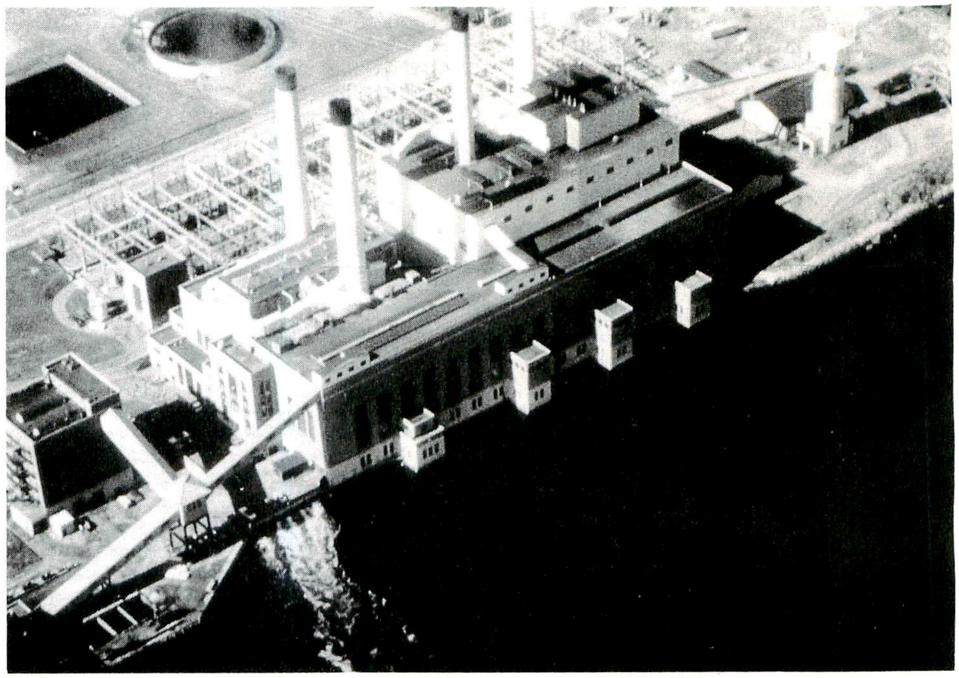
MIT Sea Grant

Quarterly Report

Cleaning Up Industrial Wastewater



People who turn up their noses at horseradish may be surprised to learn that the potent mustard may have redeeming value in laundering industrial wastewaters. Alexander Klibanov in MIT's Department of Nutrition and Food Science has discovered that horseradish, when combined with hydrogen peroxide, removes certain dangerous pollutants prevalent in the wastewaters of several common industries.

More than five million tons of industrial wastes are dumped in the nation's oceans each year. These effluents cause several pollution problems: concentration of toxic substances in dumping areas; ingestion of contaminants by marine organisms; thick deposits of foreign substances on nearshore bottom environments; and excessive growth of undesirable organisms.

The roots of the pollution problems are partly phenols and aromatic amines, chemical compounds common in the wastewater of such industries as coal conversion, resin and plastic, oil refining, textile, chemical, timber, soap, and iron and steel. Nearly all phenols and aromatic amines are toxic and some are carcinogens.

There are methods for removing these pollutants from water, but they have serious handicaps. Some of the most popular methods are adsorption on activated carbon, extraction, microbial and chemical oxidation, incineration, electrochemical techniques, and irradiation. The drawbacks are that these are relatively expensive, do not purify completely, create hazardous by-products themselves, or are not efficient enough. The new horseradish treatment may avoid these problems.

It is a simple chemical process. When peroxidase from horseradish and hydrogen peroxide are added to water loaded with phenols and aromatic amines, the peroxidase causes oxidation of the pollutants by the hydrogen peroxide. During oxidation, some of the pollutant molecules split into unstable fragments, free radicals. When a free radical and a whole molecule meet in the solution, they join to form a larger free radical, still unstable. This joining and growing continues until the expanding free radical meets a stabilizer or another free radical, which acts as a stabilizer, and the chain reaction stops. Because there are many more whole molecules than free radicals or stabilizers in the solution, the molecule grows quite large before it meets a stabilizer and the chain reaction stops. These big molecules, polymers, are not soluble in water, so they precipitate out and can easily be removed from the solution by simple filtration or sedimentation.

In the laboratory Klibanov and coworkers Barbara Alberti, from the Department of Nutrition and Food Science, and undergraduate students Evan Morris and Lee Felshin tried the new treatment against 40 phenols and aromatic amines. Many of the 40 are on the U.S. Environmental Protection Agency's list of hazardous pollutants. In about a dozen cases the horseradish treatment removed more than 99 percent of the pollutant. But in other cases as little as 63 percent was removed, and some chemicals did not respond at all. A probable explanation for the lack of response is that the result of the horseradish treatment on these stubborn chemicals is a lightweight polymer that does not precipitate out of the solution. These results were disappointing, until a breakthrough appeared in the research.

A discovery that Klibanov calls the cornerstone of the research is that when easily-removed and stubborn pollutants are together in water the stubborn chemicals respond much more positively to the treatment. This is because the free radicals of the easily-removed pollutants join with the molecules of the stubborn ones, including them in the joining and growing process described above to form mixed polymers which are heavy enough to precipitate. This discovery significantly broadened the potential application of the method. In fact, this phenomenon does not seem to be limited to phenols and aromatic amines. Some other organic pollutants, including naphthalene and azobenzene (a suspected carcinogen), also respond to the treatment when easily-removed chemicals are present (otherwise there is no response). Making sure that easily-removed substances are in real wastewater to aid the others is no problem since the real stuff contains ample variety of chemicals.

Klibanov experimented on wastewater from a chemical plant which produces flame retardant. The sample contained more than 150 different chemicals, some phenols and some non-phenolic. Total concentration of phenols in the water was 105 parts per million (ppm). One hundred units of horseradish peroxidase and 2.5 mmoles of hydrogen peroxide were used to treat the solution. After 40 hours the concentration of phenols was down to 3.7 ppm, 96.5 percent less than at pretreatment. Even with 25 units peroxidase and 2 mmoles hydrogen peroxide, 85 to 90 percent of the phenols were removed.

The usual method for treating industrial wastewater does not work in winter because cold temperatures inhibit the

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chemical process. Therefore, Klibanov was anxious to see if his treatment would work in cold water. He also wanted to try it in water with high pH since low pH causes corrosion of steel columns and metal containers used in treatment ponds. At 4° C and 7 pH the results were as good as at room temperature and lower pH.

These days, cost of pollution cleanup methods alone can determine whether they are practical. Industry already uses established methods and is reluctant to change unless the difference in cost is significant. Cost of the horseradish cleanup is not out of line, but there are ways to pare expenses. One way would be to use a crude peroxidase instead of the pure form. But Klibanov did not know if the crude would be as effective. He made a crude preparation of peroxidase by crushing whole horseradish roots and pressing them through cheesecloth to obtain juice. Results from the crude peroxidase were comparable with results using the pure form. Using crude, the cost of treating 1,000 liters of wastewater is about 69 cents. The cost of a conventional treatment, the FMC process, is at least 84 cents for 1,000 liters. With economy still in mind, Klibanov currently is trying to determine optimal working conditions for the treatment.

Limitations on the use of horseradish as the source of peroxidase have prompted Klibanov to look for other sources that are as effective, but cheaper and more dependable and controllable for large-scale use. Horseradishes are harvested only once a year, require a large area for cultivation, cannot be grown in many climates, and the price is unstable. Two other peroxidases have been tested, one from milk and one from *Caldariomyces fumago;* both were less successful than horseradish. But Klibanov is optimistic about finding bacteria that contain an effective peroxidase. He is testing different strains. If he finds the right one, the supply will be unlimited and controllable since bacteria are easily grown in the laboratory.

Industries in Britain and France, where pollution control laws are tough, have expressed interest in the new treatment. Industry in the United States, where regulations now seem to be easing, appears hesitant to invest, at least until a new source of peroxidase is found. Klibanov thinks his method holds particular promise for the up-and-coming coal conversion industry in the United States. The coal conversion process produces many of the pollutants that are no challenge to the new treatment.

Research in Undersea Teleoperators

Possibilities for doing increasingly complicated undersea jobs with unmanned work vehicles continue to unfold with technological advances in telemetry, digital control, transducers, supervisory control, artificial intelligence, and microcomputers. Eventually scientists should be able to construct a teleoperator that can perform underwater without a human pilot or a tether to connect it to a surface station. Several research efforts at MIT Sea Grant funnel towards this goal. One project in the Man-Machine Systems Laboratory in the Department of Mechanical Engineering has made it possible to test control systems without having actually to build and install them in vehicles. Another gives higher resolution to a manipulator's sense of touch.

Undersea Vehicle Simulation

Homayoon Kazerooni, a graduate student working with Professor Tom Sheridan, has fashioned a sophisticated digital computer simulator of undersea vehicles. He has modeled vehicle hull hydrodynamics, thruster capability, control system, and sonar and other sensors, all of which can be modified to resemble a number of vehicle types. In its first application he adapted the model to simulate *Alvin,* the Woods Hole Oceanographic Institution research submarine, in order to test designs for autopilots that will guide the submarine closely along a two-dimensional path on the bottom of the ocean.

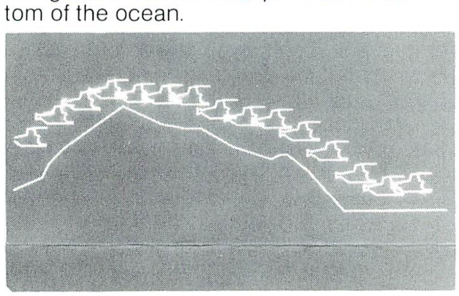

Figure 1. Graphic simulation of *Alvin* negotiating a fabricated ocean floor on autopilot.

Alvin performs sophisticated missions such as the much-publicized recent exploration of the Galapagos Spreading Center. A human pilot of *Alvin* on bottom-following missions such as this has limited vision through a small window at the front of the vehicle, and crashes into the irregular ocean floor are not uncommon. Manual piloting is also extremely slow and consumes large amounts of precious battery power.

Kazerooni designed an autopilot for *Alvin* to illustrate the usefulness of the vehicle simulator in testing control systems. The autopilot uses two sonars and a computer for data analysis and thruster control. Simulation is real time and consists of three routines that intercommunicate, called STERN, TANG, and ALVIN.

STERN simulates *Alvin's* hardware, the dynamics and kinematics of the sonars, and includes graphic simulations of the behavior of the submarine, the ocean floor, and the sonar beams. A vector display terminal shows simultaneously two perspectives, a close-up to show in detail how nearly the vehicle is paralleling the bottom, and a distant picture so the viewer can evaluate the vehicle's movements in relation to the bigger environment. The autopilot has two sonars; Sonar 1 sweeps constantly in a vertical plane from 30° below horizontal to vertical, mapping points along the path immediately ahead of the vehicle, and Sonar 2 measures the distance to a single point further ahead.

TANG is the brain of the autopilot software. TANG fetches data from Sonar 1 (angle and distance to points along the sweep), analyzes the data to determine the tangent of the ocean floor ahead, and, based on the tangent, fixes the angle of Sonar 2 between 50° above and 50° below horizontal so that Sonar 2's beam "sees" sufficiently ahead to allow time for vertical thrust if needed either to avoid a crash or to get closer to the bottom.

Once Sonar 2 has assumed the proper angle, the distance to the bottom is transmitted to computer routine ALVIN, the servocontroller for the thrusters. ALVIN engages the thrusters if the distance varies from a given value determined by TANG. If the distance is too long, the vehicle is too far from the bottom and needs to move down; if the distance is too short, the sub must move up to avoid crashing.

A separate program allows the programmer to vary the contour of the ocean floor for each test. In all likely environments tests have been successful: no crashes. The autopilot guides the submarine *Alvin* across the screen within six to twelve feet of the fabricated bottom. Another simpler, more inexpensive controller designed by graduate student Erik Vaaler also has been tested on the simulator and found effective at low speed in milder environments.

The experiments prove not only the effectiveness of the autopilots, but also that the computer simulator works as a viable time- and money-saving method of testing new technologies on undersea vehicles.

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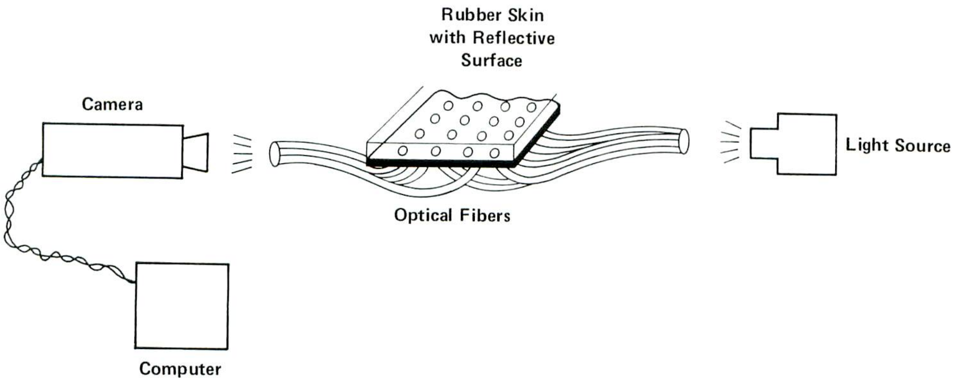

Figure 2. Current sensor design, where light is sent through one set of fibers and received through another.

Touch sensing for manipulators

Picking up a bolt and fitting it through a hole seems a simple enough affair. But it depends on a sense of touch, and touch is more complicated than we as humans, who have it naturally, may think. Even a crude sense of touch involves discerning how the bolt is picked up and whether it is grasped securely. Endowing manipulators with improved touch sensitivity is the focus of research by John Schneiter, a graduate student working with Professor Sheridan in the Man-Machine Systems Lab. Schneiter has built a touch sensor using optical fibers. A manipulator hand fitted with this sensor will be able to do such underwater maintenance and repair tasks as picking up a bolt and fitting it through a hole.

The "skin" of the sensor is a square of rubber with a reflective surface which is depressed when an object like a bolt comes in contact with it. If the manipulator could interpret the shape and depth of the depression, it could determine the position of the bolt and tell whether its grip was firm. Reflected light and optical fibers are used to provide information about the depression.

The one-half-inch square rubber skin lies across the tips of a bundle of 600 optical fibers, like a flat cover atop an upright bundle of straws. Light travels through these fibers, emerging as a pattern of individual lights at the opposite tips. If nothing is depressing the rubber skin atop the fibers, all of the points of light at the tips are of uniform intensity. But if an object presses in on the skin, the fibers directly beneath the area will transmit brighter light.

A human viewer can interpret the light pattern, but since eventually manipulators will be able to operate without human intervention, Schneiter has programmed a computer to interpret the pattern. A video camera photographs the pattern and sends the image to the computer. When the image changes, meaning something is in contact with the skin, the computer deciphers the change and can instruct the manipulator how to adjust—to grab more tightly to prevent slippage or loosen its grip to manipulate an object, such as a bolt.

Schneiter is experimenting to find the simplest way of getting light to the fibers at the sensor end. In his current design, light is provided through other optical fibers and reflected off the rubber skin (Figure 2), but he is refining this design, using a beam splitter to eliminate the need for two sets of fibers. With the beam splitter (a surface that acts both as mirror and window) the same fibers can act as light senders and receivers (Figure 3).

Advantages of the device are that it uses available technology, is easy to build, and has high resolution compared to available touch sensors, without the vulnerability of delicate electronic switches and other components exposed to abrasion and heat. If the rubber skin is damaged it is easily replaced.

This research is supported by Sea Grant and the Office of Naval Research.

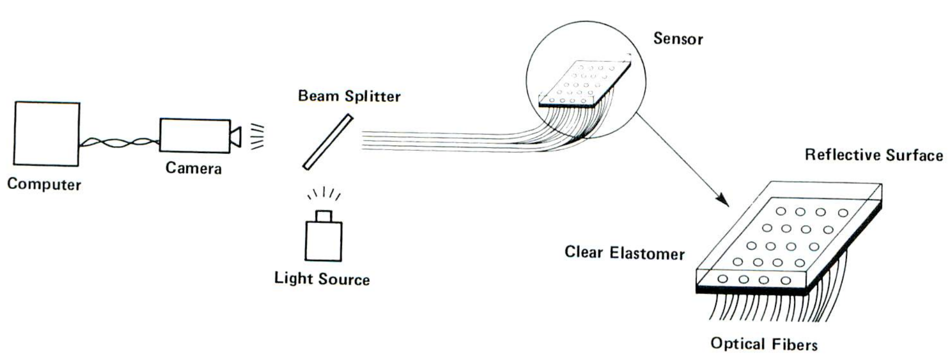

Figure 3. Refined design, where a beam splitter allows use of the same fibers as light senders and receivers.

Fishermen Join Back-to-School Movement

In the past decade more and more adults have returned to school full-time or are taking advantage of short seminars and night courses. For some, it is intellectual stretch, for others there is a professional benefit, with an economic payoff. For fishermen, the adult education trend has offered a formal educational environment where none existed before.

Traditionally, their classroom was the family boat where skills passed from father to son, uncle to nephew. Today, children from fishing families often enter other fields and their replacements are the sons and daughters of teachers, salespeople, factory workers. Even for those fishermen whose knowledge is still transmitted through family tutors, changes in technology, regulations, and marketing methods demand brand new skills.

In Buzzards Bay on the Massachusetts Maritime Academy campus, special classes, ranging from basic netmending to business management to the operation of sophisticated equipment, such as sonar fish finders, have been attracting experienced fishermen and young people, including Academy cadets. The courses were started in 1976 under the direction of David Kan, with MIT Sea Grant support, to train new, young crews for New England's fleet and to give experienced fishermen access to information that would help them expand and diversify under the newly established Federal Conservation Management Act. The classes were an instant hit in the fishing community and many were repeated to accommodate the overflow applications. In 1978 the course series was able to expand into a Fisheries Training Center with an infusion of support from the State of Massachusetts. Today the Center serves fishermen from Massachusetts and the entire New England region, an area that generates over a billion dollars in income from harvesting the ocean.

Most of the Center's classes are held in the well-equipped facilities on the MMA campus, where large diesel engines and electronic simulators provide hands-on experience. Kan has worked with the MMA library to compile and house a growing collection of periodicals and reference materials on the latest fishing gear, financial management, oceanography and fisheries biology for those students who wish to study on their own or do extra homework. A year ago a Coast Guard buoy tender was renovated as a training vessel for at-sea classes. And most recently, the fisheries courses have taken to the road, on board a converted bus equipped with industry supplied radar, Loran C, radio and other samples of the latest marine electronics.

The mobile classroom, which can be reserved by fishermen's groups or communities, will serve two particularly valuable purposes: more people can take some of the courses and the bus could become a temporary focal point for fishermen to share their own knowledge with each other. Because many spend so much time out of port, they have difficulty keeping abreast of all the new, available equipment.

Courses on the bus and informal discussions among the fishermen should help boat owners gain the familiarity needed to make informed purchasing decisions and will broaden their knowledge of their own gear. And for crews, greater knowledge hopefully will offer job opportunities.

Recently, the *National Fisherman* reported that accidents at sea are primarily caused by human error. MMA courses in navigation and seamanship are aimed at reducing mistakes. Every boat is likely to operate more safely if the entire crew is trained in the basic skills of handling and docking a vessel and reading charts and navigation aids. Knowing how to apply first aid techniques or to use lifesaving equipment properly can minimize injuries or even prevent death. Fishing captains concentrating on catching the fish and getting them to market through fair and foul weather simply don't have the time to teach these skills to continuously changing crews.

Teachers of seamanship and navigation at the MMA Center, like all instructors there, are on the Academy faculty or are recruited for their knowledge and experience. For instance, accountants and lawyers who have handled clients in the fishing industry are brought in to teach about tax law, financing and insurance options, and marketing alternatives, such as cooperatives. The business management classes are often attended by a husband and wife who are working together; he harvests the fish, she manages the money.

Making the best use of money is a motivating force for a good many of the course attendees. Fishermen, whether they're full- or part-time, save money when torn nets can be mended and put back to work at sea; lobstermen who can build their own pots or construct the nets save in buying equipment. At the diesel workshops, students learn to do tune-ups so they can invest the $50 or $100 savings in something else on their boats. Knowing how to repair a diesel can also get crew and catch safely home if a motor breaks down on a trip.

Recently the MIT Sea Grant Program surveyed the people who've attended the classes during the past years and found a growing number of non-fishermen taking part. Some, like an insurance broker, a diesel oil salesman and a marina operator, thought the knowledge would help them serve their clients better. Others, like a novice sailor and recent retirees, wanted to be better seamen and recreational fishermen.

According to Arthur B. Clifton, Manager of MIT Sea Grant's Massachusetts Liaison Service, the survey is helping to structure the course plans over the next few years. Clifton has worked with David Kan since the fisheries program started. Next year, many of the traditional basic skills will continue as the mainstays, but there will be more offered for those who have "graduated" to new levels or for those aggressive boat owners looking for new techniques that have been tried by fishermen in other parts of the world. The training vessel, *Maritime Quest,* will be a laboratory to try out various trawling methods used elsewhere and evaluate their efficiency and suitability for New England's fleets. Underwater cameras will record the operation of the gear as part of the testing process, and will likely be made available as a training tool to show fishermen the effects on doors and nets of different boat handling and speeds.

The Center will also continue to sponsor a Massachusetts Fisherman's Forum, an annual meeting designed to debate policy issues and bring all segments of the fishing industry together. This year's offerings are an insight into the complex and diverse knowledge that a competitive fisherman needs to be successful. In the two-day meeting the attendees discussed pricing, product quality, gear efficiency, and political effectiveness. They learned about migratory patterns and abundance of the major commercial species from the National Marine Fisheries Service and discussed the effects municipal planning has on fishing harbor facilities.

Educational programs, like the courses at MMA, and others at the University of Rhode Island and the Southern Maine Vocational Institute, have been helping the new generation of men and women entering the industry to gain new skills and become better managers. Art Clifton and David Kan see these young people as financial managers as well as fishermen, willing to take on not only physical risks, but hard investment decisions as well. For the future, the two men believe the ocean's rich fisheries resources will be well used to build a long list of business successes that will benefit individuals, the region and the country.

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