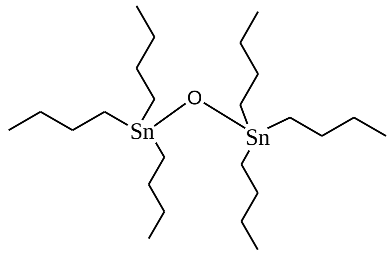
Designing of safer marine antifoulants

Pesticides are the substances (e.g. insecticides, herbicides disinfectants) employed to control a wide range of organisms such as insects plants and microorganisms. Few more examples of pesticides includes algicides, rodenticides, pisicides, fungicides, molluscicides, avicides etc. which have been used to control algae, rodents, fish, fungi, snails and slugs and birds. Some of the most well known chemical pesticides include the organochlorine insecticides (e.g. DDT, mirex, dieldrin and aldrin), the organophosphate insecticides (e.g. malathion, parathion, chlorpyrifos) and the chlorophenol derived herbicides (e.g. 2,4-D and 2,4,5-T). ***Antifoulants are generally marine pesticides used for killing the unwanted organisms. Chemical pesticides usually act by interfering with a bodily function in the target organisms.***

The ocean rocks or dock pilings are generally covered with algae and seaweed (soft foulants) and encrusted with barnacles and diatoms (hard foulants). The ship hull is constantly immersed in water for several years and these folulants gets accumualted or generated on it resulting in a significant hydrodynamic drag on the ship. This drag on a ship obstructs its passage through the water leading to higher fuel consuption and generating higher amount of greenhouse gas (i.e. CO_2) and other atmospheric pollutants (nitrogen oxides, sulphur oxides, unburned hydrocarbons, ozone etc.), causing higher operational and environmental costs. Thus, to inhibit the attachment and growth of marine organisms, the hulls of ships are generally treated with chemical compounds known as antifoulants e.g. tributyltin (TBTO) a well known organotin compound (**Figure 1**). Although, organotin compounds are effective antifoulants but they have relatively long half-lives in the environment (half-life of TBTO in seawater is > 6 months).Thus significant concentrations of these compounds can be found in ocean sediments as well as the water, and they tend to bioconcentrate in marine organisms. They are also highly toxic to marine life at the ppt level and may enter the food chain.



Tributyltin (TBTO)

Therefore an effective green marine antifoulants should possess the following properties such as rapid degradation, nonhazardous environmental concentrations, limited bioavailability, toxic only to target organisms, minimum bioconcentration (**Figure 2**).

Figure 2. Schematic representation of properties of effective green antifoulants

SEA-NINE 211

Rohm and Haas company has developed **SEA-NINE 211 as an antifoulant**. The active ingredient in Sea-Nine 211, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI), is a member of the the isothiazolone family of antifoulants (**Figure 3**). DCOI works by maintaining a hostile growing environment for marine organisms. When organisms attach to the hull (treated with DCOI), proteins at the point of attachment with the hull react with the DCOI. This reaction with the DCOI prevents the use of these proteins for other metabolic processes. The organism thus detaches itself and searches for another surface to grow.

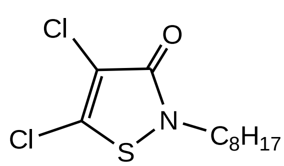


Figure 3. 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI)

Thus, environmental risk can be mitigated by reducing the toxicity of a compound and/or by reducing the exposure to the compound. DCOI, the active ingredient in Sea-Nine, by necessity is acutely toxic to a wide range of marine organisms. DCOI was found to be active against algae and diatoms at concentrations of around 10 ppb and barnacle larvae at ppm levels. However the environmental risk of DCOI is minimal because only organisms in contact with the ship's hull are exposed to toxic levels of DCOI. Although DCOI is stable as part of the coating on a ship, when it is released (leached) slowly from the hull of the ship it rapidly degrades (when in contact with seawater) to compounds that are essentially nontoxic.This decomposition is a result of microorganisms naturally occurring in sea water (**Figure 4**).

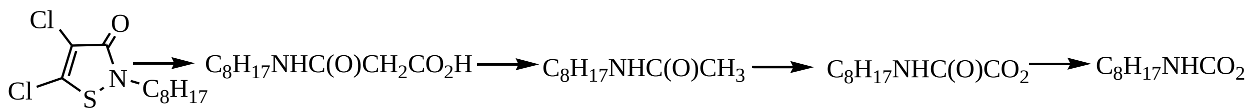


Figure 4. Decomposition of DCOI in neutral seawater

The half-life of DCOI in water at pH 7 is greater than 720 hours while in natural seawater the half-life drops to less than an hour. This rapid biodegradation leads to environmental concentrations of DCOI that are below the acute toxicity level. DCOI is also not highly toxic. The rapid biodegradation of DCOI is accompanied by rapid partitioning of DCOI to the soil/sediment. This is in part due to the low solubility of DCOI in water. The adsorption of DCOI by the soil/sediment further decreases its bioavailability**. In addition to the low bioavailability of DCOI it has a bioconcentration factor of only 13 as compared to 1500 for TBTO.** Bioconcentration levels of 100 or more are generally considered to be of significance, thus bioconcentration of DCOI is not expected to reach levels in marine organisms that would lead to concern.