Validating ecofriendly claims in marine antifouling coatings

Polymer Paints Coatings Journal
(in press)

Araceli Q. Adrias and Jonathan R. Matias

Poseidon Sciences Group

122 East 42nd Street, Suite 1700
New York, NY 10168 USA

Contact:

Jonathan R. Matias
Executive Director
jrmatias@poseidonsciences.com ; poseidonnova@aol.com
mobile: +1 646 251 1661

The years following the ban on tributyltin (TBT) antifoulants in marine paints saw the proliferation of marine coatings companies touting ecofriendly designations in their website and on their paint cans. Just how ecofriendly are marine paints? What constitutes an ecofriendly label? How does one test a marine paint for its environmental safety attributes? These are but a few of the questions that will plague the industry as consumers seek a better definition and accountability from companies that manufacture paint.

The pharmaceuticals, chemicals and cosmetic industries have been inundated with regulations, public backlash and unwanted attention from environmental groups because of chemicals that are perceived as environmentally unfriendly. These chemicals end up in the aquifers, rivers and eventually in the ocean. Besides reports on accumulation of such chemicals in the food chain, the main concern has been on those so called 'gender-bending" or "endocrine disrupting" chemicals, i.e., compounds that cause reproductive damage or intersex in animals. Remember the days when TBT became a target when imposex was detected in some snails? Imposex is a term that applies to a pathological condition in sea snails wherein the sex organs develop abnormally into the opposite sex in the presence of low levels of pollutants. The legislation against TBT has opened the way to make it much easier to legislate out the next chemicals—rightly or wrongly—based on the precautionary principle as described here [1]:

The precautionary principle states that if an action or policy has a suspected risk of causing harm to the public or to the environment, in the absence of scientific consensus that the action or policy is harmful, the burden of proof that it is not harmful falls on those who advocate taking the action. This principle allows policy makers to make discretionary decisions in situations where there is evidence of potential harm in the absence of complete scientific proof. The principle implies that there is a social responsibility to protect the public from exposure to harm, when scientific investigation has found a plausible risk. These protections can be relaxed only if further scientific findings emerge that provide sound evidence that no harm will result.

This 'precautionary principle' originated from the 1992 ethical responsibility to maintaining the natural environment. But, environmentalists interpret this principle in more stringent terms in that the company must demonstrate the absence of harm before the new technology is put into practice.

The key phrase that affects the marine paint industry is that policymakers have "discretionary decisions in situations where there is evidence of potential harm in the absence of complete information." And, since this has been made a statutory requirement in European legislations, it becomes necessary for companies to become more pro-active in making sure that their chemicals or products does not fall in the potentially harmful category or otherwise lose the business opportunity.

Since the days of aggressive environmental action against TBT and despite the new focus on cuprous oxide, the marine paint industry has largely been spared much of the limelight that has befallen cosmetics and pharma companies. **But not for long.** Unlike chemicals in plastics or biochemicals in cosmetics/ pharmaceuticals that inadvertently end up in the environment, marine paints in contrast are **intentionally** placed in the marine environment to protect ship hulls from barnacles and other fouling organisms. It is just a matter of time when the focus of the often dreaded environmentalists shifts back in earnest on marine paints once again.

Is any TBT-free or biocide-free marine paint really ecofriendly? Claiming that a product is ecofriendly may be good for marketing now, but at some point in the near future we will have to be accountable for such statements. Most responsible chemical manufacturers have done their job in complying with the obligatory safety tests. However, except for some tests on freshwater fish (such as minnows and zebra fish), most toxicity tests are done as LD_{50} studies on mammalian systems, such as rats, mice, and birds. How such ingredients affect actual marine life is rarely part of the test paradigms primarily because these organisms are inconvenient to study.

If the regulatory agencies already accept the safety test based on non-marine organisms anyway, then why would it matter? Information technology has tortoise. The public, represented by environmental groups, can sway regulatory agencies and public opinion to the detriment of the industry so easily in this electronic age. It is becoming essential as part of any strategic / marketing plan to know as much as possible about the marine environmental issues that may impact the launch of a new product or an existing one. It is much better to have compelling evidence of safety on file rather than scramble to have them later. Compared to the sizeable investment already made on developing such chemicals, taking the extra precaution is a prudent step.

Coatings comprise a diversity of polymers and a myriad of other additives. More recent environmental studies show that while individual chemicals may pose minimal risk, the combination with other chemicals and the persistence of such chemicals in the environmental can play a significant role in the overall toxicity of a finished product. Moreover, the effect may not be so easily measured by acute tests. Cuprous oxide, for example, is both a toxicant and an essential binder. While it has minimal toxicity under acute tests, sublethal chronic doses have substantial physiologic effects that can affect the survival of marine species [2]. Zinc is a common ingredient in many coating systems. However, tests on cultured fish cell lines show zinc compounds are at the top ranks of toxic compounds in cytotoxicity studies [3]. Thus, even in the absence of organic biocides, common coating ingredients can be substantially toxic on their own.

There are standardized methods in testing toxicity, such as the ASTM (American Society for Testing and Materials) E729-1996 (re-approved 2002) in the United States and other similar methods in Japan and European Union. As a marine research group, Poseidon Sciences recently began a program to create validation methods that apply specifically to the marine paint industry for claims of ecological safety. A typical test, referred here as the Marine Toxicity Sentinel Screening or MTSS, is shown in the schematic in Fig. 1 wherein a coated PVC coupon measuring 5.0 cm by 7.5 cm was suspended inside a glass container filled with 1 liter natural seawater. The marine larvae used in the toxicity studies were either from hatchery reared or wild caught specimens.

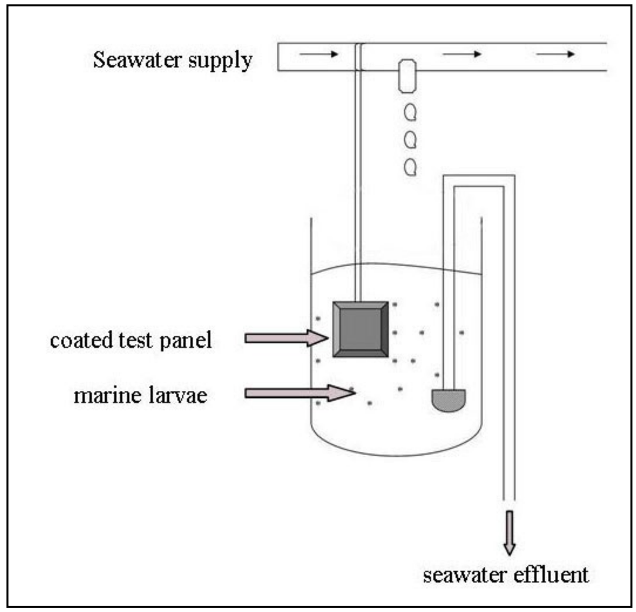

Figure 1. Schematic diagram of Poseidon's Marine Toxicology Sentinel Screening test system.

Although Poseidon Sciences facilities can access over a dozen marine larval species cultured in hatcheries and from wild collections from the natural marine environment, it is necessary to choose more convenient sentinel species that can serve as markers of the environmental impact. In this study we have chosen three cultured species: mysids, fish and shrimp larvae (Fig. 2). The mysid, *Mysidopsis bahia*, also called opossum shrimp, is a crustacean found in most of the oceans and frequently used in safety testing. About 6 mm in length, they feed voraciously on zooplanktons and in turn are prey to larger organisms. Although they superficially look like shrimps, they are in fact not shrimps and belong to a distant family. The prawn, *Penaeus monodon*, is commercially cultured food organism and found in tropical oceans. They are used in this study as post-larvae at 13 days of age. The larvae of the milkfish, *Chanos chanos*, are commonly found in the tropical waters of the Pacific Ocean. Poseidon Sciences intends to expand the sentinel species as the testing program becomes more established to include a much broader representation of the marine ecosystem.

Figure 2. Photographs of the various larvae used as sentinel organisms to measure the toxicity of coatings.

Twenty larvae of each species were introduced with the seawater and the mortality rate over 48-hour period in the presence of the coatings was compared with the control PVC coupon without any coating. Such short term acute tests can either be performed as a static or a flow-through system in which natural seawater is added while at the same time releasing an equal volume out of the system. The flow-though system simulates the dilution of the seawater in an open ocean environment. While such laboratory tests cannot possibly mimic what exactly happens in the natural environment, this method allows discrimination between highly toxic compositions and those that pose minimal risks.

In this experimental demonstration, the coatings were prepared and allowed to cure for the period of time as specified by the manufacturer. The coatings were either placed on static immersion for the toxicity test directly after curing or pre-treated by placing the panels in seawater for a one week period prior to the static toxicity test. The coating compositions used in this study only serve as examples to demonstrate the testing method and the manufacturers' names are intentionally omitted. Paint sample 1 is a copper-based coating comprising 40% cuprous oxide in an ablative coating system. Paint 2 is a chlorosulfonated polyethylene based coating. Paint 3 is a lanolin wax-based coating system. All test coatings did not contain any biocidal ingredients.

The mortality pattern of the shrimp larvae in the three three coatings when exposed directly after coating preparation is shown in Fig. 3. The lanolin-based coating (paint 3) showed the highest mortality, followed by copper based coating (paint 1) and then by the chlorosulfonated polyethylene coating (paint 2). However, when the paints were pre-treated by exposure for one week in seawater, the mortality pattern associated with the coatings was similar in relationship to each other, but occurred at a much lower rate (Fig. 4). The total mortality after 48 hours is shown for milkfish larvae (Fig 5) and mysids (figure 6) for both direct exposure and pre-treatment regimens.

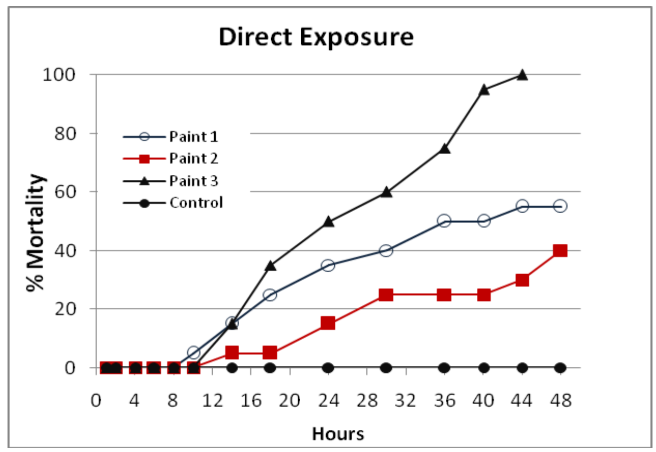

Figure 3. Effect of exposing the coated panels directly to the marine larvae of the prawn, *P. monodon*, without prior immersion to seawater.

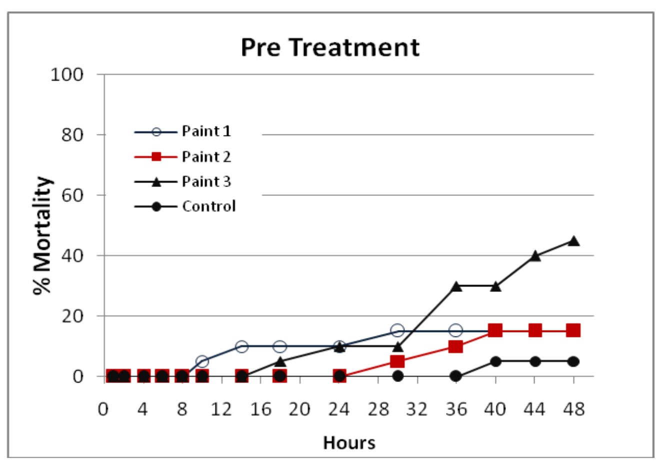

Figure 4. Effect of pre-immersion of the coated panels in seawater for 1 week prior to introduction of the panels to larvae of the prawn, *P. monodon*.

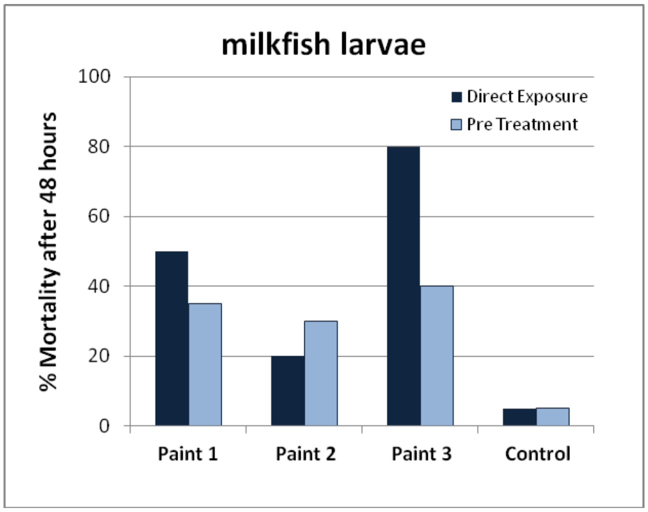

Figure 5. The total mortality of milkfish larvae after 48 hours in the presence of coated panels when exposed directly or with pre-immersion in seawater prior to the marine toxicology test.

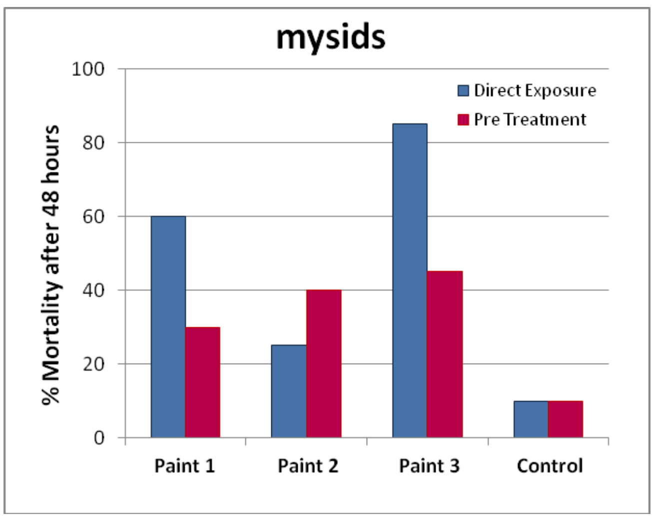

Figure 6. The total mortality of mysids after 48 hours in the presence of coated panels when exposed directly or with prior immersion in seawater prior to the marine toxicology test.

These tests show that the larval study is sensitive enough to separate the toxicity level between different types of coatings. The three selected coatings vary substantially in composition, yet in the absence of biocides, these coatings continued to express some level of toxicity to marine larvae. Pre-treatment by immersing the panel in seawater attenuated the toxic effects although they remain quantifiable. In a normal operating environment, the coatings are immersed in seawater and, presumably over a period of time, toxic ingredients are washed out or leached out of the paint. These typically comprise monomers, solvent residues and small molecule constituents that contaminate the ingredients used in the paint. The study is being expanded to determine what ideal exposure level in seawater is necessary to fully eliminate the ingredients that contribute to the toxicity effects. Also needed is to evaluate the coatings after longer periods of operational use to determine if such coating retained a level of toxicity to other non-target animals.

Evaluating a finished coating, besides its constituents, for toxicity against marine life is necessary to make a claim that the product is truly ecofriendly. The MTSS method is just a beginning in this quest for a reliable system to establish a more transparent and reasonable basis to make an ecofriendly claim.

REFERENCES:

1. http://en.wikipedia.org/wiki/precautionary_principle

2. Brown RJ, Galloway TS, Lowe D, *et al.* (2004). Diferential sensitivity of three marine invertebrates to copper assessed using multiple biomarkers. *Aquatic Toxicology*, 66: 267-278.

3. Ní Shúilleabháin S, Mothersill C, Sheehan D,*et al* (2004). In vitro cytotoxicity testing of three zinc metal salts using established fish cell lines. *Toxicology In Vitro*. 18:365-76.