Chapter 11
PROTECTION OF ALUMINIUM

11. PROTECTION

THE ALUMINIUM alloys that are used in marine applications – essentially those that belong to the 5000 and 6000 series – have excellent resistance to corrosion in a marine environment, whether they are exposed to sea air or submerged in sea water.

Unlike other common metals such as steel, they do not need to be protected by painting or any other means. Painting only the strict minimum of a boat, i.e. the quickwork and living or reception quarters, represents a major saving on cost, including maintenance, and on weight as well.

Examples of marine applications in unprotected aluminium abound, and include oyster barges, plant and machinery rooms on passenger ships and coastal installations such as floating landing stages in marinas, road signs etc. There are also many examples of craft and coastal installations that have never been protected and which have been in service for many decades.

Aluminium and its alloys are non toxic to living organisms such as marine flora and fauna (1). Protecting the quickwork of a boat with special antifouling paint is therefore essential to prevent biofouling by deposits of an animal or vegetable origin. The same applies to submerged equipment if it is to be protected from fouling (2).

In most cases apart from the quickwork, the purpose of protection is essentially decorative and aesthetic. This is true of the protection of the dead works, the masts of pleasure craft, and the hull and superstructures of commercial vessels on which the shipowner wishes to place his personal "brand".

It has long been recognised [1] that paint lasts longer on aluminium than on steel because the substrate is more resistant to corrosion (3), and this is true in a marine environment. However painting involves the regular maintenance of the paintwork with all of the surface preparation which this entails, and while this is perfectly feasible for accessible surfaces, it is less so for ballast tanks with complex shapes or surfaces that are broken up by stiffeners, frames etc., with welds making surfaces even more irregular.

One may as well say that only accessible areas should be repaired in the shipyard, as there is often little point in attempting to paint ballast tanks, water tanks etc. – once the paint here has deteriorated, it cannot be repaired.

Three types of protection are used almost exclusively in marine applications:

- anodising,
- painting, and
- cathodic protection.

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(1) This also applies to the salts and the oxide of aluminium (alumina), so even the corrosion products of aluminium are not toxic.

(2) For the effect of fouling on corrosion behaviour, refer to Chapter 10.

(3) The fact that the corrosion products of aluminium – alumina – are white, almost colourless if pitting corrosion is very superficial, has little impact on the general appearance of a painted surface on which the paint has disappeared locally under the effect of corrosion. There is no comparison with the deterioration in the look of painted steel surfaces!

YACHT MASTS

OF ALUMINIUM

1. ANODISING

Anodising is a process of surface treatment which thickens the natural oxide film and is specific to aluminium. Alloys that belong to the 5000 and 6000 series have a metallic structure and chemical composition that are suitable for anodising.

A number of anodising techniques have been developed to improve the surface properties of the metal or adapt them to particular applications: decoration, resistance to corrosion, long-lasting appearance, surface hardness, resistance to abrasion, aptitude for friction and anti-adhesion, acceptance of organic coatings (adhesives, lacquers, paints).

In marine applications, it is primarily the decorative aspect that is important. Anodising prevents tarnishing and superficial pitting corrosion. This surface treatment is applied mainly to deadworks and the masts of pleasure craft.

Sulphuric anodising is the treatment most commonly used for decoration, for obtaining hard coatings and for enhancing corrosion behaviour.

The classical treatment parameters are:

- strength of H_2SO_4: 200 ± 20 $g.l^{-1}$
- level of dissolved aluminium in the bath: 15 $g.l^{-1}$ max.
- the bath is agitated to prevent temperature exceeding 20°C
- d.c. current density: 1.5 ± 0.1 $A.dm^{-2}$

This treatment is applied discontinuously to castings (mainly for deadworks), shapes (mainly for masts) and sheet (4) or continuously to strip.

The anodic films, whose structure is determined by the type of anodising bath and the treatment conditions, consist of hexagonal cells pierced by micropores whose diameter, e.g. for a coating of 15 microns, is about one thousandth their thickness (figure 137). These porous films are ideal for absorption colouring, either by dipping in the dye or by electrolytic deposition.

(4) Surface treaments are applied in facilities with a number of treatment baths in series. The size of the tanks that contain these baths is necessarily limited, to around fifteen metres for those used to treat boat masts.

YACHT ADRIEN, GLOBAL CHALLENGE

Whether they are coloured or not, the anodic films must be sealed to close the pores and so ensure excellent resistance to corrosion. This operation is done in pure distilled boiling water containing sealing additives. The quality of the anodising, i.e. its durability, depends largely on the sealing conditions (5) (6).

Standards define classes of anodising (for building applications) as a function of thickness, and specify what classes must be used depending on the atmosphere of the particular environment (7). In practice, a minimum film thickness of 20 microns is recommended in a sea atmosphere (class 20 minimum) [2].

Provided it is regularly serviced at least once a year by removing any deposits of dust and sea salt with products suitable for anodised aluminium, the "life" of a properly sealed 20 micron film will far exceed 20 years in a marine environment.

STRUCTURE OF THE ANODISED LAYER

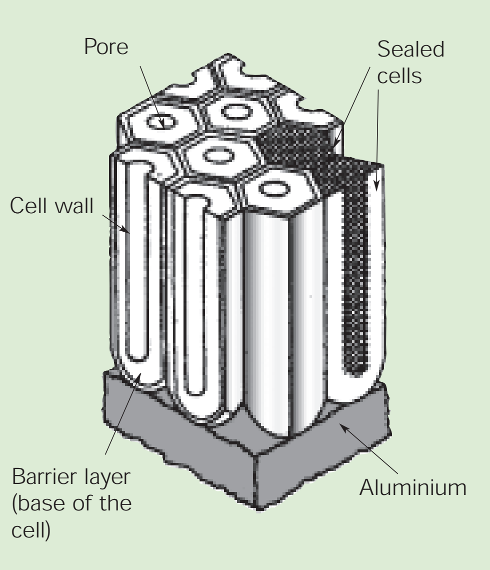

Figure 137

There are other anodising processes:
- hard anodising (with film thicknesses up to 100 microns) is normally used for technical applications as it offers good wear resistance in marine environments (8),
- thin-film phosphor anodising (a very useful surface preparation for adhesive bonding).

Note: Anodising does not remove the risk of bimetallic corrosion if an anodised aluminium piece is in contact with another metal in an aqueous medium.

(5) The anodised surface will not accept any other coating once it has been sealed – such a surface cannot be painted.

(6) In practice, the sealing time must be the same as the anodising time.

(7) Standard NF A 91-450: Anodisation (oxydation anodique) de l'aluminium et de ses alliages. Couches anodiques sur aluminium, December 1981.

International standard ISO 7599: Anodizing of aluminium and its alloys – General specifications anodic oxide coatings on aluminium, 1983.

(8) Contrary to misconception, hard anodising is not done to protect aluminium from pitting corrosion. It offers no more protection than a conventional 20 micron film because it is almost never sealed and it is also much more expensive!

2. PAINTING

It is essential to remember that the natural oxide film which always covers the surface of aluminium prevents the adhesion of paints in particular and organic coatings in general. Its surface must therefore be prepared to create sites of adhesion – "bridges" – between the oxide film and the coating. Many years of experience show that the behaviour of coatings on aluminium depends on the surface preparation [3].

Applying paint to an aluminium alloy surface involves a number of steps:

2.1 Degreasing

The purpose of degreasing is to remove all foreign bodies, including solid particles (swarf, dust) and fatty products (oils, greases), which have infiltrated the metal's natural oxide film.
Degreasing with detergents (Teepol or equivalent type) is preferable to the use of organic solvents (9). Solvents that are too "light" such as acetone are not recommended as they are tricky to handle and highly flammable.

Degreasing should be done by treating small areas at a time, using clean lint-free cloths that are frequently replaced to ensure that impurities are removed rather than just spread around!

(9) Chlorinated solvents are used less and less for health and environmental reasons, and are likely to cause subsequent corrosion unless stabilised. They are not recommended for work in boatyards or marine applications.

2.2 Surface cleaning

There are three options:
- etching,
- cleaning with abrasive jet,
- disk grinding.

Etching

This involves chemically pickling the surface layer of aluminium so that it will accept the wash primer.

The etching medium is a phosphoric acid solution that is applied liberally to all the surfaces to be treated. It is applied with a brush, cloth or sometimes a mop, taking care to protect the operator from splashes.

After application, the medium must be left to act as directed by the manufacturer, usually for 20 to 30 minutes. The surfaces are then washed off with fresh water until the wash water returns to a pH level that is equivalent to that of water from a main.

Cleaning with abrasive jet

Cleaning with the abrasive jet (10) is carried out with an abrasive suitable for use on aluminium alloys, such as corundum or any other inert abrasive. This treatment must always be done on surfaces that are clean and dry, and be followed by thorough dust removal.

Surfaces should be painted as soon as possible following abrasive treatment to prevent the oxide film from absorbing moisture or the treated surfaces from attracting impurities.

Steel shot must not be used owing to the attendant risks of pitting corrosion. Abrasives that have already been used to treat metals other than aluminium should also be avoided for the same reason.

Disk grinding

This type of preparation is used on surfaces that cannot be treated by etching or abrasive cleaning. It must be carried out with coarse grit wheels to achieve a well keyed adhesive substrate.

However, coatings do not adhere to surfaces treated in this way as well as after etching or abrasive cleaning.

2.3 Painting

Effective protection against an aggressive marine environment is obtained by multi-layer coatings in which each coat contributes to the efficiency of the system. The types of paint most widely used at present are based on polyurethane or epoxy resins.

A typical system will consist of:
- a reactive primer, usually with a vinyl resin base and containing a certain amount of phosphoric acid. The primer ensures that the coatings adhere to the aluminium,
- finish coats whose purpose is to reinforce the water tightness of the paint system and enhance its appearance.

Finish coats should be applied with a compressed air spray gun.

(10) Incorrectly called sand or shot blasting.

(11) Due mainly to distortion caused by welding. Strict adherence to the rules governing aluminium welding as discussed in Chapter 6, will minimise the amount of filler on a hull.

2.4 Fillers

Special fillers are used to repair surface imperfections (11). Preference should be given to solvent-free epoxy fillers as these are perfectly suited to immersion and will not shrink as they harden.

Fillers should never be applied directly onto the metal but instead between successive coats of epoxy primer. Application is by spatula or more often using a float.

Once it has dried, the filler should be sanded using wet or dry abrasive paper. Some fillers may require washing with fresh water after curing, especially if this occurs at low temperature. All dust should be carefully removed from the surface before the next coat is applied.

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2.5 Antifouling paints

Aluminium and its mineral compounds such as alumina $Al(OH)_3$, the corrosion product of aluminium, are non toxic to marine flora and fauna. The quickwork of an aluminium ship must therefore be coated with a marine antifouling paint in order to prevent deposits and encrustations of sea organisms such as mussels, barnacles and so forth.

As has been explained elsewhere (12), antifouling paints based on copper oxide must be avoided as they can severely corrode the underlying metal.

Since the early 1970s, the biocide used in most commercial antifouling paints has been based on a salt of tin, TBT (tributyl tin), which is compatible with aluminium.

In view of the toxicity of this biocide to the marine environment, on October 5, 2001 the IMO decided to ban TBT based antifouling paints from 1 January 2003, and from 1 January 2008 no vessel will be allowed to sail with its hull coated in these products (13).

A number of paint manufacturers have anticipated this ban and for several years have been making antifoul paints that are compatible with aluminium and that comply with the European Directive and the IMO's decision [4], e.g. JOTUN's ALUSEA being one of them.

2.6 Drinking water tanks

The chemical composition of the 5000 and 6000 series alloys that are commonly used for marine applications puts them among the "food-grade" materials (14).

They can therefore be used uncoated to make drinking water tanks. Before use however it is essential to thoroughly clean the walls of the tank and rinse them several times, preferably with hot drinking water.

Drinking water tanks may also be painted if desired, in which case the protection products must be supported by a manufacturer's certificate of safety.

2.7 Repairs and treatment procedures

There are two procedures to consider depending on the extent of the damage:

Procedure 1: the anti-corrosion primer has not been affected

- Degrease,
- Wash off carefully in fresh water,
- Dry,
- Apply filler to bring level,
- Sand with abrasive (grit 250-300) under water (generously around the damaged area but not down to the anti-corrosion primer),
- Re-apply the finish coat(s).

Procedure 2: the damage is more serious and bare metal has been exposed

- Degrease,
- Wash off carefully in fresh water,
- Sand with abrasive (grit 180-220) down to the metal, exposing a wide area around the affected zone,
- Apply wash-primer (reactive primer) to the areas of bare metal,
- Re-apply the complete paint system.

2.8 Application conditions, paint tests, health and safety requirements

As a general rule, paints should be applied:

- in a dust-free, draught-free environment,
- at temperatures above 15°C,
- at between 40 and 70% humidity.

Paint containers must be stored at approximately 20°C for at least 24 hours prior to use. Before commencing application it is advisable to ensure that the substrate is at least 3 °C above dew point.

Painting and drying operations must be programmed as part of the overall production schedule in the same way as any other operation.

2.9 Testing paints

Paints can be tested for:

- Viscosity: This test is carried out with the flow cup according to AFNOR standard NF - T 30 070 (Ford cup No. 4) and is used to adjust the viscosity of the paint to suit the application technique (e.g. brush, spraygun) for finishing coats on dead works.
- Wet thickness: Wet film thickness is measured with comb gauges. The dry film thickness is then calculated from the result of this test and from the known dry extract by volume of the paint.

(12) Chapter 10.

(13) This decision followed on from European regulations banning the use of organostannic compounds (tin salts) since 1989 (Directive 89/677/EEC dated 21.12.1989).

(14) Standard EN 602. Aluminium and aluminium alloys – Wrought products. Chemical composition of semi-finished products used for the fabrication of articles for use in contact with foodstuff.

For example, a wet coat 100 microns thick must be applied to obtain a dry film thickness of 35 microns with a paint of 35% dry extract by volume.

If the application technique requires the paint to be thinned, then the dry film thickness will obviously be reduced for the same wet thickness. In this case it is advisable to increase the number of coats applied to achieve the total dry film thickness that is required. This point is particularly important for coats of primer.

2.10 Health and safety

In their instructions, suppliers of surface treatment products and paints indicate all of the precautions that must be taken for use and storage. They are also required by law to provide safety data sheets to any user who requests this information.

2.11 Examples of procedures recommended by JOTUN

Procedures recommended by Jotun for quick work, dead work, decks and superstructures are shown in table 69 and the interior of ships in table 70.

JOTUN PROCEDURES FOR QUICKWORKS, DEAD WORKS, DECKS AND SUPERSTRUCTURE

Procedure	Quick Work	Dead works, decks, superstructure and exterior accessories
Surface preparation	Degrease with detergent (type Teepol or equivalent), Wash off with fresh water. Generally roughen all surfaces with non-metallic abrasive (corundum)*. This surface preparation must be confined to very small areas and should never be used on exterior planking.	
Primer	1 x 50 µm DFT Epoxy Primer	1 x 50 µm DFT Epoxy Primer
Finish	2 x 100 µm DFT Epoxy	1 x 100 µm DFT Epoxy 2 x 50 µm DFT Acryl Polyurethane Topcoat**
Antifouling	2 x 125 µm DFT Antifouling Selfpolishing Tin Free « special Aluminium », (non electrolytic pigments).	

** Note: Areas that cannot be roughened with non-metallic abrasive can be chemically pickled with a solution of phosphoric acid of the "deoxydine" type and then washed off.*
*** Note: A non-skid powder must be used between the two finish coats of acryl polyurethane on exterior decks.*

Table 69

JOTUN PROCEDURES FOR MACHINE COMPARTMENTS

Procedure	Ceiling divisions Interior decks	Sheet structures beneath ceilings	Sheet structures beneath engine room	Fresh water tanks
Surface preparation	Degrease with detergent type Teepol Wash off with fresh water.			
Primer	1 x 40 µm DFT Epoxy Primer			
Finishes	1 x 40 µm DFT Epoxy Undercoat White 1 x 40 µm DFT Acryl Polyurethane Topcoat	2 x 100 µm DFT Epoxy	2 x 150 µm DFT Epoxy (drinking water compliant)	

Table 70

3. CATHODIC PROTECTION

This is an electrochemical form of protection in which the metal that is to be protected acts as the cathode (figure 138) on which H^+ ions are reduced (to gaseous hydrogen) according to the reaction:

$$2H^+ + 2e^- \rightarrow H_2$$

For this reaction to take place, *e^- electrons must be transferred to the metal*. There are two ways of doing this:

- Connecting another metal (or alloy) – the anode – whose dissolution potential is more electronegative in the particular environment, and which will oxidize according to the reaction:

$$2M \rightarrow 2M^{n+} + 2e^-$$

The electrons released in this way will flow to the cathode.

This reaction consumes the metal of the anode which is known as the "consumable" or "sacrificial" anode as a result.

On ships, anodes are usually castings designed to suit their method of attachment and their position on the vessel (photo p. 174).

- Installing a direct current source that supplies the flow of electrons needed for the reduction reaction on the metal that is to be protected. This is "cathodic protection by impressed current".

3.1 Cathodic protection of aluminium

When it acts as the cathode, the metal's dissolution potential falls to values that are more electronegative than its normal dissolution potential. For an anode to be effective, the difference in potential between it and the metal which it must protect must be at least 100 to 200 mV. The impressed current system regulates both the required level of potential (relative to a reference electrode) and the flow of electrons.

The cathodic protection of aluminium is much more complex than that of steel even though the protection current for aluminium is one tenth of that needed to protect (unpainted) steel [5].

To protect aluminium, it must be reduced to levels of potential at which the reduction of ions H^+ accelerates. The effect of this reaction is to alkalinise the environment with an excess of OH^- ions, i.e. to cause local corrosion of the aluminium, referred to as "cathodic corrosion".

This "cathodic corrosion" (which is unwanted) has a particular appearance which makes it easy to recognise. On bare metal it generally develops as rounded craters whose surfaces can be quite shiny. If the metal is painted, the paint may blister (15).

Studies have shown that in order to obtain total protection, the potential of magnesium alloys such as 5083 or 5086 must be reduced to levels where – in sea water – cathodic corrosion develops strongly [6].

PRINCIPLE OF CATHODIC PROTECTION

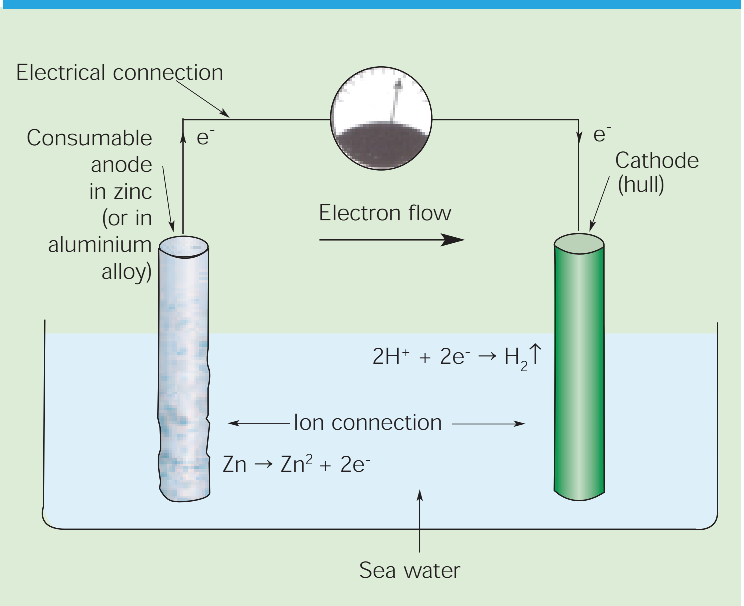

Figure 138

(15) *But the converse is not true, i.e. a paint blister is not necessarily due to "cathodic corrosion".*

3.2 Neutralisation of bimetallic couples

The very good corrosion resistance of aluminium-magnesium alloys of the 5000 and 6000 series in marine environments and specifically in immersion in sea water requires no protection in itself.

Whatever the vessel's system of propulsion however (conventional screw or hydrojet) cathodic protection will be needed to neutralise the bimetallic couple between the submerged aluminium alloy structure and propulsion components such as stainless steel shaft, bronze screw or steel hydrojet.

This is achieved by fitting sacrificial anodes whose weight and distribution on the hull will be determined individually for each craft by contractors who specialise in cathodic protection.

The task of these anodes is to reduce the electric potential of the bronze, stainless steel and other metals to more negative levels approaching those of aluminium (figure 139).

How the system works

At the working point of the composite system formed by:

- the aluminium alloy hull,
- the screw and shaft (bronze and/or stainless steel) or steel hydrojet,
- the sacrificial anodes,

the anodes release a current such that the potential E_c of the metals (bronze, stainless steel) falls, as does the potential E_{al} of the aluminium. As a result, the potential of all the metals present in the vessel find a common level E_{pc}, thereby eliminating all risk of bimetallic corrosion to the aluminium alloy hull (or other structure).

Electric current flows, and so the anodes are consumed. The life of the anodes depends on a number of factors: the propulsion system, the surface to be protected, surface conditions and the temperature of the sea water, and so it is important to check the condition of the anodes whenever the boat is careened and replace them as necessary.

Choice of anodes

The electric potential of aluminium must not be reduced by more than 200 to 300 millivolts (from its initial potential). The absolute lower limit generally accepted for the potential of aluminium is in the region of - 1100 mV SCE (16). Beyond this there is a serious risk of "cathodic corrosion".

This is why magnesium anodes should be avoided as they reduce the potential of the aluminium too far.

Anodes made from special aluminium alloys such as "Hydral" or "Mercatal" and from zinc on the other hand are very suitable and are widely used.

Notes:

For the cathodic protection of the submerged aluminium alloy structure to be effective, it is essential that:

- the boat's propulsion system is equipotentially bonded to the hull (17)
- the anodes are never painted and the anode and hull are in perfect contact.

Finally, the use of an impressed current system on an aluminium alloy ship is not advisable, as such systems are difficult to handle and pose too many risks for an aluminium hull unless they are carefully designed and correctly set up.

Everything that we have said about the cathodic protection of a ship also applies to a fixed structure that is immersed in sea water and that requires this form of protection. It goes without saying that cathodic protection will only work for the immersed part of the structure.

3.3 Quayside protection of pleasure craft

In marinas, aluminium boats may well find themselves close to or in actual contact with quays made from steel or reinforced concrete and with steel boats as well, and any sufficiently conductive contact between them can cause bimetallic corrosion of the aluminium hull.

To prevent this risk, some companies supply mobile or pendant anode systems designed to be put in place while pleasure craft are wintering. These systems are ideal for pleasure boats that are tied up at the same place for long periods of time.

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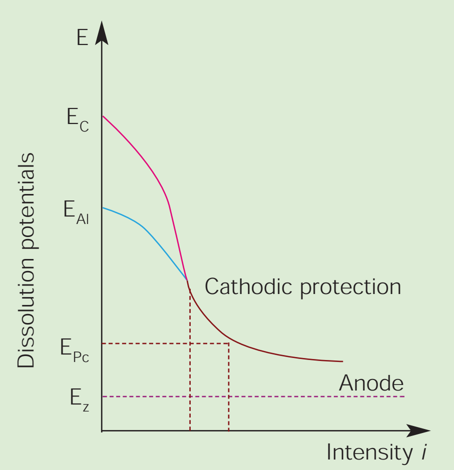
(16) mV CSE = millivolts measured versus the saturated calomel electrode.

(17) Cf. Chapter 10.

NEUTRALISATION OF BIMETALLIC COUPLES



E_C = Potential of other métal (copper, stainless steel…)
E_{AL} = Potential of aluminium
E_{PC} = Potential of the cathodic protection
E_Z = Potentiel of the anode

Figure 139

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CATHODIC PROTECTION