

Approach may offer nontoxic alternative for ship antifouling technology

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Researchers are working on a new environmentally friendly method to control tenacious shellfish that attach to the hulls of ships, increasing drag and hiking fuel consumption by as much as 50 percent. Here, a mussel is attached to a sheet of Teflon. Credit: Purdue University photo/Jonathan Wilker

A new approach represents a potential environmentally friendly method

to control tenacious shellfish that attach to the hulls of ships, increasing drag and hiking fuel consumption by as much as 50 percent.

Transoceanic shipping accounts for about 3.5 percent of annual global fossil-fuel consumption, said Jonathan Wilker, a professor of chemistry and materials engineering at Purdue University.

Shellfish are impressive in their ability to attach themselves onto nearly any surface, including Teflon. Ships are often painted with a red, copper-based "antifouling" paint to reduce attachment of animals such as oysters, mussels and barnacles. The copper leaches from the paint into the water, killing animals in their larval stages.

"Current antifouling coatings function by releasing biocidal copper, essentially killing everything in the waters around a ship," Wilker said. "All major ports in the world are polluted with high copper levels. There is great demand for environmentally benign approaches to defeating biological adhesion."

His research team has come up with a new method that hinges on interfering with the oxidation chemistry of bioadhesion.

"In recent years, we have been gaining an increased understanding of how shellfish attach," he said. "Our goal is to only stop the adhesion, rather than killing the animals."

Findings are detailed in a research paper that appeared in September in a print issue of the journal *Chemistry of Materials*, published by the American Chemical Society. The paper was authored by graduate students Chelsey A. Del Grosso and Thomas W. McCarthy; technicians Christopher L. Clark and Joshua L. Cloud; and Wilker.

The team studied how animals produce adhesives. Their research has

shown that the animals create such strong adhesion by using oxidative chemistry – or the removal of an electron from [protein molecules](#).

"If you remove an electron, the protein becomes more reactive and wants to connect with other proteins that have more electrons. This oxidative coupling is what cures the adhesive," Wilker said.

Mussels extend hairlike fibers that attach to surfaces using plaques of adhesive. Proteins in the glue contain the rare amino acid Dopa, which can be oxidized by removing an electron, facilitating the "cross-linking" of protein molecules. This mechanism suggests that an alternative to biocidal coatings could hinge on the use of antioxidant compounds to interfere with the oxidative chemistry and inhibit glue formation.

"These animals are using oxidation chemistry to cure their glue, so what happens if we go in the opposite direction and make a surface that is an antioxidant?" Wilker said. "Perhaps we can shut down the bonding."

The researchers explored this approach, creating surfaces with antioxidants and then quantifying how well the animals attached. Finding coatings capable of drying properly without consuming the antioxidant and also remaining attached to the underlying panels while underwater proved to be challenging. They tried numerous systems, eventually discovering combinations of antioxidants and a coating that worked well.

The research showed that, in coatings that have a 25 percent concentration of antioxidants, the bio-adhesion was reduced by more than a quarter.

"The adhesion went down significantly, but not all the way to zero," he said. "The main goal here was to test the idea that, with oxidative chemistry being key to formation of biological glues, reducing surfaces could decrease the bond strengths. After demonstrating this concept, we

can now move on to refining the approach for making coatings that will prove to be useful on ships."

More information: Chelsey A. Del Grosso et al. Managing Redox Chemistry To Deter Marine Biological Adhesion, *Chemistry of Materials* (2016). [DOI: 10.1021/acs.chemmater.6b03390](https://doi.org/10.1021/acs.chemmater.6b03390)

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