

Shedding light on the marine paints industry

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The marine industry is facing a number of challenges relating to the replacement of TBT. Naturally, research is continuing, but there are more issues to be addressed, such as the safe removal of TBT-containing coatings and cost issues relating to the alternatives. Jonathan Matias of Posiedon describes the latest situation in Korea and the rest of Asia.

'Without relevant regulations on the safe removal, treatment and disposal of TBT, more tin could be released to shallow navigable coastal waters than the amount that ships discharged by to the ocean during the last 40 years.'
 Michael Champ, ATRP Corporation

The Asian marine paint industry is undergoing a sea of change following the IMO treaty banning the application of tributyl tin (TBT)-based paints. The treaty, with a retroactive date of 1 January, 2003, enters into force once it is ratified by 25 states (representing 25% of the world's shipping tonnage). Experts believe that the treaty may not be fully enforced by this year, but by 2005, well before the IMO's specified total ban of 1 January, 2008.

The sentiment over reform was palpable during Poseidon Ocean Sciences' workshop in Pusan, South Korea in April 2003. More than 40 technical representatives and administrators from the major coatings and shipbuilding industries mainly from Korea and Japan attended the workshop on nontoxic antifouling strategies for the marine paint industry. The high attendance, along with robust participation from experts and participants, were testimony to the keen awareness of the dynamic changes in the regional market for antifoulants, notwithstanding the patchy recoveries of some Asian economies, the then-prevailing jitters over the Iraq war and the onset of the SARS epidemic.

REGULATORY ISSUES AND SETBACKS

Japan ratified the IMO convention in February of this year. In Australia, an agreement between the industry and government will see the phasing out of paints containing TBT by 31 July, 2003. The European Union's Council of Ministers has agreed in principle to adapt the convention into EU law. Panama, whose flag flies over 21% of the world's fleet, has indicated that it will sign the treaty.

The IMO's Marine Environment Protection Committee recently concluded its session in mid-July this year where it adopted guidelines for sampling antifouling systems and guidelines for

However, there are experts who question the wisdom of imposing the ban, given studies that show that levels of TBT have fallen and that many alternatives have yet to be tried and tested.

For one, Michael A Champ, President & CEO of ATRP Corporation, an environmental consultancy in Arlington, Virginia is concerned about the lack of appropriate regulations from the international to local levels for the safe removal, treatment and disposal of the TBT stripped from some 30,000 ships in shipyards and drydocks.

Without such regulations, more TBT could be released to shallow navigable coastal waters than the amount discharged by ships over the last 40 years to the ocean.

In the US, only the state of Virginia has discharge regulations on releases from shipyards. In Europe, several nations regulate discharges. The legislative policies enacted by these countries (mostly from the developed world) with regulations on the use of TBT to protect their local marine resources 'have had far-reaching environmental and economic impacts, which have in essence, transferred TBT contamination to those countries least able to deal with it,' said Champ.

Lacking the funding or environmental expertise available for monitoring and developing ways to deal with these high technology compounds, the 'unregulated' countries end up with more contamination because they do not have the necessary regulatory structure to prevent it, he added.

KOREAN RESEARCH

In Korea, the government has long banned the use of TBT on small ships and it is introducing a registration scheme for antifoulants. But a study by Won Joon Shim of the Korea Ocean Research and Development Institute found that TBT contamina-

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in Korean waters, particularly near TBT source areas such as its harbours and shipyards. A logistic regression risk assessment model was run with expected TBT concentrations in coastal waters, along with a survey on toxicological data of TBT.

Professor Shim's studies showed that based on the acute and chronic toxicity data, more than 95% of marine species could be protected from TBT contamination. But around 15% of species could be affected by TBT contamination in chronic threshold toxicity levels.

Other chronic problems remain: Alternatives to tributyl tin are more expensive, the effectivity of such products is under question, and nature sometimes pulls surprises.

In China, for instance, it was found that water from the rivers Yangtze and Hwangpu contained sulphides that diminished the efficacy of antifoulants being applied on ships docked in shipyards along these rivers.

Kumgang Korea Chemical warned that after conducting two years of raft tests on its own and competing tin-free products, the contaminated water from the rivers had all but cracked, delaminated or diminished the solubility of antifoulants. In one shipyard, low concentrations of sulphur resulted in blackened coatings in six months.

Although copper-based coatings are the mainstay of the shipping industry for now, the cost of the coatings is two to three times more expensive than TBT-based paints. It was clearly evident during the workshop in Pusan that the industry viewed copper-based antifouling paints as transitional technology; a stop-gap option until more novel nontoxic alternatives are developed.

A GROWTH INDUSTRY

Manufacturers pursue the development of various types of antifouling paints, whether ablative or water-based, with the end-goal of products being environmentally friendly. Coatings companies hope to expand their roles as global players; through acquisitions or the introduction of products to new markets. The Freedonia Group estimates that the world demand for biocides used as preservatives in paints and coatings is projected to increase 6.3% per year through 2006.

The Asian marine paint market is growing rather than contracting. This is evidenced by the flurry of activities among raw material suppliers and coatings manufacturers. In May this year, Dow Chemical of the US opened its 25 million-dollar epoxy resin plant in Zhangjiagang, China.

Among the products of this unit are solid solution epoxy resins for liquid marine paints. Demand for products such as these is growing by double-digits in China where the economy is growing and businesses are relocating.

The new unit will supply China, Asia and Australia. Kansai Paint of Japan is constructing a paint production facility in China that is expected to raise its marine paint production capacity to 78,000 tons per year from 48,000 tonnes per year. Kansai also said it expects sales from marine paints to rise to ¥8.5 billion from ¥6.0 billion this year.

Akzo Nobel continues its expansion, signing a contract with specialty chemicals producer NOF of

Japan to acquire the worldwide marine and aerospace coatings businesses of its subsidiaries – US Paint in St. Louis and NOF Europe.

These two businesses produce the 'Awlgrip' brand for marine coatings systems and posted total sales of US\$30 million in 2001. The move is expected to position Akzo Nobel as a major player in the market for professional above-water topside coatings. The firm's joint venture with its partner in Korea, DPI, has been split into two -- a powder coatings venture and a marine and protective coatings concern.

Despite a patent dispute between Chugoku Marine Paints and Chokwang Jotun, Chugoku Marine Paint reported a rise in profit to ¥717 million (US\$6m) in the year ended March 2003, a turnaround from a loss of ¥1.07 billion.

RESEARCH ACTIVITIES

Despite hindrances and skepticism, research and production forge ahead. Chinese scientists have developed nontoxic coating for watercraft by combining organic clay and bioactive substances extracted from natural and unpolluted pepper (capsaicin). This particular coating, reported by the China Chemical Reporter in November 2002, tested on seven ships in the South China Sea, has shown to minimize navigation resistance, thus reducing energy consumption.

Isuzu Ceramics Research Institute, a unit of the Japan's Isuzu Motors, hopes to have a barnacle-reducing ship coating made from epoxy resin on the market in 2004. This resin is a hydrophilic ceramic that reacts with seawater to produce a small quantity of ammonia that barnacles dislike. The coating reduces drag by 3-5% on its own, and reduces barnacle adhesion by 70-80%.

Altex Coatings, a dominant player in the marine paint industry in New Zealand, is completing its research exploring potential uses of algal toxin as an antifoulant. The algal toxin attacked Wellington harbor in 1998 and has been isolated and cultured from the harbor for experimental purposes.

ASSESSING NEW ANTI-FOULING CHEMICALS

The Tropical Marine Science Institute at the National University of Singapore continues to develop bioassays to assess new antifouling chemicals and materials, while extracting from local marine organisms compounds that may be effective and nontoxic in fighting off biofoulers.

A similar effort is being undertaken at the Hong Kong University of Science and Technology's Dept. of Biology. Professor Pei-Yuan Qian and his research team have isolated and identified bioactive substances that act as nontoxic antifoulants against major fouling organisms in Hong Kong's waters.

By using the bioassay-guided isolation and purification of antifouling compounds they have successfully purified some bioactive compounds for the induction and inhibition of larval settlement of major foulers (including 50 marine soft-bodied organisms such as seaweeds, sponges, soft corals, and tunicates).

In addition, over 150 species of marine bacterial species have been also screened. Non-toxic antifouling compounds have been isolated and

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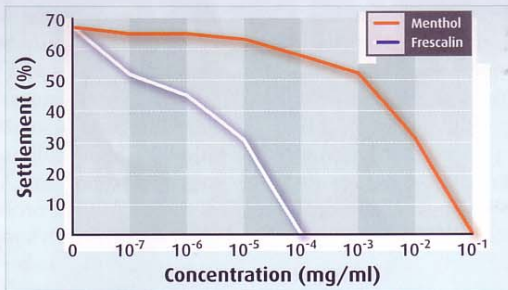


Figure 1: The inhibition of the settlement of the cyprid larvae of the barnacle, *Balanus amphitrite Darwin*, in the presence of Frescalin and menthol. Frescalin was three orders of magnitude more effective than menthol.

purified from some of the bacterial species. The research has also led to the creation of a large collection and database of bacterial culture from tropical and subtropical environment.

Dr Qian believes that bacterial metabolites are the best sources of non-toxic antifouling compounds for industry application.

DOLPHINS AND SEAL MIMICS

Among the test coatings being evaluated by the US Navy is a combination of polymers – one smooth and hydrophilic; the other 'water-avoiding' and complex – which, when analyzed on nanometer-scale dimensions, resembled the rippled skin of dolphins. The dolphin's rippled skin is cited as reason why barnacles do not adhere to it. The concept of combining the polymers came from Karen Wooley, a chemist and professor at Washington University in St. Louis. 'Different formulas give us different compound surface properties, so if we tweak the size of the surface features to what's needed, perhaps we'll finally have outwitted the barnacle,' Wooley told the *Ocean News and Technology* magazine.

The concept of mimicking the method by which marine mammals protect their skins is also evident in SealCoat AF, a product of Shanghai-based company SealCoat. The coating, developed by Swedish inventor Kjell Alm more than 10 years ago, is based on the application of synthetic microfibers sprayed onto a surface coated with a layer of epoxy-free solvent adhesives. The fibers prevent hardfouling from settling in, the same manner that seals can protect their fur. This year, the company hopes to operate in 20 major marine markets around the world.

In June this year, Poseidon Ocean Sciences signed a strategic alliance with international flavor and fragrance producers Symrise to produce and market Frescalin. This is a nontoxic antifouling additive for use in marine paints, contains a novel menthol analogue, menthol propylene glycol carbonate, which is specifically targeted against hard fouling organisms, such as barnacles.

Antifouling co-biocides, such as Sea-Nine 211 or Zinc Omadine, are effective against soft-fouling organisms, but relatively weak against hard foulers. While high copper concentrations are commonly used as a means of preventing hard fouling, the future direction of antifouling marine coatings will be in the development of low copper paints and eventually metal-free systems.

This creates a market opportunity for a variety

of compounds that can be used to prevent attachment via a repellent type system.

Poseidon's research in prevention of hard fouling spans a period of over 10 years. This research started from the isolation and identification of active ingredients from marine sponges, identification of the active portions of large antifouling chemicals and screening of naturally occurring analogues using the barnacle settlement assay.

Through the Natural Bioproducts Screening Program, Poseidon's team was able to identify a class of biochemicals that mimic the biological action of naturally occurring, hard to synthesize biochemicals, such as juncline.

One structure that produces a biological effect of inhibiting barnacle settlement was menthol. When screened for biological activity, menthol and menthol analogues inhibited barnacle settlement through a repellent action without any toxic effects by rendering surfaces unpleasant for barnacles to settle. The next challenge was to develop novel compounds that can remain in the paint for longer periods of time.

Hence, the development of Frescalin, which has a higher boiling point and greater biological action than menthol (see Figure 1). Ongoing field studies on Frescalin in many marine exposure conditions show greater efficacy than the naturally occurring menthol. Frescalin is registered in Korea and in the process of being registered in many other countries.

PROSPECT FOR THE FUTURE

Given the ongoing research and ventures pursued, we remain optimistic of the prospects of antifouling coatings in the Asia Pacific region.

It remains a fact that Asia accounts for up to 70% of the global marine paints market. Over 60% of new ships are being built in Korea, Japan and China. Of the 60,000 commercial ships of all types plying the world's oceans, over 60% are still being drydocked in ship repair facilities throughout the Asia Pacific region.

While the industry strives for low copper and ideally metal-free paints, it is becoming clear that there is no such thing as a 'magic bullet' that will take care of all the fouling problems that marine coatings may experience as the ship goes from one port environment to another.

Gone are the days of toxic paints, including TBT-laced paints, that kill all types of fouling. The future antifoulant will likely be a combination of biologically safe active compounds that prevent attachment of organisms selectively.

Frescalin is one of the first generation of compounds that will be in this family of antifoulants. Combinations of Frescalin with others will create new market opportunities for biocide makers in the future.

A way to enhance the competitiveness and accelerate new developments is communication among the research institutions and the marine paints industry. One idea resulting from our Pusan conference is the formation of a Biofouling Association in the Asia Pacific region, which can begin to address these key issues for the industry.

The Asia Pacific market is the dynamic playing field for such ideas and new technologies. APCJ