direction.

Passive
Non Reactive or Inert.

Passivation
Rendering a metal unreactive or inert to a specific corrosive solution. Sometimes used to describe removal of osmotic compounds from glassfibre laminates.

Peeling
A defect where a dry paint film curls away from a surface.

Phosphates
Salts derived from phosphoric acid.

Phthalic Acid
A white, soluble crystalline substance used in the manufacture of dyes and resins.

Pickling
Cleaning and preparation of metals for painting by immersion in strong acids. This method is little used now due to environmental concern and for reasons of Health and Safety.

Pickling
An effect where a paint or varnish film wrinkles, usually due to incompatibility with previous coatings, too rapid overcoating or **Solvent Entrapment**.

Pickling
An effect where a paint or varnish film wrinkles, usually due to incompatibility with previous coatings, too rapid overcoating, or **Solvent Entrapment**.

Pigment
A fine powder used to provide colour and opacity in paint films.

Pigment Volume Concentration or PVC.
The percentage of the volume of dried paint which is represented by the pigment.

Pimpling
Small Blisters present in a Paint Film.

Pin Holes
Small holes or voids in a paint finish or gel-coat.

Plasticisers
Most paints and plastics contain plasticisers to improve flexibility. With time, and exposure to the elements these are slowly depleted, and the films become brittle. Soft plastics like PVC fenders contain large quantities of plasticisers, often forming a sticky surface film. This should be washed off regularly to prevent attraction of abrasive dirt and grit.

Ply Wood
A laminate consisting of a number of thin layers of wood glued together so that the grain of each layer is at right angles to that of its neighbour.

Poise
A unit of Viscosity measured under specified conditions of shear, named after the physicist Poiseuille.

Poly
A prefix used in chemistry meaning many, e.g. Polyester or Polyurethane.

Poly Vinyl Chloride or PVC
A very widely used Polymer of vinyl chloride. Commonly used for plastic piping and gutters as well as fenders for yachts.

Polyester
A Form Of Reactive Resin having many Ester groups. Used in paints and structural resins.

Polyhydric
Compounds containing many Hydroxyl (OH) groups. Other descriptions including Dihydric (two) and Trihydric (three) are also used to denote the number of hydroxyl groups present in each molecule.

Polymerisation
Synonymous with **Curing** or **cross Linking**.

Polymers
These are large molecules made by the polymerisation of up to four Monomers.

Polyurethane Resins
Polymers formed by a reaction between hydroxylated **Resins** and **Isocyanates**. Most polyurethane coatings have exceptional durability in a marine environment.

Porosity
A measure of how efficient a material is in "soaking up" a liquid or gas. This is different to Permeability, which describes the ability to permit transmission.

Pot Life
The duration for which a two component product will maintain its application properties after mixing, (usually quoted at a specified temperature).

Primer
Paint used to gain optimum **Adhesion** to, and protection of a Substrate.

Profile
Surface contour of a **Substrate** or Paint Film when viewed edge-on.

R

Radical
A reactive group of Atoms present in organic compounds which keep their arrangement during chemical reactions, even though the whole compound may be altered. Reaction stimulant.

Reclaimed Solvent
Reclaimed solvent is recovered from paint waste by distillation. As it generally contains a mixture of solvents, its use is generally limited to equipment cleaning.

Reduction
Chemical reactions in which oxygen is removed from a molecule by Oxidation of a secondary reagent.

Reduction
Viscosity reduction by thinning.

Resin
A common term used to describe a binder, polymer or media used in the manufacture of paints and varnishes. See also Alkyd Resin, Oleoresinous, Polyurethane, Epoxy Resin, etc.

Reversible Spray Tip
An Airless Spray Gun Tip which may be easily reversed to clear blockages.

Rheology
A science concerned with the behaviour of fluids such as paint when subjected to various shearing forces i.e. stirring, brushing, spraying. See also **Thixotropic**, and **Newtonian**.

Paint Roller
Implement used to apply paint to large, flat surfaces, usually from a special tray.

Rust
An oxide of iron caused by the process of **Corrosion**.

S

Sags
Surface defect caused by wet paint moving under the effects of gravity, usually on vertical or inclined surfaces.

Saponification
Breakdown of an Ester by an Alkali to form a soap. Can occur if Conventional paints are used underwater, particularly on metal.

Satin (Finish)
Term used to describe a paint or varnish with a low gloss (but not matt) finish.

Sediment
Solid paint components such as pigments and extenders which may form a deposit in the bottom of a container.

Sensitiser
Any material that can cause an allergic reaction by repeated contact or exposure, such as epoxy and polyurethane curing agents. Also known as Allergens

Settling
Effect whereby solids in a paint (such as pigments) fall out of suspension, usually due to gravity, forming a mass at the bottom of the tin called Sediment.

Sheen
Measure of the amount of Gloss a finish possesses.

Shelf Life
Length of time that a product will remain useable if kept in an unopened container. A storage temperature range is sometimes specified.

Shell (Fouling)
Type of hard-backed type of fouling species such as a barnacle or mussel.

Shop Primer
A protective primer applied to steel plate which has been grit blasted at the steel mill. These primers provide good anticorrosive protection during storage and newbuilding, and usually carry approvals for welding. Some Shop Primers can be overcoated with a full coating scheme, however, it is usually recommended that they are removed by sweep blasting or discing, and a new **Holding Primer** applied.

Silicone Alkyds
Type of Resin where an Alkyd is reacted with Silicone Resin to enhance application characteristics and gloss retention.

Silicone Resins
Range of Compounds comprising Hydrocarbons, Silicon and Oxygen which have been Polymerised. Used in Caulking compounds and heat resistant finishes.

Sleepy (Finish)
Dull, less than full Gloss.

Slime
Fouling caused by strand-like marine organisms.

Slurry Blasting
Abrasive cleaning of substrates by suspending abrasive particles in a high pressure jet of water, or air and water. This method is often used in the preparation of GRP hulls with osmosis, as it is less aggressive than dry grit blasting.

Solids
Non-volatile portion of a paint or varnish.

Solubility
A measure of how easily a substance will dissolve in a specific **Solvent.**

Soluble Matrix
Antifouling Paint in which the Binder is sparingly soluble in water.

Solvent
Liquid which is capable of dissolving substances. Many solvents are specific to a particular resin type and may be used in the manufacture of "Selective" paint strippers such as those used to remove antifoulings from GRP hulls.

Solvent Entrapment
If Solvent does not evaporate before a paint film cures, it can become trapped within the coating scheme. Solvent Entrapment is typically caused by excessive film thicknesses or too rapid overcoating, and causes soft paint films and poor gloss. It may also lead to premature failure due to **Splitting.**

Spattering
The deposition of large paint droplets rather than a fine spray mist, normally caused by applying paint with too high a viscosity, incorrect atomising air pressure, or incorrect fluid tip selection.

Splitting
Defect where a paint coating fails due to poor cohesive strength, rather than poor adhesion. Splitting is usually caused by **Solvent Entrapment** and/or **Undercure** of the affected paint film.

Spray Fog
Synonymous with Overspray or Spray Mist, and refers to the atomised paint which fails to reach the target surface.

Spray Gun
Apparatus which converts liquid paint into a fine mist by **Atomisation.**

Spray Pattern
Shape and size of the spray pattern emerging from a Spray Gun, usually when held at a specified distance from the surface being sprayed.

Spraygun Nozzle Assembly
A combination of Needle, Tip and Air Cap in a Spray Gun.

Spreading Rate
See Coverage.

Stain
A liquid used alter the colour of wood, whilst allowing the natural grain to remain visible.

Steel
An alloy of iron, carbon and other elements, possessing high tensile strength.

Substrate
Surface on to which paint is applied. The term substrate is usually used to describe the yachts basic construction material, i.e. Steel, Alloy, Timber or GRP.

Superstructure
That part of a boat above deck level, i.e. the cabin roof, wheelhouse and mast.

Surface Contamination
Oil, grease, dirt or other undesirable matter which reduces adhesion of a paint film, or spoils its appearance.

Syneresis
A condition where the resin and extenders in a filler separate during storage, allowing the lighter extenders to float to the surface and form a crust. Syneresis is most likely to occur in hot storage conditions.

Synthetic
Man-made.

T

Tak Rag
A special cloth impregnated with linseed oil, which can be used to remove traces of dust from surfaces immediately before painting.

Teredo
Type of marine worm. See also Gribble.

Thinners
Liquids added to paints or varnishes in order to reduce Viscosity, (also known as a "Reducer"). Thinners are usually a blend of several **Solvents**.

Thixotropy
False high viscosity which breaks down when stirred or brushed. Thixotropy is the fundamental property of "non-drip" paints.

Thou
Abbreviation for one thousandth of an inch, generally used in the engineering industry. Equal to 25.4 Microns.
See also **Mil** and **µM**.

Time Weighted Average (or TWA)
Occupational Exposure Limits are often quoted as Time Weighted Average figures to

Toluene
An Aromatic Hydrocarbon Solvent, used mainly in two pack polyurethane paints and varnishes. Highly Inflammable

Top Coat
Final paint-Film applied to a system of two or more products.

Topsides
Area of exterior hull above the waterline, but below decks.

Tram Lines
Parallel lines at the top and bottom of an Airless Spray pattern. Tram Lining is inherent with the Airless application method, but is worsened by applying paint which is too cold and/or too viscous. Incorrect choice of fluid tip and insufficient fluid pressure can also promote this defect.

Transfer Efficiency (Spray)
A measure of how much paint is actually applied by a spray gun, compared with the quantity of paint used. Conventional Sprayguns are very inefficient, having typical Transfer Efficiencies of only 25 ~ 40%, the remainder being lost as **Spray Fog**. Environmental concern and legislation is now driving the trend towards more efficient application methods such as **HVLP** and **Air Assisted Airless**, which offer Transfer Efficiencies of 60% and above.

Transparent
Completely unobstructive to light transmission.

Trigger
Finger operated lever on a Spray Gun which regulates the flow of Atomising air to the nozzle.

Trowel
Implement used for applying Fillers to a surface.

Two Component Spraygun
A Spray Gun which had two separate fluid passages to the Spray Head, and is designed to keep the **Base** and **Curing Agent** separate until they are actually applied. (Sometimes called a Plural Spraygun). Used to apply two component products with short pot lives.

U

Ultra Violet (Light)
Electromagnetic energy having a wavelength of between 0.03 to 0.4 μM, (which is invisible to the human eye). Ultra violet light is very destructive to paint films and plastics because of its short wavelength, and causes fading and loss of gloss, i.e. **Ultra Violet Degradation**.

Ultra Violet Degradation
Fading, Loss of Gloss and ultimately **Chalking**, caused by exposure of paint films to ultra violet light.

Undercoats
These are similar to finishes, but contain more extenders to aid obliteration, and to make them easier to sand.

Urethane Alkyds
Conventional **Alkyd Resins** that have been modified or "reinforced" by partial reaction with isocyanate monomers. Urethane alkyds generally dry faster, and have harder films than standard alkyds, although their gloss retention is not quite as good.

V

Varnish
A transparent **Resin** without any colouring pigment, generally used to decorate and protect timber.

Viscosity
Measure of how "thick" a liquid is and how well it flows. There are a number of viscosity measuring systems used world wide. The simplest measure the time taken for a measured quantity of fluid to flow through an orifice in a **Viscosity Cup**.

Visible Light
Electromagnetic energy having a wavelength of between 0.4 to 0.7 μM, which is visible to the human eye. Violet light has the shortest wavelength at about 0.4 μM, followed by blue, green yellow orange and red light, which has a wavelength of about 0.62 μM. Wavelengths above and below these figures are invisible to the human eye, although they sometimes affect our perception of colours.

Voids
See **Pin Holes**.

Volatile Content
Percentage of materials which evaporate from a given quantity of a paint or varnish. These are usually **Solvents**.

Volatile Content
Percentage of materials which evaporate from a given quantity of a specific type of paint or varnish. These are usually organic solvents, and are sometimes referred to as **Volatile Organic Compounds** or **VOC's**.

Volume Solids
Measure of percentage of a paint which remains after the solvent has evaporated.

W

Warping
Distortion of a material, usually timber.

Wash Primer
A very thin primer (such as a Self Etch Primer) used to provide good adhesion for a full coating scheme, usually by chemical reaction with the substrate. Wash primers provide little or no protection by themselves, and most need to be overcoated within a short period. It is important that wash primers are not applied too thickly, or more than a single coat applied, as this may cause failure.

Water Blasting
Cleaning method utilising powerful jets of water, particularly useful for removal of heavy fouling, corrosion, and water soluble salts.

Water Spotting
Surface defect caused by water-droplets affecting the paint film during and/or after drying.

Weed
Form of water borne Fouling of plant origin.

Weld Spattering
Beads of metal left adjoining a weld.

Welding Slag
Deposits of flux and oxides remaining after welding. These are often strongly alkaline in nature, and must be removed before painting if localised corrosion is to be avoided.

Wet Edge Time
Period during which adjacent coats of paint can merge without leaving brush marks. Application after the

Wet Film Thickness
Depth of a paint film immediately after application measured using a 'comb' gauge. See also **Dry Film Thickness**.

Wet Film Thickness Gauge
Sometimes known as a Wet Film Thickness Comb, these are used to measure the depth of the wet paint film immediately after application, and before significant solvent evaporation has taken place. Film thickness is usually measured in Microns or µM.

Wet or Dry (Abrasive Paper)
Waterproof abrasive paper.

Wet Rot
Decay of timber by fungi. Caused by excessive moisture in timber, aggravated by poor ventilation.

White Spirit
Aliphatic hydrocarbon used as a replacement for traditional turpentine, and sometimes referred to "Turpentine Substitute". This is a petroleum derivative and is flammable.

X - Y - Z

Xylene or Xylol
Aromatic hydrocarbon distillate used as a solvent or diluent for a wide variety of coatings. This is a petroleum derivative and is highly flammable.

Zahn Cup
A viscosity cup used in the United States, similar to British Standard and Din cups.

Zinc Spraying
Similar to Galvanising, molten zinc is sprayed onto prepared steel using a special heated spraygun. Zinc sprayed surfaces are difficult to paint satisfactorily, and severely limit the choice of antifouling.

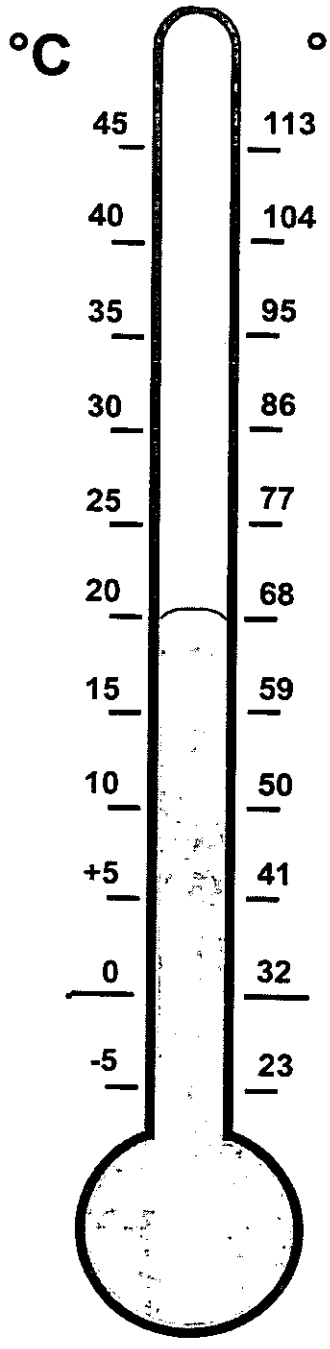
Useful Conversion Tables

Length	Equivalent
1 Thou or 1 Mil ≡	25.4 Microns or µM
1 Inch ≡	25.4 Millimetres
	25,400 Microns or µM
1 Yard ≡	914.4 Millimetres
1 Metre °	1000 Millimetres/100 Centimetres
	1000,000 Microns or µM
	39.37 Inches
	1.0936 Yards

Area	Equivalent
1 Square Metre ≡	1.196 Square Yards
1 Square Inch ≡	645.16 Square Millimetres
	6.4516 Square Centimetres

Capacity and Volume	Equivalent
1 Litre ≡	1000 Millilitres/Cubic Centimetres
	1.76 Imperial Pints
	35.2 Fluid Ounces
	2.11 US Pints
1 Imperial Pint ≡	568 Millilitres/Cubic Centimetres
	20 Fluid Ounces
1 Fluid Ounce ≡	28.4 Millilitres
1 US Pint ≡	473 Millilitres
	16 Fluid Ounces
1 Imperial Gallon ≡	4.546 Litres
1 US Gallon ≡	3.785 Litres

Painting Thermometer



- Many paints will be found difficult to apply at temperatures much above 30 °C. Tropical or High Temperature reducers should be used if applying paint by spray.
- Some paints, (particularly two component polyurethanes) tend to "drag" at temperatures above 25 °C owing to their short wet edge times. Use a slower reducer or a retarder if one is available, and avoid working in direct sunlight.
- Paint viscosity should always be measured at 20 °C.
- 15 ~ 16 °C is an ideal temperature for brush application. It is also the recommended minimum for many solvent free epoxy treatments to avoid the risk of undercure and surface sweating.
- Two component polyurethanes should not be applied at less than 12 °C. Most epoxies cure very slowly at less than 10 °C, and their curing mechanism can fail altogether at 4 ~ 7 °C. There is also a risk of blooming and blushing owing to surface condensation.
- Most paints will have a consistency like treacle at less than 10 °C, and can be very difficult to apply. For best results, warm the paint to 20° C or slightly above before use.
- 0 °C/32 °F - Freezing Point: only those paints specialy formulated for low temperature use (such as Vinyl Tars and some Chlorinated Rubber paints) should be applied at less than 5 °C.

Wegemt
10 Upper Belgrave Street
LONDON
SW1X 8BQ
UK

Telephone: +44 (0)20 7838 9149
Fax: +44 (0)20 7838 9147