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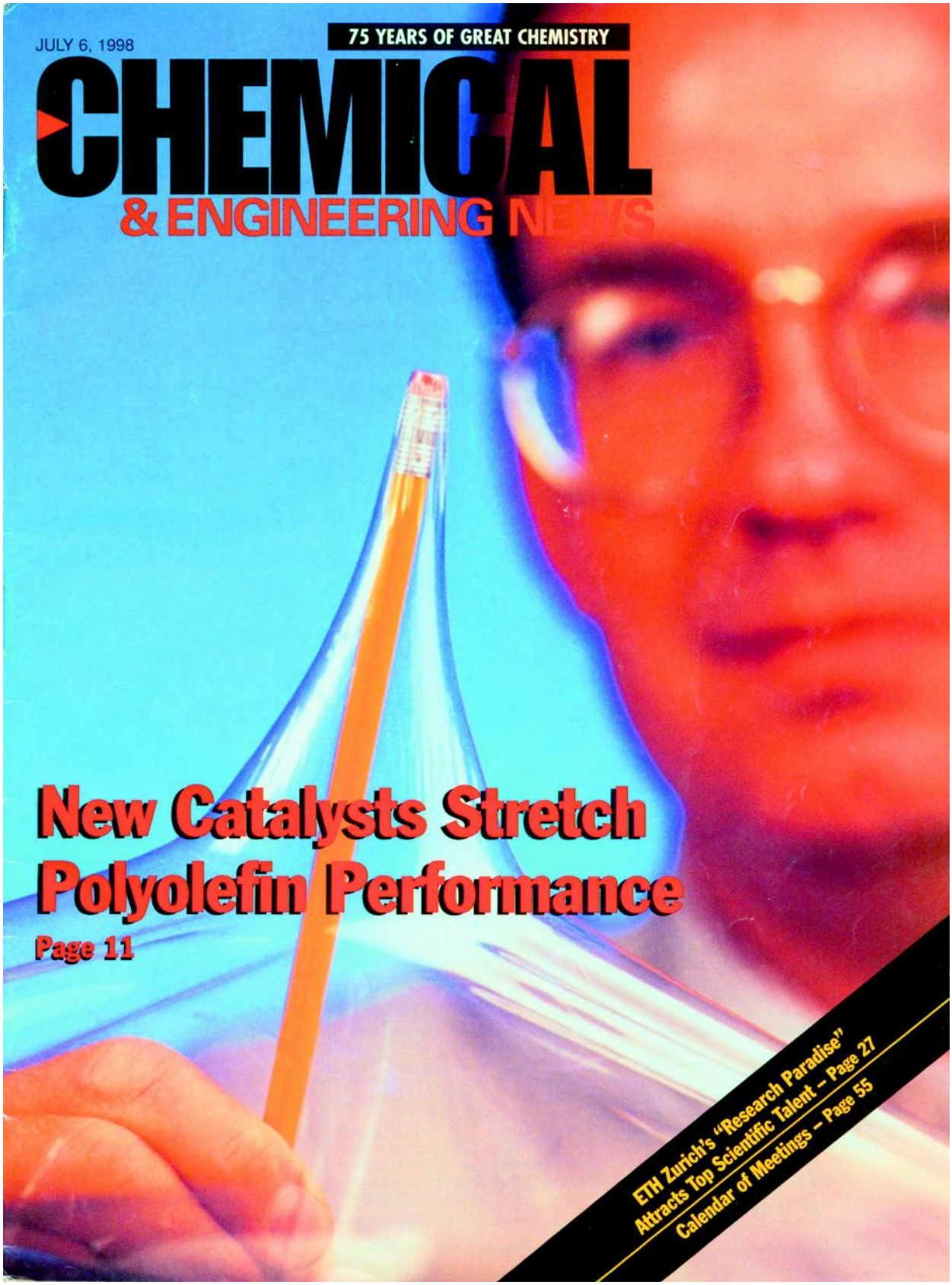

science/technology

GREEN CHEMISTRY HERE TO STAY

Scientists receive presidential awards for chemistry that protects the environment by reducing waste, conserving resources

Linda R. Raber
C&EN Washington

The third annual Presidential Green Chemistry Challenge Awards were presented June 29 at ceremonies at the National Academy of Sciences in Washington, D.C. The awards recognize three chemical companies, one national laboratory, and two academic groups for outstanding accomplishments that bring chemistry to bear on pollution reduction.

The awards—which are the only presidential awards specifically recognizing work in the chemical sciences—are the result of a partnership among the Environmental Protection Agency, the American Chemical Society, the Council for Chemical Research, and the National Research Council.

Pyrocool Technologies, Lynchburg, Va., was selected to receive a Presidential Green Chemistry Challenge Award in the small-business category. The company has developed and commercially introduced Pyrocool FEF (fire extinguishing foam), an environmentally responsible fire extinguishing and cooling agent.

Pyrocool technology replaces less environmentally sound methods. Halon gases, hailed as a tremendous advance in fire fighting when introduced, are especially destructive to Earth's protective ozone layer in the stratosphere. And aqueous-film-forming foams, developed by the Navy in the 1960s to combat pooled surface volatile hydrocarbon fires, release both toxic hydrofluoric acid and fluorocarbons when used. The fluorosurfactants that make these agents so effective have a detrimental effect on anaerobic bacteria and often lead to groundwater contamination and failure of wastewater treatment systems.

Pyrocool FEF technology, which relies on specialized surfactants, eliminates the need for traditional fire extinguishing agents. And because Pyrocool FEF is mixed with water at only 0.4%, an 87 to 93% reduction in product use is realized compared with conventional extinguishing agents typically used at 3 to 6%. "This lets more water get to the fire to do its job," says Pyrocool President Robert E. Tinsley Jr.

"The foam can be used on all sorts of fires—including fires under pressure, like a ruptured fuel line in an engine or in an engine room of a ship," says Tinsley. "It also can put out simple fires like house fires and wildfires. It is so frustrating for us to see the fires burning in northern Florida and be unable to use Pyrocool because we do not have federal certification for its use on wildfires."

Pyrocool FEF was used in 1994 to extinguish the most recent large oil tanker fire at sea. It put out the fire on board the *Nassia* in the Bosphorous Straits in just 12.5 minutes (a fire originally estimated by Lloyd's of London to require 10 days to extinguish). As a result, 80% of the ship's cargo was saved and 78,000 tons of crude oil didn't end up in the sea.

Stanford University chemistry professor Barry Trost received a Green Chemistry Challenge Award in the academic category for developing the concept of atom economy. "There is more to synthetic efficiency than simply addressing the issue of selectivity," says Trost. "You also have to address the issue of the economy of use of your materials."

Currently, the practicality of a chemical process is generally dictated by economics, which are, in turn, dictated by product yield. Typical yield calculations account for how much product is formed from a chemical process, but don't take into account how much waste is generated. In other words, yield calculations do not compare the total quantity of raw materials required for a process with the quantity of product produced. As a result, many chemical processes are considered high yield when in fact they are wasteful from the standpoint of atom economy.

Trost believes that the presidential award is important because it recognizes that green chemistry can be an important aspect of basic research. "For the long term, you want a repertoire of synthetic reactions that intrinsically are more efficient," he says.

Courtesy of Argonne National Laboratory

Argonne developers (from left) Tsai, Mike Henry, and Rathin Datta with the pilot demonstration system (membrane unit at top), fermentation broth feedstock (dark), and ethyl lactate product (clear). Development team member Jim Frank was not available for the photo.

Flexsys America, Akron, Ohio, a joint venture of Solutia and Akzo Nobel's rubber chemicals operations, was selected as the winner in the alternative synthetic pathway category for developing an environmentally friendly process for the synthesis of an important chemical in the manufacture of rubber products.

Rubber tires exposed to ozone crack and fail unless an additive such as 4-aminodiphenylamine (4-ADPA) is present. Currently, 4-ADPA manufacture is based on the chlorination of benzene. But because none of the chlorine used in the process ends up in the final product, the pounds of waste generated in the process per pound of product produced is highly unfavorable. A significant portion of the waste is in the form of an aqueous stream that contains high levels of inorganic salts contaminated with organics.

In the award-winning process, aniline and nitrobenzene react to produce 4-nitrodiphenylamine and 4-nitrosodiphenylamine. The mixture is then hydroge-

nated to make 4-aminodiphenylamine. Aniline reacts directly with nitrobenzene without any added oxidizing agent such as chlorine or bromine. This pathway eliminates a large waste problem that exists in the current process, explains Roger K. Rains, Flexsys technology manager.

Compared with the process traditionally used to synthesize 4-ADPA, the Flexsys process generates 74% less organic waste, 99% less inorganic waste, and 97% less wastewater. In global terms, if just 30% of the world's capacity to produce 4-ADPA and related materials was converted to the Flexsys process, 74 million lb per year less chemical waste and 1.4 billion lb per year less wastewater would be generated, according to EPA's description of the process.

Argonne National Laboratory, in Illinois, was selected to receive an award in the alternative reaction conditions category. Researchers at the laboratory have developed an economically viable process for producing lactate esters—which can be used as nontoxic and biodegradable solvents—from carbohydrate feedstocks.

"For many years, there was just no way of producing ethyl lactate at a low enough cost to allow it to compete with the more conventional petrochemical-derived solvents," says Argonne chemical engineer Shih-Perng Tsai. Despite their excellent properties, lactate esters traditionally have been too expensive for widespread use. The new Argonne membrane-based process requires little energy input, is highly efficient and selective, and eliminates the large volumes of salt waste produced by conventional processes.

The Argonne process should make it technically and commercially feasible for industry to use lactate esters in place of about 80% of the 3.8 million tons of solvents currently used in the U.S. each year in applications that include electronics manufacturing, paints and coatings, textiles, cleaners and degreasers, adhesives, printing, de-inking, and many other industrial, commercial, and household applications, explains Tsai.

Rohm and Haas, Philadelphia, was selected for an award in the category of designing safer chemicals, for its diacylhydrazine insecticides. One of these insecticides, Confirm, is harmless to just about everything but caterpillars. The value of crops destroyed worldwide by these pests exceeds tens of billions of dollars each year. Over the past 50 years, only a handful of classes of insecticides have been discovered to combat this destruction.

Courtesy of Pyrocool Technologies

Pyrocool FEF being used to extinguish a pressurized, obstructed, multilevel military jet fuel engine fire at Tyndall Air Force Base in Florida. Test duplicates an actual crash at Travis AFB in California that took hours to extinguish. The test fire was extinguished in 34 seconds.

Confirm effectively and selectively controls caterpillars without posing significant risk to the applicator, the consumer, or the ecosystem. Diacylhydrazines offer farmers, consumers, and society a safer technology that is effective for insect control in turf and a variety of crops, according to EPA. Confirm will replace many older, less effective, more hazardous insecticides and has been classified by EPA as a reduced-risk pesticide.

According to Robert H. Larkin of Rohm and Haas's Agricultural Chemicals business, Confirm has low toxicity to mammals by ingestion, inhalation, and topical application, and has been shown to be completely nononcogenic, nonmutagenic, and without adverse reproductive effects. It is safe for a wide range of nontarget organisms such as mammals, birds, earthworms, plants, and various aquatic organisms. It also is remarkably safe to a wide range of key beneficial, predatory, and parasitic insects such as honeybees, lady beetles, predatory bugs and beetles, and spiders.

Karen M. Draths and John W. Frost, a wife and husband research team in the department of chemistry at Michigan State University, received an award in the academic category for using genetically manipulated microbes as environmentally benign catalysts in the synthesis of important industrial chemicals.

For example, the use of microbial catalysts in the synthesis of adipic acid and catechol allows glucose to be used as a starting material. Glucose, in turn, is derived from renewable carbohydrate feedstocks such as starch, cellulose, and hemicellulose. Water is used as the primary reaction solvent, and the generation of toxic intermediates and environment-damaging by-products is avoided.

More than 4.2 billion lb of adipic acid is produced annually and used in the manufacture of nylon-6,6. Most commercial syntheses of adipic acid use benzene derived from the benzene/toluene/xylene fraction of petroleum refining as the starting material. The Draths-Frost team has modified its procedures to produce shikimic acid, an intermediate in the synthesis of aromatic amino acid synthesis, among other compounds.

"We tend to use the tools of molecular biology, biochemistry, and cloning, but we look at it from a chemist's standpoint," says Draths. "We look at genes, but we're not so interested in the regulation of the genes and the evolution of these genes as a biochemist would be. We look at the chemicals and ask how can we turn this chemical into a different chemical. That's the value of what we're doing—creating these pathways as chemists."

Also at the award ceremonies, ACS Immediate Past-President Paul S. Anderson announced the first recipient of the ACS Division of Environmental Chemistry's Kenneth G. Hancock Memorial Scholarship in Green Chemistry. Hancock, who died in 1993, was director of the National Science Foundation's Chemistry Division and one of the early advocates of environmentally benign chemical synthesis.

The scholarship, which recognizes students who are furthering the goals of environmentally benign chemistry, was presented to graduate student Jeanne M. Jennings of the University of South Carolina, who, under the guidance of professor Thomas Bryson, has focused on devising new environmentally friendly methods for executing organic reactions and syntheses using supercritical water as a solvent and reagent.

"The award-winning advances that we recognize tonight are a clear sign that green chemistry has arrived and is here to stay, because green chemistry puts cutting-edge science to work for consumers, for industry, and, best of all, it uses innovation rather than regulation to achieve important environmental goals," Anderson said.◀