Jonathan R Matias, Executive Director, Poseidon Sciences Group discusses the recent trends in coatings R&D on biocides

Perspectives on biocides

For the general public, the word 'biocide' is almost like a dirty word. Yet biocides remain an essential part of modern life, protecting the very same public that decry it from the host of bacteria and viruses in food, household items, such as cosmetics and toiletries, to swimming pools, paints and medical supplies. By definition, a biocide can mean a chemical or micro-organism that not just kill but also prevent, deter or render ineffective any organism (micro-organisms or any harmful larger life form). The word thus covers a broad range of bioactive ingredients, such as pesticides, repellents, disinfectants, antimicrobials, anti-fungals, algaecides, anti-virals and anti-parasites. Though much maligned by environmentalists, biocide manufacturers continue to provide a critical and often thankless service.

Imagine our world without biocides. Contact lenses would no longer function because of bacterial growth. Toothpastes won't work anymore and cavities would increase. Most superficial wounds would become deadly and serious wounds automatically become fatal. The food we eat and the cosmetics we use would no longer be stored; medicines won't last longer than a few weeks on the shelf. Wood products would rot because of decaying fungus. Architectural paint even in the can would become fouled during storage and those painted on surfaces covered by mould/mildew in a matter of weeks. Container ships slow down to half speed and ship transport would cost twice as much because of barnacle overgrowth on its submerged hull. Our lifestyle reverts back to pre-World War II days when a common infection, otherwise non-lethal, would decimate people by tens of thousands.

Biocides, now a US$7bn market on a global scale, are a necessary 'evil' that is aggressively regulated each passing year, making older biocides obsolete from an environmental protection viewpoint and new ones prohibitively costly to develop under the new guidelines. The environmental issues that cause all these difficulties arise for a variety of reasons, most of them justifiable under our modern understanding of how chemicals, in general, impact health and environment. These unforeseen secondary effects include endocrine disruption (gender-bending) effects seen in lower animals in which biocides can cause sex changes in aquatic animals, toxicity to non-target animals and bioaccumulation in higher life forms including human beings. In defence of the industry, these environmental consequences of biocide use are as new to the industry as to any other scientific disciplines. It is not always possible to predict all the possible negative effects or even test for them in advance. Part of this problem is that the regulatory requirements to registering biocides in the past did not include such unforeseen consequences.

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Inherently, a biocide is like a double-edged sword – with one side slicing off unwanted organisms, while the other side is doing the exact same thing to other unintended targets. The trick of creating 'safer' biocides is like a man in a circus, balancing on a high wire, precariously trying to stay on without falling on either side. This balancing act can be seen with relatively newer compounds, such as SeaNine 211 and Econea, with very short half-life in the environment but nevertheless designed to be as toxic as the rest of the biocides in the market.

BIOLOGICAL RESISTANCE TO BIOCIDES

An emerging trend that will disastrously impact the biocide industry in years to come is the phenomenon of resistance. A biocide is rarely 100% lethal and the idea that a tiny population of organisms survive the biocide exposure to procreate and form a new and increasingly resistant population is decades old. This trend is increasing at an unprecedented level, with micro-organisms showing resistance to antibiotics and insects being resistant to pesticides. However, even in human beings, resistance to drugs is common, particularly in cancer cells exposed to toxic anti-tumour pharmaceuticals or normal cells being resistant to insulin after prolonged exposure. This phenomenon is universal. No one as yet has seriously looked at resistance happening on mould and mildew in paints or barnacles on marine coatings. But rest assured that it is happening as organisms evolve even faster by the introduction of biocides as a catalyst of biological change.

NEW TRENDS IN NANOTECHNOLOGY AND BIOCIDES IN COATINGS

In the wake of biological resistance and the environmental issues of biocide use are new directions in research. The past decade has seen a flurry of activities in creating surfaces that resist fouling through nano-structured shapes on the surface of a coating, through chemical modifications that repel organisms and the use of permanently bound biocides that do not leach out of the paint. While such applications represent a tiny fraction of the overall biocide industry in general, this new trend will have an impact especially on the future of coatings.

Foul release coatings to prevent barnacles from attaching to surfaces have been around for a number of years and are slowly gaining ground. These fluoropolymer coatings, pio-

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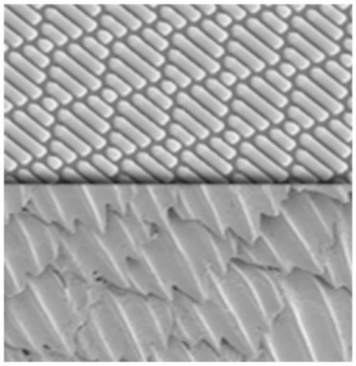

Fig 1. Microtopography of the Sharklet pattern (above) and shark skin (below). Photo: Sharklet Inc

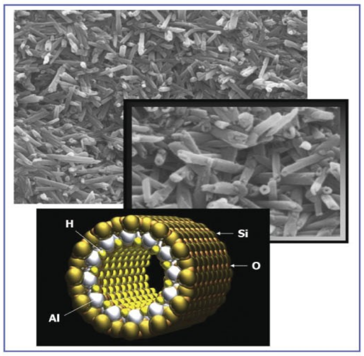

Fig 2. Scanning electron micrographs showing the tubular structure of halloysite clay and a schematic representation of the chemical structure of the microtubule. Photo courtesy of Applied Minerals, Inc

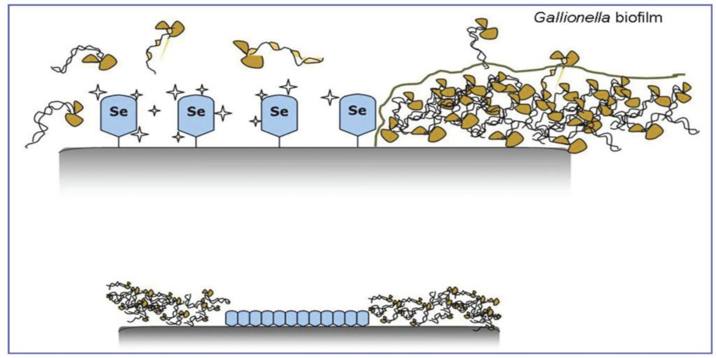

Fig 3. Schematic representation of iron degrading bacteria, Galionella sp, avoiding surfaces with covalently bound selenium

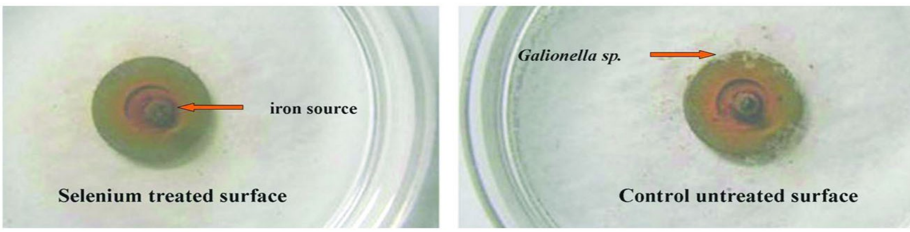

Fig 4. The presence of covalently bound selenium prevents growth of Gallionella sp overgrowth over metallic surface after nine days of immersion in Galionella rich culture

Suggested reading
http://www.appliedminerals.com/
http://news.rpi.edu/update.do?artcenterkey=2759
http://www.paintsquare.com/news/article_news.cfm?id=4686&nl_versionid=684&trackid=19765310
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neered commercially by International Paints, serve as a benchmark for other companies developing fluoropolymer chemistries with the objective of creating tougher coating matrices than conventional silicone-based products.

Nanotechnology is becoming a new paradigm in biocide research. Scientists from the US Naval Research Laboratory, Massachusetts Institute of Technology and Penn State University recently engineered a water-repellent film by a process that deposits nanorods on a thin film. This method, published in Nature Materials (December 2010), created a smooth surface that may be useful in preventing biofouling adhesions.

On a different track this year, scientists at Rensselaer Polytechnic Institute demonstrated a biocidal effect by inserting lysostaphin, a naturally occurring microbial-derived defensive enzyme, in a carbon nanotube. Once incorporated in latex paints, this combination of enzyme-nanotube complex eradicated methicillin resistant Staphylococcus aureus (MRSA) on surfaces without leaching to the surface of the coating.

Both recent technologies mentioned here, once commercially developed, open new opportunities in coatings that rely on nature-inspired technologies. However, they will need to overcome the commercial hurdles that Sharklet Technologies has already gone through and now moving towards commercial promise. The Sharklet pattern, developed by Anthony Brennan at the University of Florida, was based on mimicking the microscopic topography of shark skin, forming a ridge pattern designed to discourage organisms, such as bacteria and barnacles, from settling (**figure 1**).

Adhesive-backed 'skins' can now be placed on surfaces to prevent bacteria from transferring in high touch areas, particularly in a hospital setting. Whether these patterns can be employed in the more aggressive environment of a ship's hull or the surfaces of architectural coatings, where biocides play a dominant role, will need to be further demonstrated in the future.

DELIVERY SYSTEMS FOR BIOCIDES

There are a number of new delivery systems in the form of sophisticated micro- and nano-capsules. However, these systems tend to be quite expensive for applications in paints and coatings where price consideration is a high priority compared to pharmaceuticals or cosmetics. Promising new materials for controlled release actually comes from Mother Nature in the form of tubular mineral clays called halloysite wherein natural weathering processes created pores with a 30nm diameter and one micrometer length (**figure 2**). These naturally occurring microtubules permit entrapment of bioactive ingredients at a much higher loading capacity than conventional porous materials and at a much cheaper price than synthetically produced carbon nanotubes. Initially developed as an inexpensive controlled release technology for biocides in marine paints by the US Naval Research Laboratory, this technology has recently been licensed to Applied Minerals, the world's largest producer of halloysite clay, for a broader range of uses. Halloysite combines this controlled release advantage with its added potential as a rheology modifier and filler in coatings.

ALTERNATIVE BIOCIDAL AND NON-BIOCIDAL TECHNOLOGIES

Research at Poseidon Sciences follows similar trends but using totally different approaches.

In biocide research, Poseidon scientists have entered into R&D collaboration with Selenium Ltd (Texas) in developing new applications using covalently bonded selenium [Se]. Compared to copper or silver, Se can be permanently attached to the surface yet continues to be biologically active. Se is a nutritional supplement and also possesses anti-bacterial properties through the release of reactive oxygen species, such as hydrogen peroxide. Upon contact with Se-treated surface, the reactive oxygen released by Se kills the bacteria, thereby preventing biofilm formation (**figure 3**). This killing effect is short range and does not extend far from the coated surface. This proprietary technology already achieved FDA 510(k) approval for two separate Class II medical devices and the first coated antimicrobial orthodontic products were introduced to the market in 2009 to prevent dental plaque. Because it is bound permanently to the surface and yet remains bioactive, Se does not have to leave the coating to exert its antimicrobial action. Thus, leaching of the biocide to the environment is prevented.

The most urgent environmental issue in recent years involves the hydraulic fracturing process to extract oil and

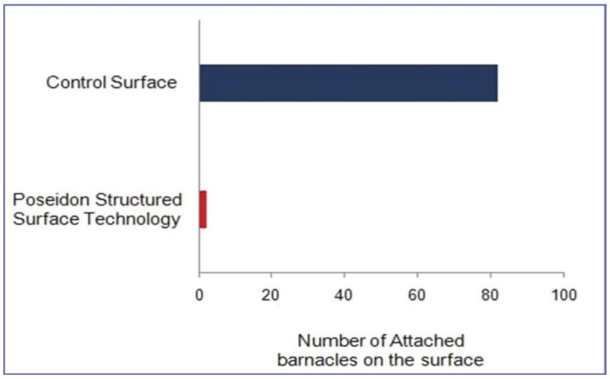

Fig 5. Barnacle settlement on panels expressing PSST surface structure compared to control surface. Immersion for 30 days conducted in Tuticorin Bay, India

natural gas in USA, Europe and other countries with commercially viable shale oil deposits. Hydraulic fracturing, a method pioneered by Halliburton, involves sending high pressure fluid containing sand through a well bore deep in an oil/gas bearing shale formation to cause fracture. This is followed by injection of proppants typically composed of ceramic beads that are lodged inside the shale to keep the fracture open. The fractured shale allows afree flow of natural gas and oil into the pipeline that brings them to the surface for collection.

Anaerobic iron and sulphate degrading bacteria rapidly proliferate in the fracturing fluids, causing corrosion of the pipes and clogging of the proppants. Biocides are typically included in the fracturing fluid to inhibit bacterial growth. However, over the years, there has been a tremendous public concern about the environmental impact associated with hydraulic fracturing and, in particular, the possible contamination of aquifers and nearby streams by biocides and other chemicals present in the fracturing fluid. Considering the economic and strategic value of oil-gas reserves, an alternative technology needs to be developed as soon as possible to solve this environmental concern. A biocidal approach is still the best method to keep Gallionella and Desulfovibrio bacteria from clogging the wells and corroding the pipes. However, the biocidal material should be environmentally friendly and must not freely diffuse away from the borehole.

The Poseidon-Selenium collaboration is aimed at developing coating technologies that would prevent this type of fouling without the need for biocidal treatment that places the environment at risk. Recent studies have shown that Se-treated metal prevent the migration of the iron degrading bacteria over this surface and prevent concomitant degradation of the metal surface (**figure 4**). While research is continuing, emerging data from the laboratory shows that ceramic proppants can be coated with Se to prevent biofilm formation and eventual clogging.

In structured surfaces, Poseidon scientists are continuing to develop a new concept in structured coatings, referred to as Poseidon Structured Surface Technology (PSST), that no longer rely on nano-sized topography but on an understanding of barnacle cyprid attachment behaviour in relation to surface patterns. Data from field exposure of such structured coatings in the barnacle-rich tropical ocean environment of Tuticorin Bay in India, show overwhelming inhibition of barnacle adhesion in the absence of biocides (**figure 5**).

What does all this research mean to the biocide industry? This research is pointing in the same direction that the industry is already pursuing – better, more eco-friendly approaches. Although these new ideas will take years to become part of mainstream business, it is meant to complement the industry by enabling these technologies to find niches where conventional biocides may present environmental issues. Structured coatings, controlled delivery systems that minimise release of biocides to the environment and covalently bonded biocides will eventually become part of the mix of technologies that make up the biocide industry of the future.