WHITE PAPER

BALMORAL COPPERCLAD™ MARINE ANTIFOULING SYSTEM

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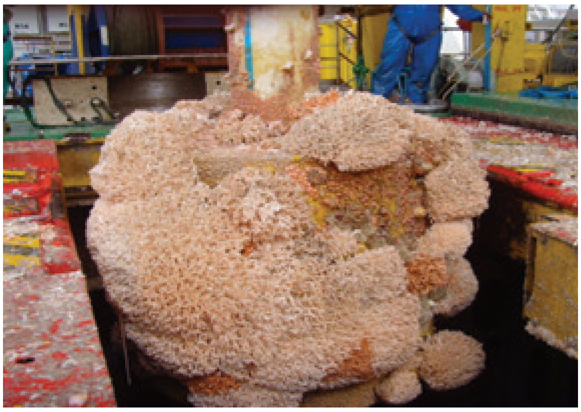
1 INTRODUCTION

Marine biofouling is an issue which must be seriously considered when installing any structure or launching any vehicle into an aquatic environment. Biofouling may be divided into microfouling - biofilm formation and bacterial adhesion - and macrofouling - attachment of larger organisms; of which, the main culprits are barnacles, mussels, polychaete worms, bryozoans, and seaweed.

1.1 **Microfouling** The initial process in biofouling is the formation of a 'conditioning film' on the substrate surface. This film formation commences immediately upon immersion. The composition of the conditioning film varies with the composition of the water and the substrate but typically develops through the absorption of organic molecules (eg, humic substances, polysaccharides and proteins) and ions onto the substrate surface. Subsequent colonisation of the conditioning film by bacteria, fungi and microalgae to form the initial biofilm occurs within minutes, and is rapidly followed by the attachment of macroalgae and protozoa. Microbial cell adhesion follows the attachment of these microorganisms. These microbes produce proteins, glycoproteins and lipids, polysaccharides and other so-called 'extracellular polymeric substances' (EPS) to produce a matrix which binds together the microbes and other microfouling species. The EPS provides a substrate and nutrients for diatoms and algae which in turn facilitate the settlement of other fouling species.

1.2 **Macrofouling**The presence of the EPS microbial film promotes the settlement and survival of drifting invertebrate planktonic larvae and early life forms of macro-organisms such as polychaetes, hydroids, molluscs and barnacles. The 'hard fouling' filter feeders form dense colonies with high growth rates and in appropriate environmental conditions, cause a particularly severe fouling problem.

The biological nature and degree of marine fouling is strongly influenced by environmental factors such as temperature, salinity, light levels and nutrient levels, as well as geographical location. In most marine service environments, 'hard fouling' in significant thicknesses only extends down to 30-50msw, with 'soft fouling' in progressively reducing thicknesses thereafter, down to typically around 100msw. There are however a significant number of locations worldwide where 'hard fouling', specifically by deepwater corals, is known to flourish down to extreme depths. The primary species, Lophelia pertusa has a main depth distribution band of 200–1000msw (particularly 200-400msw), although the species has been identified down to 3000msw. As Lophelia corallites grow 5-10mm pa, major accumulations can accumulate on marine installations during project lifetimes.



Recovered Distributed Buoyancy Module Fouled with Lophelia perusa

Accumulation of such fouling organisms leads to increases in submerged weight, but far more importantly, such fouling has significantly affected the hydrodynamic performance of subsea structures and equipment.

A range of coating systems and technologies has been developed to prevent marine biofouling on all susceptible structures and equipment

2 TYPES OF MARINE ANTIFOULING COATINGS

Marine antifouling systems are of three generic types:

2.1 Biocide release systems, based on dissolution or hydrolysis of the binder. These systems release the biologically-active ingredient at a slow rate, the rate depending upon the identity of the binder system and the local environmental conditions. These are relatively new systems, with somewhat restricted track record however the performance is often outstanding, providing long term resistance to all types of fouling organisms. Some of these treatments are now specified for up to (& even beyond) 20 years untended service.

2.2 External coatings with 'low surface energy' characteristics which prevent strong fouling adherence. When newly applied, the surface is so 'slick' that any initial adherence of fouling species is readily removed by the hydrodynamic drag resulting from vessel movement. However, there is no track record to support the use of such systems in permanent (eg, 20+ years') service & indeed it would appear likely that general wear & tear of the thin (150mic DFT) fouling resistant coating from continual fouling detachment will gradually degrade the surface coating. It is therefore standard practice is for vessels A/F-treated with these materials to be dry-docked and the 'old' coating removed & replaced at 2 (max 4-5) year intervals. Importantly, for effective operation the coating needs significant water movement across the surface (>2.5m/s) to sweep away initial deposits. Where this surface water velocity is not routinely achieved (eg, as would be the case with tethered systems such as risers), periodic cleaning by water jetting or brushing using a ROV is essential. It should be noted that this cleaning operation is likely in itself to damage the very soft and fragile coating and thereby reduce subsequent antifouling performance and coating longevity.

2.3 Inherently toxic surfaces, which inhibit the deposition or growth of the EPS pre-film essential for the deposition of all macro-fouling species. The standard systems of this type are based on copper metal or alloys which are inherently toxic to marine fouling organisms and are subject to ultra-slow dissolution into seawater- these properties deliver outstanding long term marine antifouling service

The primary antifouling systems using this technology are solid 90:10 CuNi alloy sheeting bonded to Neoprene-coated steelwork and systems using CuNi granules embedded in Neoprene sheet cold-bonded or vulcanised onto a neoprene coated substrate. Both solid CuNi sheeting and Cuproprene have massive track record, in many cases going back 25 years, for splashzone antifouling protection of platform jacket steelwork. Neither is suitable for use on complex shapes such as buoyancy modules nor on moulded polymer products such as VIV mitigation strakes.

3 BALMORAL COPPERCLAD™ MARINE ANTIFOULING SYSTEM

Whilst copper-nickel alloy systems are unique in their combination of outstanding antifouling performance and extended service track record, neither of the current standard systems are suitable for use on complex shapes, due to their supply in flat sheet form. Although the 'Low Surface Energy' coatings can be applied to complex shapes, the requirement for a high water current velocity (minimum 2.5m/s) to ensure self-cleaning of incipient fouling precludes their use in static or low water current environments.

Where cross-surface water velocity is either too low or too irregular to ensure self-polishing of a non-toxic surface, or where dry-docking for coating replacement is not an option, those systems whose antifouling properties are based on a continuous and controlled release of biocides from the surface provide effective and predictable performance. Slow-release biocide systems based on tri-butyl tin (TBT) were extensively used in the late 20th century, however, on account of TBT toxicity and persistence in the water column, its use was prohibited in 2003.

Modern 'slow biocide release' antifouling systems are routinely copper-based, usually cuprous oxide, and often in association with copper-organic complexes. The particular benefits of copper are its potency towards marine at the coating/water interface and its limited bioavailability.

Whilst historic 'slow release' antifouling systems relied upon migration of the biocidal chemicals to a permanent surface, as the surface layers become progressively leached, the migration rate of the biocidal components inevitably declines until all antifouling performance is lost, even when substantial reserves of biocidal component remain deep in the antifouling coating. The modern approach is to utilise a binder system which slowly hydrolyses or dissolves, so that the antifouling surface is continuously renewed and the availability of the biocidal component adjacent to the coating surface is maintained. By balancing the binder dissolution rate with the toxic chemical diffusion rate, a stable toxic chemical release rate can be maintained through the service life. For systems of this type, the service life is determined by the applied dry film thickness and, given adequate coating thickness, antifouling service life in excess of 25 years is achievable.

A range of 'slow biocide release' antifouling systems is commercially available; however all were developed for the overwhelmingly-dominant market of antifouling protection of marine vessel hulls. Here, the A/F coating is applied onto an underlying steel anticorrosion coating typically based on epoxy resin. The A/F systems are bonded to this chemically-active epoxy coating using specially-developed bridging primer systems. Being developed specifically to bond to the chemically-activer epoxy substrate, the standard A/F primer systems are unsuitable for bonding to very different, and generally 'low surface energy/activity' substrates such as polyethylene and polyurethane as dominantly-used in marine buoyancy and polymer products.

Balmoral has worked with a market-leading marine antifouling paint supplier to develop Balmoral CopperClad which a complete coating and application system specifically designed to achieve outstanding bonding performance between polyethylene or polyurethane substrates and a market-leading 'slow biocide release' antifouling coating system. The antifouling coating is one of the Jotun SeaQuantum range, and which is based upon a silyl-acrylate binder which exhibits continuous slow solution and slow hydrolysis in seawater. This dissolution & hydrolysis of the binder continually renews the surface concentration of the biocide system and gradually releases biocide components into the surface/water interface to ensure continuous protection of the coated structure.

The unique aspects of the Balmoral CopperClad system are a proprietary multistage procedure used to prepare and activate the polymer surface, and the selection of primer/binder system.

4 COPPERCLAD APPLICATION PROCESS

The surface preparation procedures are confidential; however the antifouling top coat is applied by conventional air-powered spraying. In order to ensure the essential drying conditions required to avoid soft coatings and subsequent cracking, the required final film thickness is applied in a number of coats each 250-300mic WFT and each producing a final coating thickness of 125-150mic DFT. The drying duration between coats is critically dependent upon both ambient temperature and air movement rate and in order to provide both tight control of these parameters and high production efficiency, Balmoral has developed an automated coating line where individual products index past individual work stations for surface preparation, surface activation and multilayer coating application, all under temperature-controlled conditions.

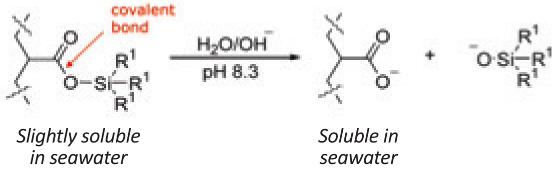
5 BALMORAL COPPERCLAD SYSTEM IN SERVICE

The CopperClad antifouling system comprises a modified epoxy primer/tie coat to provide the bond between the polymer (PE or PU) substrate and the copper-containing antifouling layer. The antifouling layer is built up to the required thickness for the project service life under the project service conditions and as a number of individual coats.

There are 3 discrete stages in the service life of the Balmoral CopperClad system:

Stage 1

Conversion of the hydrophobic covalent silyl acrylate polymer surface to an ionic acrylate surface.



This conversion process enables water penetration into the coating.

Stage 2

Solubilisation of copper oxide through conversion to copper ions and subsequent copper depletion of the immediate surface layer. This is accompanied by slow hydrolysis and solubilisation of the acrylate moiety into seawater. Leaching of the copper oxide initially proceeds at a faster rate than the hydrolysis/solution of the acrylate polymer, allowing the progressive development of a layer of copper-depleted acrylate polymer at the surface. The increasing thickness of this ‘leached layer’ progressively retards diffusion of copper to the coating surface.

Stage 3

Stabilisation of the thickness of the copper-depleted acrylate polymer layer on the surface. At the end of Stage 2 above, a steady-state situation develops where the thickness of the ‘leached acrylate layer’ becomes sufficient to stabilise copper diffusion at a very low level. Thereafter, through Stage 3 to the end of service life, the hydrolysis & solubilisation of the acrylate layer and the diffusion of copper ions come into a balance where the thickness of the leached layer and the copper loss rate reach mutual stability. The presence of this copper-depleted layer is shown below. In this cross-section through the coating after a simulated service test, a section of the coating (on left side) is protected from erosion by an epoxy paint barrier coat (shown as white layer). 85 microns of the adjacent CopperClad coating (on right side) has been eroded/dissolved away and on the top of this can be seen the thin (approx. 10 microns) and paler-coloured ‘leached layer’.

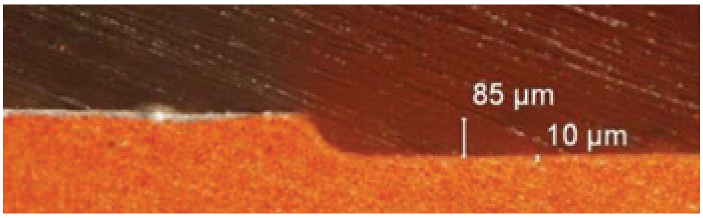
This steady erosion of coating thickness for a given set of service conditions of temperature and water velocity allows the design of required coating thickness to suit project conditions.

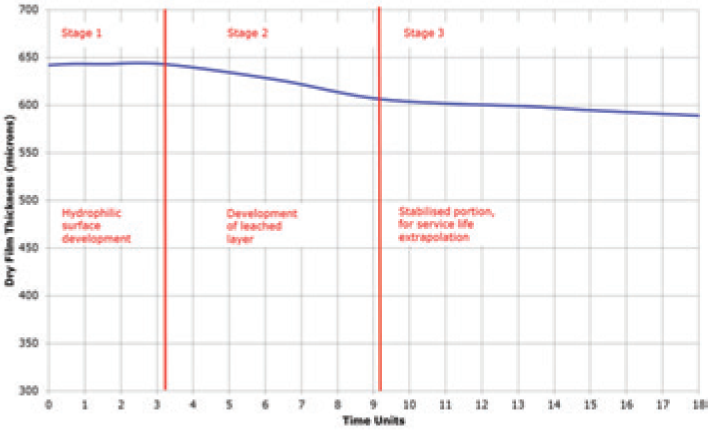
These 3 stages in the service life can be identified by monitoring coating thickness during service. The graph below shows the change in coating thickness during the early months of service.

During the initial phase ('Stage 1'), the coating thickness remains essentially unchanged, whilst the hydrophobic silyl acrylate surface is converted to hydrophilic acrylate.

During the next stage ('Stage 2'), rapid solubilisation of copper occurs, leading to relatively rapid thickness erosion until the copper-depleted 'leached layer' has formed.

Finally, a 'steady state' condition of balanced solubilisation of acrylate binder and solubilisation/diffusion/release of copper is achieved. The very slow and stabilised rates of binder and copper solubilisation result in an essentially linear reduction of coating thickness with time through to end of life. This linear Thickness vs. Time relationship can be used to determine the required coating thickness for project service conditions and life.



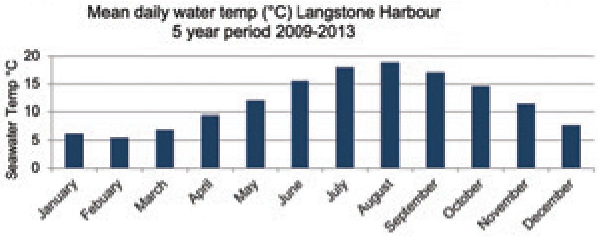


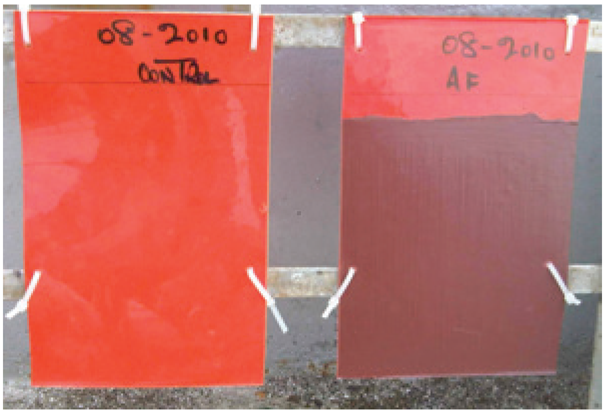
Change of Coating Thickness with Time under 'Temperature Acceleration' conditions

6 PERFORMANCE IN FIELD TRIALS

The antifouling performance of Balmoral CopperClad has been monitored in marine field trials by the Institute of Marine Science, University of Portsmouth, on trials raft in Langstone Harbour, UK. The CopperClad was applied onto orange polyether polyurethane sheets.

Environmental conditions at the test site over the test period were as follows:





Control and CopperClad-treated sheets before immersion

Control and CopperClad-treated sheets after 1 year immersion

Control and CopperClad-treated sheets after 2 year immersion

7 COATING ADHESION

The standard substrates used in marine polymer products are rotationally moulded polyethylene (eg, buoyancy module shells) and cast polyether polyurethane (pipe/cable protection products and buoyancy module coatings). Adhesion testing has been performed on sheet samples of each substrate.

As CopperClad is a soft polymer coating, standard adhesion tests such as ‘dolly pluck’ cannot be used. Jotun recommends adhesion testing using ISO 16276-2:2007, ie, ‘X-Cut’. Adhesion testing on CopperClad applied to the two substrates gave results as below.

Substrate	**Test**	**Standard**	**Result**	**Comment**
Polyethylene	X-Cut	ISO 16276-2:2007	Level 0 (no coating removal)	Pass
Polyurethane	X-Cut	ISO 16276-2:2007	Level 0 (no coating removal)	Pass

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