# Cotton, Fleece, and Beads

### *Sopping up oil with unconventional sponges*

By JANET RALOFF

There's no shortage of products to remove oil spills from water. "But there surely aren't any magic bullets out there," notes Daniel F. Sheehan, who chairs the federal Interagency Coordinating Committee on Oil Pollution Research and directs the Coast Guard's National Pollution Funds Center in Arlington, Va.

Indeed, he says, "I don't think there have been significant technological advances in the oil-spill recovery field in the last 15 years."

But several research teams seek to change that. Two groups in Texas, for instance, have begun investigating an unusual source of materials for environmentally friendlier oil-cleanup products. These spill-eating materials are wastes: fly ash left over from coal burning, and poor-quality cotton and fleece.

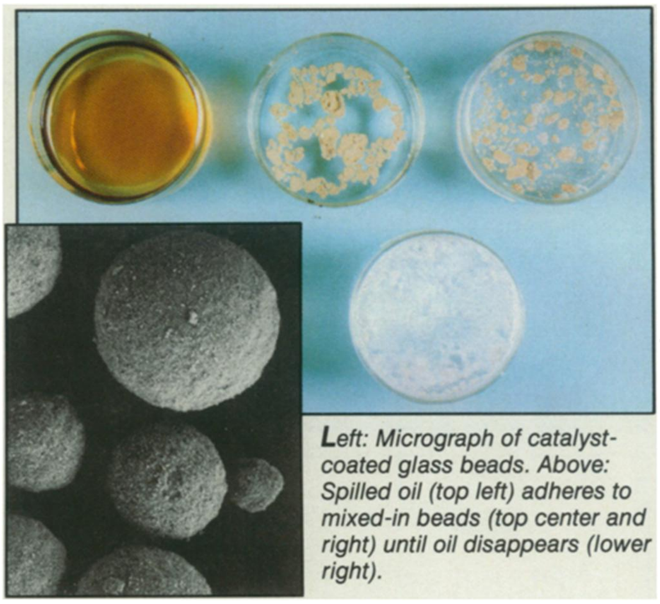
Adam Heller spearheads one of these programs at the University of Texas at Austin. For the past year, his team has coated buoyant, microscopic glass bubbles with titanium dioxide. The primary pigment in white paints, this chemical also functions as an efficient photocatalyst, dramatically speeding the sunlight-mediated breakdown of many chemicals, including toxic hydrocarbons.

After baking the pigment onto the glass microbeads, Heller's group adds a water-repelling surface film. When sprinkled on a small pool of crude oil floating atop a dish of water and then stirred vigorously, these tiny beads bind nearly half their weight in hydrocarbons. Quickly, the black oil begins bleaching. Eventually, all that remains visible are white beads floating on water.

Heller explained the magic behind this transformation at the 1993 International Oil Spill Conference, held last month in Tampa, Fla.

In the presence of sunshine or another source of near-ultraviolet light, the titanium dioxide coating accelerates a normal, sunlight-driven reaction with water. This produces highly reactive molecular fragments known as free radicals, which in turn foster a reaction between the oil and oxygen in the air.

A cascade of subsequent reactions, initiated by the free radicals, decomposes the compound into nothing but carbon dioxide and water, Heller says. The process does generate some short-lived, intermediate-size molecules, but these chemicals remain adsorbed onto the beads until the decomposition process runs its course.



Left: Micrograph of catalyst-coated glass beads. Above: Spilled oil (top left) adheres to mixed-in beads (top center and right) until oil disappears (lower right).

Images: Heller

Sunlight alone catalyzes some decomposition of many hydrocarbons. But Heller says his tests indicate that the surface reactions on the glass bubbles yield far fewer toxic materials and a more complete breakdown than sunlight-only decomposition. The beads themselves — having the same composition as sand — are nontoxic, he adds. Even the titanium dioxide is nontoxic. Heller points out that instant vanilla-pudding mixes, many toothpastes, and cosmetics contain this relatively inexpensive compound.

"There is no reason why we could not apply these beads even to the most environmentally sensitive areas," he says, although he adds that "this remains to be proved." Indeed, he speculates that a dry bath with these beads might safely cleanse the feathers of oiled waterfowl.

Scooping up the oxygen it needs from its local environment, "each of these bubbles is a catalytic reactor," Heller says. How quickly they break down oil depends on their access to sun and oxygen. Because churning water helps deliver both, Heller argues that the roiling waves that can render booms and skimmers useless on stormy seas (such as those encountered when the tanker *Braer* ran aground off Scotland's Shetland Islands in January) might actually improve the oil-breakdown efficiency of the microbeads.

In theory, these beads could eliminate their weight in oil each hour, he says. In the laboratory experiments Heller's team has conducted to date, however, the beads took a week or two to decompose oil.

The researchers have successfully used the beads to break down five different oils, though never in batches of more than a few ounces. In April, a firm licensed to market this technology began pilot-scale production of the beads. When larger quantities become available, Heller hopes to launch field tests using the beads to clean up hydrocarbons in industrial waste ponds.

The beads can be manufactured to the desired size — probably about 50 to 80 microns in diameter, Heller says. However, he notes that fly ash from burning coal contains similar glassy spheres, which, though heavier, might function almost as well. Using these far less expensive alternatives might create a new market for some of the nearly 58 million tons of coal ash now destined annually for costly burial in U.S. landfills.

Harry Whittaker, a chemical engineer with Environment Canada in Ottawa, regards the microbead technology as potentially useful but contends its promise "is being oversold."

Whittaker heads his federal agency's applied R&D program on technologies for cleaning up oil spills, chemical spills, and leaking chemical landfills. While he and his colleagues haven't tested microbeads, they have explored titanium dioxide's potential for cleaning hydrocarbon-tainted waters since 1987. Their research indicates that not all hydrocarbons degrade quickly to carbon dioxide and water, or as completely as Heller suggests. "Some are very recalcitrant," Whittaker says.

He also suspects that if birds and other animals ingest any of the floating glass beads, they may suffer toxic consequences. Ingestion will shut off the beads' access to sunlight, he notes, preventing further degradation of any toxic hydrocarbons they carry.

If Whittaker can obtain beads for study from the company licensed by the University of Texas to make them, he will gauge the rates at which different hydrocarbons decompose "and look for potential byproducts of incomplete destruction, which may come off when you try to use these beads on various chemicals," he says. "We're also going to figure out whether there is any loss of [treated hydrocarbons] due to absorption into the glass bead itself."

Despite these questions, Whittaker says he is genuinely interested in the technology. His lab is currently exploring the use of fiberglass filters impregnated with titanium dioxide to remove and break down water pollutants. If his studies verify claims by Heller's group, the Canadian research program might switch to microbeads too, he says.

A separate group, led by Harry W. Parker of Texas Tech University in Lubbock, is investigating more mundane materials for cleaning up oil.

Cotton harvesting each year yields millions of pounds of fibers too short to interest fabric manufacturers. Weavers of wool shun similar quantities of too-thick fibers because of their inherent scratchiness. If Parker has his way, both fibers, currently considered wastes, will ultimately find commercial appeal as sorbents of spilled hydrocarbons.

In their raw form, both fibers meet or exceed the absorbency of materials currently marketed to sop up spilled oil, Parker's studies show. But unlike the synthetic materials usually sold for this purpose, his wool and cotton are biodegradable. In lab tests using 1- or 2-liter fermentation reactors, Parker says, microbes readily degraded the natural fibers, even those heavily coated with diesel or crude oil. Indeed, he says, his team's biological studies demonstrate that this breakdown of the fibers conveniently releases the sopped-up oil, allowing it to float to the top of the bioreactors.

Cleanup managers could separate this oil and run it through an additional fermentation cycle, this one populated with oil-noshing bacteria, he suggests. Alternatively, the oil could be reused.

Without question, notes Parker, it's cheaper to dispose of soiled sorbents in landfills than to biodegrade them. But if the Environmental Protection Agency succeeds in its current bid to reclassify oil-soaked materials as hazardous wastes, the costs of burying them could skyrocket, making his scheme an economical and "greener" alternative, he says.

By October, Parker and his colleagues hope to have pilot-scale fermentation under way in 50- to 250-gallon bioreactors. Only larger trials such as these can establish the potential limits and promise of biodegradable sorbents, he says.

In preparation for an international meeting last year, Sheehan's interagency committee compiled a database of oil-cleanup research. "I was surprised at how little, internationally, there is," he told SCIENCE NEWS.

Although spill managers have identified many notable gaps in their arsenal of cleanup technologies, they have lacked financing for R&D programs to fill those gaps, according to research analysts who spoke at the First International Oil Spill R&D Forum, held last June in McLean, Va.

For instance, France — scene of the catastrophic *Amoco Cadiz* tanker spill in 1978 — "has had no funding for oil R&D," notes a report presented at the forum by Jean-Francois Levy, of the Interministerial Mission de la Mer in Paris.

Recent federal spending on oil-spill R&D in the United States, a world leader in this area, has averaged about $30 million per year, Sheehan notes — "not much." However, federal agencies have drawn up a five-year R&D plan to address some of the most pressing research gaps. It spells out "how we would spend money if we could get more," Sheehan says. "And indeed, we hope the [new Oil Pollution Act] will begin to provide certainty of funding, [because] the farther in time you get away from a major oil spill, the less interest there is in oil-spill R&D." □