United States
Environmental Protection
Agency

Presidential Green Chemistry Challenge

Award Recipients

EPA
United States
Environmental Protection
Agency

EPA744-K-02-002
June 2002
www.epa.gov/greenchemistry

Office of Pollution Prevention and Toxics (7406M)

Presidential Green Chemistry Challenge

Award Recipients

Printed on paper that contains at least 50 percent postconsumer fiber.

Contents

Introduction

The Presidential Green Chemistry Challenge Awards Program is an opportunity for individuals, groups, and organizations to compete for annual awards in recognition of innovations in cleaner, cheaper, smarter chemistry. The Challenge Awards Program provides national recognition for outstanding chemical technologies that incorporate the principles of green chemistry into chemical design, manufacture, and use, and that have been or can be utilized by industry to achieve its pollution prevention goals. Five winners are typically honored each year, one in each of the following categories:

- Academia.
- Small business.
- The use of alternative synthetic pathways for green chemistry, such as catalysis/biocatalysis; natural processes, including photochemistry and biomimetic synthesis; or alternate feedstocks that are more innocuous and renewable (e.g., biomass).
- The use of alternative reaction conditions for green chemistry, such as the use of solvents that have a reduced impact on human health and the environment, or increased selectivity and reduced wastes and emissions.
- The design of safer chemicals that are, for example, less toxic than current alternatives or inherently safer with regard to accident potential.

This booklet presents the 1996 through 2002 Presidential Green Chemistry Challenge Award recipients and describes their award-winning technologies. The winners each demonstrate a commitment to designing, developing, and implementing green chemical technologies that are scientifically innovative, economically feasible, and less hazardous to human health and the environment. The Presidential Green Chemistry Challenge Program is looking forward to adding next year's winners to the growing list of chemists and chemical companies who are on the cutting edge of pollution prevention.

Academic Award

Professor Eric J. Beckman
University of Pittsburgh

Design of Non-Fluorous, Highly CO_2-Soluble Materials

Carbon dioxide, an environmentally benign and nonflammable solvent, has been investigated extensively in both academic and industrial settings. Solubility studies performed during the 1980s had suggested that CO_2's solvent power was similar to that of *n*-alkanes, leading to hopes that the chemical industry could use CO_2 as a "drop-in" replacement for a wide variety of organic solvents. It was learned that these solubility studies inflated the solvent power value by as much as 20 percent due to the strong quadrupole moment of CO_2 and that carbon dioxide is actually a rather feeble solvent compared to alkanes. As the 1980s drew to a close, a number of research groups began to explore the design of CO_2-philic materials, that is, compounds that dissolve in CO_2 at significantly lower pressures than do their alkyl analogs. These new CO_2-philes, primarily fluoropolymers, opened up a host of new applications for CO_2, including heterogeneous polymerization, protein extraction, and homogeneous catalysis.

Although fluorinated amphiphiles allow new applications for CO_2, their cost (approximately $1 per gram) reduces the economic viability of CO_2 processes, particularly given that the use of CO_2 requires high-pressure equipment. Furthermore, data have recently shown that fluoroalkyl materials persist in the environment leading to the withdrawal of certain consumer products from the market. The drawbacks inherent to the use of fluorinated precursors, therefore, have inhibited the commercialization of many new applications for CO_2, and the full promise of CO_2-based technologies has yet to be realized. To address this need, Professor Eric Beckman and his group at the University of Pittsburgh have developed materials that work well, exhibiting miscibility pressures in carbon dioxide that are comparable or lower than fluorinated analogs and yet contain no fluorine.

Drawing from recent studies of the thermodynamics of CO_2 mixtures, Professor Beckman hypothesized that CO_2-philic materials should contain three primary features: (1) a relatively low glass transition temperature, (2) a relatively low cohesive energy density, and (3) a number of Lewis base groups. Low glass transition temperature correlates to high free volume and high molecular flexibility, which imparts a high entropy of mixing with CO_2 (or any solvent). A low cohesive energy density is primarily a result of weak solute-solute interactions, a necessary feature given that CO_2 is a rather feeble solvent. Finally, because CO_2 is a Lewis acid, the presence of Lewis base groups should create sites for specific favorable interactions with CO_2.

Professor Beckman's simple heuristic model was demonstrated on three sets of materials: functional silicones; poly(ether-carbonates); and acetate-functional polyethers. Poly(ether-carbonates) were found to exhibit lower miscibility pressures in CO_2 than perfluoropolyethers, yet are biodegradable and 100 times less expensive to prepare. Other families of non-fluorous CO_2-philes will inevitably be discovered using this model, further broadening the applicability of CO_2 as a greener process solvent.

Small Business Award

SC Fluids, Inc.

SCORR – Supercritical CO_2 Resist Remover

The semiconductor industry is the most successful growth industry in history, with sales totaling over $170 billion in the year 2000. The fabrication of integrated circuits (ICs) relies heavily on photolithography to define the shape and pattern of individual components. Current manufacturing practices use hazardous chemicals and enormous amounts of purified water during this intermediate step, which may be repeated up to 30 times for a single wafer. It is estimated that a typical chip-fabrication plant generates 4 million gallons of waste water and consumes thousands of gallons of corrosive chemicals and hazardous solvents each day.

SC Fluids, in partnership with Los Alamos National Laboratory, has developed a new process, SCORR, that removes photoresist and post-ash, -etch, and -CMP (particulate) residue from semiconductor wafers. The SCORR technology outperforms conventional photoresist removal techniques in the areas of waste minimization, water use, energy consumption, worker safety, feature size compatibility, material compatibility, and cost. The key to the effectiveness of SCORR is the use of supercritical CO_2 in place of hazardous solvents and corrosive chemicals. Neat CO_2 is also utilized for the rinse step, thereby eliminating the need for a deionized water rinse and an isopropyl alcohol drying step. In the closed loop SCORR process, CO_2 returns to a gaseous phase upon depressurization, leaving the silicon wafer dry and free of residue.

SCORR is cost-effective for five principal reasons. It minimizes the use of hazardous solvents, thereby minimizing costs required for disposal and discharge permits. It thoroughly strips photoresists from the wafer surface in less than half the time required for wet-stripping and far outperforms plasma, resulting in increased throughput. It eliminates rinsing and drying steps during the fabrication process, thereby simplifying and streamlining the manufacturing process. It eliminates the need for ultra-pure deionized water, thus reducing time, energy, and cost. Supercritical CO_2 costs less than traditional solvents and is recyclable.

SCORR will meet future, as well as current technology demands. To continue its astounding growth, the semiconductor industry must develop ICs that are smaller, faster, and cheaper. Due to their high viscosity, traditional wet chemistries cannot clean small feature sizes. Vapor cleaning technologies are available, but viable methods for particle removal in the gas phase have not yet been developed. Using SCORR, the smallest features present no barriers because supercritical fluids have zero surface tension and a "gaslike" viscosity and, therefore, can clean features less than 100 nm. The low viscosity of supercritical fluids also allows particles less than 100 nm to be removed. The end result is a technically enabling "green" process that has been accepted by leading semiconductor manufacturers and equipment and material suppliers.

SCORR technology is being driven by industry in pursuit of its own accelerated technical and manufacturing goals. SCORR was initially developed through a technical request from Hewlett Packard (now Agilent). A joint Cooperative Research and Development Agreement between Los Alamos National Laboratory and SC Fluids has led to the development of commercial units (SC Fluids' Arroyo™ System). Other industry leaders, such as IBM, ATMI, and Shipley, are participating in the development of this innovative technology.

Alternative Synthetic Pathways Award

Pfizer, Inc.

Green Chemistry in the Redesign of the Sertraline Process

Sertraline is the active ingredient in the important pharmaceutical, Zoloft®. Zoloft® is the most prescribed agent of its kind and is used to treat an illness (depression) that each year strikes 20 million adults in the U.S. and that costs society $43.7 billion (1990 dollars). As of February 2000, more than 115 million Zoloft® prescriptions had been written in the U.S.

Applying the principles of green chemistry, Pfizer has dramatically improved the commercial manufacturing process of sertraline. After meticulously investigating of each of the chemical steps, Pfizer implemented a substantive green chemistry technology for a complex commercial process requiring extremely pure product. As a result, Pfizer significantly improved both worker and environmental safety. The new commercial process (referred to as the "combined" process) offers substantial pollution prevention benefits including improved safety and material handling, reduced energy and water use, and doubled overall product yield.

Specifically, a three-step sequence in the original manufacturing process was streamlined to a single step in the new sertraline process. The new process consists of imine formation of monomethylamine with a tetralone, followed by reduction of the imine function and in-situ resolution of the diastereomeric salts of mandelic acid to provide chirally pure sertraline in much higher yield and with greater selectivity. A more selective palladium catalyst was implemented in the reduction step, which reduced the formation of impurities and the need for reprocessing. Raw material use was cut by 60 percent, 45 percent, and 20 percent for monomethylamine, tetralone, and mandelic acid, respectively.

Pfizer also optimized its process using the more benign solvent ethanol for the combined process. This change eliminated the need to use, distill, and recover four solvents (methylene chloride, tetrahydrofuran, toluene, hexane) from the original synthesis. Pfizer's innovative use of solubility differences to drive the equilibrium toward imine formation in the first reaction of the combined steps eliminated approximately 140 metric tons/yr of the problematic reagent titanium tetrachloride. This process change eliminates of 100 metric tons of 50 percent NaOH use, 150 metric tons of 35 percent HCl waste, and 440 metric tons of solid titanium dioxide wastes per year.

By eliminating waste, reducing solvents, and maximizing the yield of key intermediates, Pfizer has demonstrated significant green chemistry innovation in the manufacture of an important pharmaceutical agent.

Alternative Solvents/ Reaction Conditions Award

Cargill Dow LLC

NatureWorks™ PLA Process

Nature Works™ polylactic acid (PLA) is the first family of polymers derived entirely from annually renewable resources that can compete head-to-head with traditional fibers and plastic packaging materials on a cost and performance basis. For fiber consumers, this will mean a new option for apparel and carpeting applications: a material that bridges the gap in performance between conventional synthetic fibers and natural fibers such as silk, wool, and cotton. Clothing made with Nature Works™ fibers features a unique combination of desirable attributes such as superior hand, touch, and drape, wrinkle resistance, excellent moisture management, and resilience. In packaging applications, consumers will have the opportunity to use a material that is natural, compostable, and recyclable without experiencing any tradeoffs in product performance.

The Nature Works™ PLA process offers significant environmental benefit in addition to the outstanding performance attributes of the polymer. Nature Works™ PLA products are made in a revolutionary new process developed by Cargill Dow LLC that incorporates all 12 green chemistry principles. The process consists of three separate and distinct steps that lead to the production of lactic acid, lactide, and PLA high polymer. Each of the process steps is free of organic solvent: water is used in the fermentation while molten lactide and polymer serve as the reaction media in monomer and polymer production. Each step not only has exceptionally high yields (>95 percent), but also utilizes internal recycle streams to eliminate waste. Small (ppm) amounts of catalyst are used in both the lactide synthesis and polymerization to further enhance efficiency and reduce energy consumption. Additionally, the lactic acid is derived from annually renewable resources, PLA requires 20–50 percent less fossil resources than comparable petroleum-based plastics, and PLA is fully biodegradable or readily hydrolyzed into lactic acid for recycling back into the process.

While the technology to create PLA in the laboratory has been known for many years, previous attempts at large-scale production were targeted solely at niche biodegradable applications and were not commercially viable. Only now has Cargill Dow been able to perfect the Nature Works™ process and enhance the physical properties of PLA resins to compete successfully with commodity petroleum-based plastics. Cargill Dow is currently producing approximately 4,000 metric tons of PLA per year to meet immediate market development needs. Production in the first world-scale 140,000 metric ton/yr plant began November 1, 2001.

The Nature Works™ process embodies the well-known principles of green chemistry by preventing pollution at the source through the use of a natural fermentation process to produce lactic acid, substituting annually renewable materials for petroleum-based feedstock, eliminating the use of solvents and other hazardous materials, completely recycling product and byproduct streams, and efficiently using catalysts to reduce energy consumption and improve yield. In addition, Nature Works™ PLA products can be either recycled or composted after use.

CSI

ACQ Preserve®: The Environmentally Advanced Wood Preservative

The pressure-treated wood industry is a $4 billion industry, producing approximately 7 billion board feet of preserved wood per year. More than 95 percent of the pressure-treated wood used in the United States is currently preserved with chromated copper arsenate (CCA). Approximately 150 million pounds of CCA wood preservatives were used in the production of pressure-treated wood in 2001, enough wood to build 435,000 homes. About 40 million pounds of arsenic and 64 million pounds of hexavalent chromium were used to manufacture these CCA wood preservatives.

Over the past few years, scientists, environmentalists, and regulators have raised concerns regarding the risks posed by the arsenic that is either dislodged or leached from CCA-treated wood. A principal concern is the risk to children from contact with CCA-treated wood in playground equipment, picnic tables, and decks. This concern has led to the increased demand for and use of alternatives to CCA.

Chemical Specialties, Inc. (CSI) developed its alkaline copper quaternary (ACQ) wood preservative as an environmentally advanced formula designed to replace the CCA industry standard. ACQ formulations combine a bivalent copper complex and a quaternary ammonium compound in a 2:1 ratio. The copper complex may be dissolved in either ethanolamine or ammonia. Carbon dioxide (CO_2) is added to the formulation to improve stability and to aid in solubilization of the copper.

Replacing CCA with ACQ is one of the most dramatic pollution prevention advancements in recent history. Because more than 90 percent of the 44 million pounds of arsenic used in the U.S. each year is used to make CCA, replacing CCA with ACQ will virtually eliminate the use of arsenic in the United States. In addition, ACQ Preserve® will eliminate the use of 64 million pounds of hexavalent chromium. Further, ACQ avoids the potential risks associated with the production, transportation, use, and disposal of the arsenic and hexavalent chromium contained in CCA wood preservatives and CCA-treated wood. In fact, ACQ does not generate any RCRA* hazardous waste from production and treating facilities. The disposal issues associated with CCA-treated wood and ash residues associated with the burning of treated wood will also be avoided.

In 1996, CSI commercialized ACQ Preserve® in the United States. More than 1 million active pounds of ACQ wood preservatives were sold in the U.S. in 2001 for use by thirteen wood treaters to produce over 100 million board feet of ACQ-preserved wood. In 2002, CSI plans to spend approximately $20 million to increase its production capacity for ACQ to over 50 million active pounds. By investing in ACQ technology, CSI has positioned itself and the wood preservation industry to transition away from arsenic-based wood preservatives to a new generation of preservative systems.

* RCRA - Resource Conservation and Recovery Act

Academic Award

Professor Chao-Jun Li
Tulane University

Quasi-Nature Catalysis: Developing Transition Metal Catalysis in Air and Water

The use of transition metals for catalyzing reactions is of growing importance in modern organic chemistry. These catalyses are widely used in the synthesis of pharmaceuticals, fine chemicals, petrochemicals, agricultural chemicals, polymers, and plastics. Of particular importance is the formation of C–C, C–O, C–N, and C–H bonds. Traditionally, the use of an inert gas atmosphere and the exclusion of moisture have been essential in both organometallic chemistry and transition-metal catalysis. The catalytic actions of transition metals in ambient atmosphere have played key roles in various enzymatic reactions including biocatalysis, biodegradation, photosynthesis, nitrogen fixation, and digestions, as well as the evolution of bioorganisms. Unlike traditionally used transition-metal catalysts, these "natural" catalytic reactions occur under aqueous conditions in an air atmosphere.

The research of Professor Chao-Jun Li has focused on the development of numerous transition-metal-catalyzed reactions both in air and water. Specifically, Li has developed a novel [3+2] cycloaddition reaction to generate 5-membered carbocycles in water; a synthesis of beta-hydroxyl esters in water; a chemoselective alkylation and pinacol coupling reaction mediated by manganese in water; and a novel alkylation of 1,3-dicarbonyl-type compounds in water. Li's work has enabled rhodium-catalyzed carbonyl addition and rhodium-catalyzed conjugate addition reactions to be carried out in air and water for the first time. A highly efficient, zinc-mediated Ullman-type coupling reaction catalyzed by palladium in water has also been designed. This reaction is conducted at room temperature under an atmosphere of air. In addition, a number of Barbier-Grignard-type reactions in water have been developed; these novel synthetic methodologies are applicable to the synthesis of a variety of useful chemicals and compounds. Some of these reactions demonstrate unprecedented chemoselectivity that eliminates byproduct formation and product separation. Application of these new methodologies to natural product synthesis, including polyhydroxylated natural products, medium-sized rings, and macrocyclic compounds, yields shorter reaction sequences.

Transition-metal catalyzed reactions in water and air offer many advantages. Water is readily available and inexpensive, and is not flammable, explosive, or toxic. Consequently, aqueous-based production processes are inherently safer with regard to accident potential. Using water as a reaction solvent can save synthetic steps by avoiding protection and deprotection processes that affect overall synthetic efficiency and contribute to solvent emission. Product isolation may be facilitated by simple phase separation rather than energy-intensive and organic-emitting processes involving distillation of organic solvent. The temperature of reactions performed in aqueous media is also easier to control since water has such a high heat capacity. The open-air feature offers convenience in operations of chemical synthesis involving small-scale combinatorial synthesis, large-scale manufacturing, and catalyst recycling. As such, the work of Li in developing transition-metal-mediated and -catalyzed reactions in air and water offers an attractive alternative to the inert atmosphere and organic solvents traditionally used in synthesis.

Small Business Award

EDEN Bioscience Corporation

Messenger®: A Green Chemistry Revolution in Plant Production and Food Safety

In today's competitive agricultural environment, growers must maximize crop productivity by enhancing yield and minimizing crop losses. The Food and Agriculture Organization of the United Nations estimates annual losses to growers from pests reach $300 billion worldwide. In addition to basic agronomic practices, growers generally have two alternatives to limit these economic losses and increase yields: (1) use traditional chemical pesticides; or (2) grow crops that are genetically engineered for pest resistance. Each of these approaches has come under increasing criticism from a variety of sources worldwide including environmental groups, government regulators, consumers, and labor advocacy groups. Harpin technology, developed by EDEN Bioscience Corporation, provides growers with a highly effective alternative approach to crop production that addresses these concerns.

EDEN's harpin technology is based on a new class of nontoxic, naturally occurring proteins called harpins, which were first discovered by Dr. Zhongmin Wei, EDEN's Vice President of Research, and his colleagues during his tenure at Cornell University. Harpin proteins trigger a plant's natural defense systems to protect against disease and pests and simultaneously activate certain plant growth systems without altering the plant's DNA. When applied to crops, harpin increases plant biomass, photosynthesis, nutrient uptake, and root development and, ultimately, leads to greater crop yield and quality.

Unlike most agricultural chemicals, harpin-based products are produced in a water-based fermentation system that uses no harsh solvents or reagents, requires only modest energy inputs, and generates no hazardous chemical wastes. Fermentation byproducts are fully biodegradable and safely disposable. In addition, EDEN uses low-risk ingredients to formulate the harpin protein-based end product. Approximately 70 percent of the dried finished product consists of an innocuous food grade substance that is used as a carrier for harpin protein.

The result of this technology is an EPA-approved product called Messenger®, that has been demonstrated on more than 40 crops to effectively stimulate plants to defend themselves against a broad spectrum of viral, fungal, and bacterial diseases, including some for which there currently is no effective treatment. In addition, Messenger® has been shown through an extensive safety evaluation to have virtually no adverse effect on any of the organisms tested, including mammals, birds, honey bees, plants, fish, aquatic invertebrates, and algae. Only 0.004 to 0.14 pounds of harpin protein per acre per season is necessary to protect crops and enhance yields. As with most proteins, harpin is a fragile molecule that is degraded rapidly by UV and natural microorganisms and has no potential to bioaccumulate or to contaminate surface or groundwater resources.

Deployment of harpin technology conserves resources and protects the environment by reducing total agricultural inputs and partially replacing many higher risk products. Using environmentally benign harpin protein technology, growers for the first time in the history of modern agriculture will be able to harness the innate defense and growth systems of crops to substantially enhance yields, improve crop quality, and reduce reliance on conventional agricultural chemicals.

Alternative Synthetic Pathways Award

Bayer Corporation and Bayer AG

Baypure™ CX: Iminodisuccinate
An Environmentally Friendly and Readily Biodegradable Chelating Agent

Chelating agents are used in a variety of applications, including detergents, agricultural nutrients, and household and industrial cleaners. Most traditionally used chelating agents, however, are poorly biodegradable. Some are actually quite persistent and do not adsorb at the surface of soils in the environment or at activated sludge in wastewater treatment plants. Because of this poor biodegradability combined with high water solubility, traditionally used chelators are readily released into the environment and have been detected in the surface waters of rivers and lakes and in make-up water processed for drinking water.

As part of its commitment to Responsible Care®, Bayer Corporation manufactures a readily biodegradable and environmentally friendly chelating agent, D,L-aspartic-N-(1,2-dicarboxyethyl) tetrasodium salt, also known as sodium iminodisuccinate. This agent is characterized by excellent chelation capabilities, especially for iron(III), copper(II), and calcium, and is both readily biodegradable and benign from a toxicological and ecotoxicological standpoint. Sodium iminodisuccinate is also an innovation in the design of chemicals that favorably impact the environment. This accomplishment was realized not by "simple" modification of molecular structures of currently used chelating agents, but instead by the development of a wholly new molecule. Sodium iminodisuccinate is produced by a 100 percent waste-free and environmentally friendly manufacturing process. Bayer AG was the first to establish an environmentally friendly, patented manufacturing process to provide this innovative chelant commercially.

Sodium iminodisuccinate belongs to the aminocarboxylate class of chelating agents. Nearly all aminocarboxylates in use today are acetic acid derivatives produced from amines, formaldehyde, sodium hydroxide, and hydrogen cyanide. The industrial use of thousands of tons of hydrogen cyanide is an extreme toxicity hazard. In contrast, Bayer's sodium iminodisuccinate is produced from maleic anhydride (a raw material also produced by Bayer), water, sodium hydroxide, and ammonia. The only solvent used in the production process is water, and the only side product formed, ammonia dissolved in water, is recycled back into sodium iminodisuccinate production or used in other Bayer processes.

Because sodium iminodisuccinate is a readily biodegradable, nontoxic, and non-polluting alternative to other chelating agents, it can be used in a variety of applications that employ chelating agents. For example, it can be used as a builder and bleach stabilizer in laundry and dishwashing detergents to extend and improve the cleaning properties of the 8 billion pounds of these products that are used annually. Specifically, sodium iminodisuccinate chelates calcium to soften water and improve the cleaning function of the surfactant. In photographic film processing, sodium iminodisuccinate complexes metal ions and helps to eliminate precipitation onto the film surface. In agriculture, chelated metal ions help to prevent, correct, and minimize crop mineral deficiencies. Using sodium iminodisuccinate as the chelating agent in agricultural applications eliminates the problem of environmental persistence common with other synthetic chelating agents. In summary, Bayer's sodium iminodisuccinate chelating agent offers the dual benefits of producing a biodegradable, environmentally friendly chelating agent that is also manufactured in a waste-free process.

Alternative Solvents/ Reaction Conditions Award

Novozymes North America, Inc.

BioPreparation™ of Cotton Textiles: A Cost-Effective, Environmentally Compatible Preparation Process

In textiles, the source of one of the most negative impacts on the environment originates from traditional processes used to prepare cotton fiber, yarn, and fabric. Fabric preparation consists of a series of various treatments and rinsing steps critical to obtaining good results in subsequent textile finishing processes. These water-intensive wet processing steps generate large volumes of wastes, particularly from alkaline scouring and continuous/batch dyeing. These wastes include large amounts of salts, acids, and alkali. In view of the 40 billion pounds of cotton fiber that are prepared annually on a global scale, it becomes clear that the preparation process is a major source of environmentally harsh chemical contribution to the environment.

Cotton wax, a natural component in the outer layer of cotton fibers, is a major obstacle in processing textiles and must be removed to prepare the textile for dyeing and finishing. Conventional chemical preparation processes involve treatment of the cotton substrate with hot solutions of sodium hydroxide, chelating agents, and surface active agents, often followed by a neutralization step with acetic acid. The scouring process is designed to break down or release natural waxes, oils, and contaminants, and emulsify or suspend these impurities in the scouring bath. Typically, scouring wastes contribute high BOD loads during cotton textile preparation (as much as 50 percent).

Novozymes' BioPreparation™ technology is an alternative to sodium hydroxide that offers many advantages for textile wet processing, including reduced BOD/COD and decreased water use. BioPreparation™ is an enzymatic process for treating cotton textiles that meets the performance characteristics of alkaline scour systems while reducing chemical and effluent load. Pectate lyase is the main scouring agent that degrades pectin to release the entangled waxes and other components from the cotton surface. The enzyme is also compatible with other enzymatic preparations (amylases, cellulases) used to improve the performance properties of cotton fabrics.

The practical implications that BioPreparation™ technology has on the textile industry are realized in terms of conservation of chemicals, water, energy, and time. Based on field trials, textile mills may save as much as 30-50 percent in water costs by replacing caustic scours or by combining the usually separate scouring and dyeing steps into one. This water savings results because BioPreparation™ uses fewer rinsing steps than required during a traditional caustic scour. Significant time savings were also demonstrated by combining treatment steps. A recent statistical survey determined that 162 knitting mills typically use 89 million m^3/yr of water in processing goods from scouring to finishing; the BioPreparation™ approach would save from 27-45 million m^3/yr of water. In addition, field trials established that BOD and COD loads are decreased by 25 and 40 percent, respectively, when compared to conventional sodium hydroxide treatments. Furthermore, these conservation measures translate directly into costs savings of 30 percent or more. As such, this patented process provides an economical and environmentally friendly alternative to alkaline scour systems currently used in the textile industry.

Designing Safer Chemicals Award

PPG Industries

Yttrium as a Lead Substitute in Cationic Electrodeposition Coatings

PPG Industries introduced the first cationic electrodeposition primer to the automotive industry in 1976. During the succeeding years, this coating technology became very widely used in the industry, such that today, essentially all automobiles are given a primer coat using the chemistry and processing methods developed by PPG. The major benefits of this technology are corrosion resistance, high transfer efficiency (low waste), reliable automated application, and very low organic emissions. Unfortunately, the high corrosion resistance property of electrocoat has always been dependent on the presence of small amounts of lead salts or lead pigments in the product. As regulatory pressure on lead increased and consumer demand for improved corrosion resistance grew, lead was regularly exempted from regulation in electrocoat because there were no cost-effective substitutes. This is especially important in moderately priced cars and trucks where the high cost of using 100 percent zinc-coated (galvanized) steel could not be tolerated. Lead is very effective for protecting cold-rolled steel, which is still a common material of construction in automobiles.

For more than 20 years, PPG and other paint companies have sought a substitute for lead in this application. This search led to PPG's discovery that lead can be replaced by yttrium in cationic electrocoat without any sacrifice in corrosion performance. Yttrium is a common element in the environment, being widely distributed in low concentrations throughout the earth's crust and more plentiful in the earth's crust than lead and silver. Although yttrium is much less studied than lead, the available data on yttrium indicate orders of magnitude lower hazard. As a dust hazard, yttrium is 100 times safer than lead at typical levels of use.

Numerous other benefits are realized when yttrium is used in electrocoat applications. Yttrium is twice as effective as lead on a weight basis, allowing the formulation of commercial coatings that contain half the yttrium by weight relative to lead in comparably performing lead-containing products. In addition, it has been found that as yttrium is deposited in an electrocoat film, it deposits as the hydroxide. The hydroxide is converted to yttrium oxide during normal baking of the electrocoat. The oxide is extraordinarily nontoxic by ingestion as indicated by the LD_{50} of >10g/kg in rats, which is in stark contrast to lead. The ubiquitous nature of yttrium in the environment and the insoluble ceramic-like nature of the oxide combine to make it an unlikely cause of future environmental or health problems.

An environmental side benefit of yttrium is its performance over low-nickel and chrome-free metal pretreatments. In automotive production, a metal pretreatment is always applied to the body prior to electrocoat, which is designed to assist in adhesion and corrosion performance. This process generates significant quantities of chromium- and nickel-containing waste and, like lead, is also a concern to recyclers of the finished vehicle. By using yttrium in the electrocoat step, chrome can be completely eliminated using standard chrome-free rinses and low-nickel or possibly nickel-free pretreatments, both of which are commercially available today. This should be possible without concern of compromising long term vehicle corrosion performance. For PPG pretreatment customers, this should result in the elimination of up to 25,000 pounds of chrome and 50,000 pounds of nickel annually from PPG products. As PPG customers implement yttrium over the next several years, approximately one million pounds of lead (as lead metal) will be removed from the electrocoat applications of PPG automotive customers.

Academic Award

Professor Chi-Huey Wong
The Scripps Research Institute

Enzymes in Large-Scale Organic Synthesis

Organic synthesis has been one of the most successful of scientific disciplines and has contributed significantly to the development of the pharmaceutical and chemical industries. New synthetic reagents, catalysts, and processes have made possible the synthesis of molecules with varying degrees of complexity. The types of problems at which nonbiological organic synthesis has excelled, ranging from stoichiometric reactions to catalysis with acids, bases, and metals, will continue to be very important. New synthetic and catalytic methods are, however, necessary to deal with the new classes of compounds that are becoming the key targets of molecular research and development.

Compounds with polyfunctional groups, such as carbohydrates and related structures, pose particular challenges to nonbiological synthetic methods, but are natural targets for biological methods. In addition, biological methods are necessary to deal with increasing constraints imposed by environmental concerns. Transition metals, heavy elements, and toxic organic solvents are often used in nonbiological processes. When these materials are used with great care and efficiency, they may still be environmentally acceptable, but their handling and disposal pose problems. The ability to use recombinant and engineered enzymes to carry out environmentally acceptable synthetic transformations that are otherwise impossible or impractical offers one of the best opportunities now available to chemistry and the pharmaceutical industry.

Professor Chi-Huey Wong at the Scripps Research Institute has pioneered work on the development of effective enzymes and the design of novel substrates and processes for large-scale organic synthesis. The methods and strategies that Professor Wong has developed have made possible synthetic transformations that are otherwise impossible or impractical, especially in areas vitally important in biology and medicine, and have pointed the way toward new green methodologies for use in large-scale chemistry. A recent study by the Institute for Scientific Information ranked Professor Wong in the top 15 of the most-cited chemists in the world for the period 1994 to 1996. According to this study, he is also the most-cited chemist worldwide working in the area of enzymes.

Some of the strategies and methods developed by Professor Wong are breakthrough achievements that laid the framework for much of the current use of enzymes as catalysts in large-scale organic synthesis. The techniques and reagents developed in this body of pioneering work are used widely today for research and development. The scope of contributions ranges from relatively simple enzymatic processes (e.g., chiral resolutions and stereoselective syntheses) to complex, multi-step enzymatic reactions (e.g., oligosaccharide synthesis). For example, the irreversible enzymatic transesterification reaction using enol esters in environmentally acceptable organic solvents invented by Wong represents the most widely used method for enantioselective transformation of alcohols in pharmaceutical development. The multi-enzyme system based on genetically engineered glycosyltransferases coupled with in situ regeneration of sugar nucleotides developed by Professor Wong has revolutionized the field of carbohydrate chemistry and enabled the large-scale synthesis of complex oligosaccharides for clinical evaluation. All of these new enzymatic reactions are carried out in environmentally acceptable solvents, under mild reaction conditions, at ambient temperature, and with minimum protection of functional groups. The work of Professor Wong represents a new field of green chemistry suitable for large-scale synthesis that is impossible or impractical to achieve by nonenzymatic means.

Small Business Award

RevTech, Inc.

EnvirogluvTM: A Technology for Decorating Glass and Ceramicware With Radiation-Curable Environmentally Compliant Inks

Billions of products are sold in glass containers in the United States every year. Most, if not all, of these glass containers are labeled in some fashion. Typically, decorative indicia are applied to glass using paper labels, decals, or a process known as applied ceramic labeling (ACL). ACL involves first printing the glass with an ink composition that contains various heavy metals such as lead, cadmium, and chromium, then bonding the ink to the glass by baking in an oven known as a lehr at temperatures of 1,000 °F or more for several hours.

All of these processes have disadvantages. Paper labels are inexpensive, but can be easily removed if the container is exposed to water or abrasion. In addition, paper labels do not provide the aesthetics desired by decorators who want rich, expensive-looking containers. Decals are expensive and difficult to apply at the high line speeds that are required in the decoration of most commercial containers. More important, decals are made from materials that are not biodegradable, which causes serious problems in the recycling of glass containers that are decorated by this method. The use and disposal of the heavy metals required in ACL presents serious environmental concerns. Moreover, the high-temperature lehr ovens required in ACL decorating utilize substantial amounts of energy and raise safety issues with respect to workers and plant facilities that use this equipment. The inks used in ACL decorating also tend to contain high levels of volatile organic compounds (VOCs) that can lead to undesirable emissions.

Clearly there has been a need in the glass decorating industry for a decorated glass container that is aesthetically pleasing, durable, and obtained in a cost-effective, environmentally friendly, and energy-efficient manner. EnvirogluvTM technology fills that need. EnvirogluvTM is a glass decorating technology that directly silk screens radiation-curable inks onto glass, then cures the ink almost instantly by exposure to UV light. The result is a crisp, clean label that is environmentally sound, with a unit cost that is about half of that achieved with traditional labeling.

Envirogluv™ technology offers many human health and environmental benefits. The ink compositions used in the Envirogluv™ process do not contain any heavy metals and contain little to no VOCs. All pigments used are biodegradable. The Envirogluv™ inks are cured directly on the glass by exposure to UV radiation, eliminating the high-temperature baking in a lehr oven associated with the ACL process. This provides additional safety and environmental benefits, such as reduced energy consumption and reduced chance of worker injury. In addition, there is less raw material use and the process does not generate any waste ink. Furthermore, Envirogluv™ decorated glass containers eliminate the need for extra packaging and are completely recyclable. Applications suitable for the Envirogluv™ process include tableware, cosmetics containers, and plate glass.

Alternative Synthetic Pathways Award

Roche Colorado Corporation

An Efficient Process for the Production of Cytovene®, A Potent Antiviral Agent

The design, development, and implementation of environmentally friendly processes for the large-scale production of pharmaceutical products is one of the most technically challenging aspects of business operations in the pharmaceutical industry. Roche Colorado Corporation (RCC), in establishing management and operational systems for the continuous improvement of environmental quality in its business activities, has, in essence, adopted the Presidential Green Chemistry Challenge Program's basic principles of green chemistry: the development of environmentally friendly processes for the manufacture of pharmaceutical products. In particular, RCC has successfully applied these principles to the manufacture of Cytovene®, a potent antiviral agent used in the treatment of cytomegalovirus (CMV) retinitis infections in immunocompromised patients, including patients with AIDS, and also used for the prevention of CMV disease in transplant recipients at risk for CMV.

In the early 1990s, Roche Colorado Corporation developed the first commercially viable process for the production of Cytovene®. By 1993, chemists at RCC's Boulder Technology Center designed a new and expedient process for the production of Cytovene®, which at the time had an estimated commercial demand of approximately 50 metric tons per year. Leveraging the basic principles of green chemistry and molecular conservation into the design process, significant improvements were demonstrated in the second-generation Guanine Triester (GTE) Process. Compared to the first-generation commercial manufacturing process, the GTE Process reduced the number of chemical reagents and intermediates from 22 to 11, eliminated the (only) two hazardous solid waste streams, eliminated 11 different chemicals from the hazardous liquid waste streams, and efficiently recycled and reused four of the five ingredients not incorporated into the final product. Inherent within the process improvements demonstrated was the complete elimination of the need for operating and monitoring three different potentially hazardous chemical reactions. Overall, the

GTE Process provided an expedient method for the production of Cytovene®, demonstrating a procedure that provided an overall yield increase of more than 25 percent and a production throughput increase of 100 percent.

In summary, the new GTE Process for the commercial production of Cytovene® clearly demonstrates the successful implementation of the general principles of green chemistry: the development of environmentally friendly syntheses, including the development of alternative syntheses utilizing nonhazardous and nontoxic feedstocks, reagents, and solvents; elimination of waste at the source (liquid waste: 1.12 million kg/yr and solid waste: 25,300 kg/yr); and elimination of the production of toxic wastes and byproducts. The process establishes new and innovative technology for a general and efficient method for the preparation of Cytovene® and other potent antiviral agents. It is registered with the U.S. Food and Drug Administration (FDA) as the current manufacturing process for the world's supply of Cytovene®

Alternative Solvents/ Reaction Conditions Awards

Bayer Corporation and Bayer AG

Two-Component Waterborne Polyurethane Coatings

Two-component (2K) waterborne polyurethane coatings are an outstanding example of the use of alternative reaction conditions for green chemistry. This technology is achieved by replacing most or all of the volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) used in conventional 2K solventborne polyurethane coatings with water as the carrier, without significant reduction in performance of the resulting coatings. This may seem an obvious substitution, but due to the particular chemistry of the reactive components of polyurethane, it is not that straightforward.

Two-component solventborne polyurethane coatings have long been considered in many application areas to be the benchmark for high-performance coatings systems. The attributes that make these systems so attractive are fast cure under ambient or bake conditions, high-gloss and mirror-like finishes, hardness or flexibility as desired, chemical and solvent resistance, and excellent weathering. The traditional carrier, however, has been organic solvent that, upon cure, is freed to the atmosphere as VOC and HAP material. High-solids systems and aqueous polyurethane dispersions ameliorate this problem, but do not go far enough.

An obvious solution to the deficiencies of 2K solventborne polyurethanes and aqueous polyurethane dispersions is a reactive 2K polyurethane system with water as the carrier. In order to bring 2K waterborne polyurethane coatings to the U.S. market, new waterborne and water-reducible resins had to be developed. To overcome some application difficulties, new mixing/spraying equipment was also developed. For the technology to be commercially viable, an undesired reaction of a polyisocyanate crosslinker with water had to be addressed, as well as problems with the chemical and film appearance resulting from this side reaction. The work done on the 2K waterborne polyurethanes over the past several years has resulted in a technology that will provide several health and environmental benefits. VOCs will be reduced by 50–90 percent and HAPs by 50–99 percent. The amount of chemical byproducts evolved from films in interior applications will also be reduced, and rugged interior coatings with no solvent smell will now be available.

Today, 2K waterborne polyurethane is being applied on industrial lines where good properties and fast cure rates are required for such varied products as metal containers and shelving, sporting equipment, metal- and fiberglass-reinforced utility poles, agricultural equipment, and paper products. In flooring coatings applications where the market driving force is elimination of solvent odor, 2K waterborne polyurethane floor coatings provide a quick dry, high abrasion resistance, and lack of solvent smell (<0.1 lb/gal organic solvent). In wood applications, 2K waterborne polyurethane coatings meet the high-performance wood finishes requirements for kitchen cabinet, office, and laboratory furniture manufacturers while releasing minimal organic solvents in the workplace or to the atmosphere. In the U.S., the greatest market acceptance of 2K waterborne polyurethane is in the area of special-effect coatings in automotive applications. These coatings provide the soft, luxurious look and feel of leather to hard plastic interior automobile surfaces, such as instrument panels and air bag covers. Finally, in military applications, 2K waterborne polyurethane coatings are being selected because they meet the demanding military performance criteria that include flat coatings with camouflage requirements, corrosion protection, chemical and chemical agent protection, flexibility, and exterior durability, along with VOC reductions of approximately 50 percent.

Designing Safer Chemicals Award

Dow AgroSciences LLC

Sentricon™ Termite Colony Elimination System, A New Paradigm for Termite Control

The annual cost of termite treatments to the U.S. consumer is about $1.5 billion, and each year as many as 1.5 million homeowners will experience a termite problem and seek a control option. From the 1940s until 1995, the nearly universal treatment approach for subterranean termite control involved the placement of large volumes of insecticide dilutions into the soil surrounding a structure to create a chemical barrier through which termites could not penetrate. Problems with this approach include difficulty in establishing an uninterrupted barrier in the vast array of soil and structural conditions, use of large volumes of insecticide dilution, potential hazards associated with accidental misapplications, spills, off-target applications, and worker exposure. These inherent problems associated with the use of chemical barrier approaches for subterranean termite control created a need for a better method. The search for a baiting alternative was the focus of a research program established by Dr. Nan-Yao Su of the University of Florida who, in the 1980s, had identified the characteristics needed for a successful termite bait toxicant.

The unique properties of hexaflumuron made it an excellent choice for use in controlling subterranean termite colonies. The Sentricon™ Termite Colony Elimination System, developed by Dow AgroSciences in collaboration with Dr. Su, was launched commercially in 1995 after receiving U.S. EPA registration as a reduced-risk pesticide. Sentricon™ represents truly novel technology employing an Integrated Pest Management approach using monitoring and targeted delivery of a highly specific bait. Because it eliminates termite colonies threatening structures using a targeted approach, Sentricon™ delivers unmatched technical performance, environmental compatibility, and reduced human risk. The properties of hexaflumuron as a termite control agent are attractive from an environmental and human risk perspective, but more important, the potential for adverse effects is dramatically reduced because it is present only in very small quantities in stations with termite activity. The comparisons to barrier methods show significant reduction in the use of hazardous materials and substantial reduction in potential impacts on human health and the environment.

The discovery of hexaflumuron's activity with its unique fit and applicability for use as a termite bait was a key milestone for the structural pest control industry and Dow AgroSciences. The development and commercial launch of Sentricon™ changed the paradigm for protecting structures from damage caused by subterranean termites. The development of novel research methodologies, new delivery systems, and the establishment of an approach that integrates monitoring and baiting typify the innovation that has been a hallmark of the project. More than 300,000 structures across the U.S. are now being safeguarded through application of this revolutionary technology, and adoption is growing rapidly.

Academic Award

Professor Terry Collins
Carnegie Mellon University

TAML™ Oxidant Activators:
General Activation of Hydrogen Peroxide for Green Chemistry

Twenty years of research by Professor Terry Collins at Carnegie Mellon University have led to the successful development of a series of environmentally friendly oxidant activators based on iron. These TAML™ (tetraamido-macrocyclic ligand) activators catalyze the reactions of oxidants in general. Their activation properties with hydrogen peroxide in water are of greatest environmental significance. TAML™ activators arise from a design process invented by Professor Collins which is complementary to that employed by Nature to produce powerful oxidizing enzymes. The activators promise extensive environmental benefits coupled with superior technical performance and significant cost savings across a broad-based segment of oxidation technology. Users of TAML™ peroxide activators will range from huge primary extractive-processing industries to household consumers throughout the world. In laboratory tests, the Collins activators have shown this potential in the major industrial application of wood-pulp delignification and in the broad-based consumer process of laundry cleaning.

Annually, bleached pulp has a global value of approximately $50 billion. The key to quality papermaking is the selective removal of lignin from the white fibrous polysaccharides, cellulose, and hemicellulose. Wood-pulp delignification has traditionally relied on chlorine-based processes that produce chlorinated pollutants. It has been clearly demonstrated that TAML™ activators can provide the Pulp and Paper Industry (P&PI) with the first low-temperature hydrogen peroxide-based delignification technology for treating pulp. The new process moves the elemental balance of pulp delignification closer to what Nature employs for degrading lignin, a strategy reflected in the industry's recent development of totally chlorine free (TCF) bleaching procedures. TAML™- activated peroxide delignification proceeds rapidly and efficiently at 50 °C indicating that minimal capital will be required to retrofit existing mills for its use. The new technology is more selective than any other TCF process and, except at low lignin content, is as selective as the current dominating delignification technology based on chlorine dioxide. These parameters show that the new technology can significantly reduce persistent pollutants associated with chlorine-containing delignifying agents by enabling the industry to use peroxide to remove the majority of lignin from kraft pulp more selectively and more rapidly.

In the laundry field of use, most household bleaches are based upon peroxide. Here, TAML™ activators enable the most attractive dye transfer inhibition processes ever developed. Almost all the approximately 80 dyes used on commercial textiles are safe from TAML™-activated peroxide while they are bound to a fabric. But in almost every case, should a dye molecule escape a fabric, the same TAML™-activated peroxide will intercept and destroy it before it is able to transfer to other fabrics. This attribute and the improved stain removal properties of TAML™-activated peroxide offer significant commercial advantages for laundry products producers. In addition, the combined features translate to both direct and indirect environmental benefits by enabling laundering that replaces stoichiometric with catalytic procedures and that requires less water. Numerous other uses are anticipated; some are currently being developed including the use of TAML™- peroxide activators for water disinfection.

Small Business Award

Biofine, Inc.

Conversion of Low-Cost Biomass Wastes to Levulinic Acid and Derivatives

Using biomass rather than petroleum to manufacture chemicals has numerous advantages. Renewable biomass contributes no net CO_2 to the atmosphere, conserves fossil fuels, and leads to a secure domestic supply of feedstocks capable of making a huge array of chemical products. Biofine, Inc. has developed a high-temperature, dilute-acid hydrolysis process that converts cellulosic biomass to levulinic acid (LA) and derivatives. Cellulose is initially converted to soluble sugars, which are then transformed to levulinic acid. The process is economical even without receiving waste disposal fees for feedstock, and wet feedstocks can be used without drying, thereby saving energy.

In August 1997, Biofine, the U.S. Department of Energy, the New York State Energy Research and Development Authority, and Biometics, Inc. began manufacturing LA from paper mill sludge at a one-ton-per-day demonstration plant at Epic Ventures, Inc. in South Glen Falls, New York. Biofine's process had already been demonstrated on a smaller scale with a variety of cellulosic feedstocks, including municipal solid waste, unrecyclable municipal waste paper, waste wood, and agricultural residues. Biofine hopes to serve the growing need for environmentally acceptable waste disposal options.

LA niche markets provide excellent small-scale opportunities; large-scale opportunities will open up as Biofine lowers the price of this highly versatile chemical intermediate. LA's worldwide market is about one million lb/yr at a price of \$4–6/lb. Full-scale commercial plants are feasible at 50 dry ton/day of feedstock. At this scale, LA could be produced at \$0.32/lb and converted into commodity chemicals such as succinic acid and diphenolic acid, which sell for \$2/lb or less, or acrylic acid, which sells for \$0.50/lb. Eventually, Biofine hopes to build larger plants to convert 1,000 dry ton/day of feedstock into LA at \$0.04–0.05/lb. The worldwide commercial market for LA and its derivatives could reach 1 trillion lb/yr. Full-scale plant opportunities are being assessed for several locations in the U.S. and worldwide. One full-scale commercial plant using 1,000 dry ton/day of feedstock could manufacture more than

160 million lb/yr of product. Fortunately, Biofine's technology is economical for a broad range of plant sizes; even the one-ton-per-day demonstration plant is self-sufficient at LA's existing price.

Because LA is a platform chemical, it need not be sold as a commodity chemical. Derivatives are the key to marketability, and markets exist for such LA derivatives as tetrahydrofuran, butanediol, γ-butyrolactone, succinic acid, and diphenolic acid. Fortunately, many economical conversion processes are possible. The National Renewable Energy Laboratory (NREL), Pacific Northwest National Laboratory (PNNL), and Rensselaer Polytechnic Institute (RPI) are developing market applications and production methods for other derivatives, including methyltetrahydrofuran (MTHF), a gasoline fuel additive; δ-amino levulinic acid (DALA), a broad-spectrum, nontoxic, and biodegradable pesticide; and new biodegradable polymers.

Alternative Synthetic Pathways Award

Lilly Research Laboratories

Practical Application of a Biocatalyst in Pharmaceutical Manufacturing

The synthesis of a pharmaceutical agent is frequently accompanied by the use and generation of a large amount of hazardous substances. This should not be surprising, as numerous steps are commonly necessary, each of which may require feedstocks, reagents, solvents, and separation agents. An example of an effort to reduce these hazards, employed by Lilly Research Laboratories, is the use of an alternate synthetic pathway designed for the environmentally responsible production of a LY300164, a central nervous system compound in the early stages of development. The original synthesis, which was employed to support early clinical development, proved to be an economically viable manufacturing process. The approach, however, involved several problematic steps. The process required the use of large solvent volumes and chromium oxide (a cancer suspect agent), which led to the generation of disproportional quantities of chromium waste compared to drug produced. These points provided compelling incentive to pursue an alternate synthetic approach.

The new synthetic pathway successfully increased worker safety and limited environmental impact by offering a strategy that more appropriately controlled oxidation state adjustments. The new synthesis involved the implementation of several inventive steps on large scale. In particular, keto-reductase activity of a common microorganism, *Zygosaccharomyces rouxii*, was discovered that led to excellent stereocontrol in the asymmetric reduction of a dialkyl ketone. Implementation of the biocatalytic process was enabled on a large scale by employing a novel, yet simple, three-phase reaction system. The protocol overcame long-standing limitations preventing the practical application of yeast-mediated reductions by allowing high concentrations of the substrate to be charged to the aqueous reaction medium and by providing a facile method for product isolation. An unprecedented autoxidation reaction of a C-1 aryl isochroman, which involved the treatment of the substrate with air and sodium hydroxide, was also discovered that eliminated the use of transition metal oxidants.

The new process was developed by combining innovations from chemistry, microbiology, and engineering. The process circumvented the use of non-recycled metal and significantly reduced solvent usage. For example, when conducted on a scale to generate 100 kg of LY300164, the new process avoids the use of approximately 34,000 liters of solvent and eliminates production of approximately 300 kg of chromium waste. In addition, the synthetic scheme proved more efficient as well, with yield climbing from 16 to 55 percent. The inventive steps of the process represent low cost and easily implemented technology, which should find broad manufacturing applications.

Alternative Solvents/ Reaction Conditions Award

Nalco Chemical Company

Water-Based Liquid Dispersion Polymers

Annually, at least 200 million pounds of water-soluble, acrylamide-based polymers are used to condition and purify water in various industrial and municipal operations. These water-soluble polymers assist in removing suspended solids and contaminants and effecting separations. Conventionally, in order to prepare such polymers in liquid form for safety and ease of handling, the water-soluble monomers, water, and a hydrocarbon (oil) and surfactant "carrier" mixture are combined in approximately a 1:1:1 ratio to form an emulsion. The monomers are then polymerized. Regrettably, the oil and surfactant components of these inverse emulsions lend no value to the performance of the polymers; they simply allow their manufacture in liquid form. This means that approximately 90 million pounds of oil and surfactant are introduced into the environment (at the current consumption rates) as a consequence of their use. Until now, there has been no alternative technology available to manufacture liquid polymers without the obvious environmental disadvantages associated with the oil- and surfactant-based carrier systems.

In order to overcome the disadvantages of conventional liquid emulsion polymers, Nalco has developed a series of new polymer products that are produced through a unique polymerization technology that permits the manufacture of these widely used polymers as fine particles dispersed in aqueous solutions of the inorganic salt ammonium sulfate. Thus, while the chemistry of the active polymer component is the same, the technology allows for the production of the polymers as stable colloids in water. Since these dispersion polymers are liquid, they retain the virtues of ease and safety of handling, but employing aqueous salt solutions instead of hydrocarbons and surfactants as the reaction medium and polymer carrier means that no oil or surfactants are released into the environment when the polymers are used in the water treatment application.

By choosing to manufacture water-based dispersions instead of water-in-oil emulsions, Nalco has conserved over one million pounds of hydrocarbon solvent and surfactants since 1997 on just two polymers in the product line. There are also benefits over the water-in-oil emulsion polymers for the users of these products as a consequence of their water-based formulations. For example, as the products contain no oil, they are safer to transport and use because they are nonflammable and emit no volatile organic compounds (VOCs).

As mentioned, the water-based dispersion polymers make use of ammonium sulfate salt, a waste byproduct from the manufacture of caprolactam, the precursor to nylon. The preparation of water-based dispersion polymers instead of water-in-oil emulsions allows Nalco to recycle and make use of this byproduct from another industry for water treatment and purification. Choosing to produce these polymers as water-based dispersions instead of as water-in-oil emulsions allowed Nalco to utilize over 3.2 million pounds of caprolactam-produced ammonium sulfate in 1998 alone.

Finally, because these new polymers are water-based, they dissolve readily in water without the complex and relatively expensive mixing and feeding equipment that is required for the use of water-in-oil polymers. This distinct advantage provides new opportunities for medium- and smaller-sized operations to treat wastewater streams cost-effectively.

Designing Safer Chemicals Award

Dow AgroSciences LLC

Spinosad, A New Natural Product for Insect Control

Estimates of monetary losses in crops as a result of uncontrolled insect infestations are staggering, far in excess of the current $12 billion market for insect control products. Man's continuing quest to control damaging insect pests in crops or on property has spawned several eras of agricultural insect control, most recently the advent of synthetic organic chemicals as insecticides. However, the development of resistance has reduced the effectiveness of many of the currently available insecticides, and more stringent environmental and toxicological hurdles have restricted the use of others.

It was against this backdrop that researchers at Eli Lilly and Company introduced high-volume testing of fermentation isolates in agricultural screens in the mid-1980s. From this program, the microorganism *Saccaropolyspora spinosa* was isolated from a Caribbean island soil sample, and the insecticidal activity of the spinosyns, a family of unique macrocyclic lactones, was identified and developed by Dow AgroSciences as a highly selective, environmentally friendly insecticide.

In Latin, "saccharopolyspora" means "sugar-loving, with many spores", and "spinosa" refers to the spiny appearance of the spores. The microorganism is an aerobic, gram-positive bacterium that is not acid fast, motile, or filamentous. Most of the activity is produced by a mixture of spinosyn A and spinosyn D, assigned the common name of spinosad. Spinosad combines highly efficacious control of many chewing insect pests in cotton, trees, fruits, vegetables, turf, and ornamentals with a superior environmental profile, including mammalian and nontarget safety. Insects exposed to spinosad exhibit classical symptoms of neurotoxicity, including lack of coordination, prostration, tremors, and other involuntary muscle contractions, eventually leading to paralysis and death. Detailed investigations of the symptomology and electrophysiology have indicated, however, that spinosad is not acting through any known mechanism. It appears to affect insect nicotinic and γ-aminobutyric acid receptor function through a novel mechanism.

Spinosad presents a favorable environmental profile. Spinosad does not leach, bioaccumulate, volatilize, or persist in the environment. Hundreds of innovative product development trials conducted over several years have characterized the activity and determined that spinosad leaves 70–90 percent of beneficial insects and predatory wasps unharmed. The low levels of mammalian toxicity result in reduced risk to those who handle, mix, and apply the product. Similarly, relatively high margins of safety for avian and aquatic species translate into reduced or nonexistent buffer zones and fewer regulated nontarget compliance measures. These advantages allow growers to control damaging crop pests with fewer concerns about human or environmental safety and costly secondary pest outbreaks.

The first product containing spinosad (Tracer Naturalyte™ Insect Control) received expedited review by the U.S. EPA and was granted registration as a "reduced risk" insect control product for cotton in early 1997. Additional registrations, introduced as SpinTor™, Success™, Precise™, and Conserve™, have recently been granted for insect control in vegetable and tree crops and in the urban environment for control of turf and ornamental plant nests.

Academic Award

Professor Barry M. Trost
Stanford University

The Development of the Concept of Atom Economy

The general area of chemical synthesis covers virtually all segments of the chemical industry—oil refining, bulk or commodity chemicals, fine chemicals, including agrochemicals, flavors, fragrances, etc., and pharmaceuticals. Economics generally dictates the feasibility of processes that are "practical". A criterion that traditionally has not been explicitly recognized relates to the total quantity of raw materials required for the process compared to the quantity of product produced or, simply put, "how much of what you put into your pot ends up in your product". In considering the question of what constitutes synthetic efficiency, Professor Barry M. Trost has explicitly enunciated a new set of criteria by which chemical processes should be evaluated. They fall under two categories—selectivity and atom economy.

Selectivity and atom economy evolve from two basic considerations. First, the vast majority of the synthetic organic chemicals in production derive from non-renewable resources. It is self-evident that such resources should be used as sparingly as possible. Second, all waste streams should be minimized. This requires employment of reactions that produce minimal byproducts, either through the intrinsic stoichiometry of a reaction or as a result of minimizing competing undesirable reactions, i.e., making reactions more selective.

The issues of selectivity can be categorized under four headings—chemoselectivity (differentiation among various functional groups in a polyfunctional molecule), regioselectivity (orientational control), diastereoselectivity (control of relative stereochemistry), and enantioselectivity (control of absolute stereochemistry). These considerations have been readily accepted by the chemical community at large. In approaching these goals, little attention traditionally has been paid to the question of what is required. In too many cases, efforts to achieve the goal of selectivity led to reactions requiring multiple components in stoichiometric quantities that are not incorporated in the product or reagents, thus intrinsically creating significant amounts of byproducts. Consideration of how much of the reactants ends up in the product, i.e., atom economy, traditionally has been ignored. When Professor Trost's first paper on atom economy appeared in the literature, the idea generally was not adopted by either academia or industry. Many in industry, however, were practicing this concept without explicitly enunciating it. Others in industry did not consider the concept because it did not appear to have any economic consequence. Today, all of the chemical industry explicitly acknowledges the importance of atom economy.

Achieving the objectives of selectivity and atom economy encompasses the entire spectrum of chemical activities—from basic research to commercial processes. In enunciating these principles, Professor Trost has set a challenge for those involved in basic research to create new chemical processes that meet the objectives. Professor Trost's efforts to meet this challenge involve the rational invention of new chemical reactions that are either simple additions or, at most, produce low-molecular-weight innocuous byproducts. A major application of these reactions is in the synthesis of fine chemicals and pharmaceuticals, which, in general, utilize very atom-uneconomical reactions. Professor Trost's research involves catalysis, largely focused on transition metal catalysis but also main group catalysis. The major purpose of his research is to increase the toolbox of available reactions to serve these industries for problems they encounter in the future. However, even today, there are applications for which such methodology may offer more efficient syntheses.

Academic Award

Dr. Karen M. Draths and Professor John W. Frost
Michigan State University

Use of Microbes as Environmentally Benign Synthetic Catalysts

Fundamental change in chemical synthesis can be achieved by elaboration of new, environmentally benign routes to existing chemicals. Alternatively, fundamental change can follow from characterization and environmentally benign synthesis of chemicals that can replace those chemicals currently manufactured by environmentally problematic routes. Examples of these design principles are illustrated by the syntheses of adipic acid and catechol developed by Dr. Karen M. Draths and Professor John W. Frost. The Draths-Frost syntheses of adipic acid and catechol use biocatalysis and renewable feedstocks to create alternative synthetic routes to chemicals of major industrial importance. These syntheses rely on the use of genetically manipulated microbes as synthetic catalysts. Nontoxic glucose is employed as a starting material, which, in turn, is derived from renewable carbohydrate feedstocks, such as starch, hemicellulose, and cellulose. In addition, water is used as the primary reaction solvent, and the generation of toxic intermediates and environment-damaging byproducts is avoided.

In excess of 1.9 billion kg of adipic acid is produced annually and used in the manufacture of nylon 66. Most commercial syntheses of adipic acid use benzene, derived from the benzene/toluene/xylene (BTX) fraction of petroleum refining, as the starting material. In addition, the last step in the current manufacture of adipic acid employs a nitric acid oxidation resulting in the formation of nitrous oxide as a byproduct. Due to the massive scale on which it is industrially synthesized, adipic acid manufacture has been estimated to account for some 10 percent of the annual increase in atmospheric nitrous oxide levels. The Draths-Frost synthesis of adipic acid begins with the conversion of glucose into *cis,cis*-muconic acid using a single, genetically engineered microbe expressing a biosynthetic pathway that does not exist in nature. This novel biosynthetic pathway was assembled by isolating and amplifying the expression of genes from different microbes including *Klebsiella pneumoniae, Acinetobacter calcoaceticus,* and *Escherichia coli.* The *cis,cis*-muconic acid, which accumulates extracellularly, is hydrogenated to afford adipic acid.

Yet another example of the Draths-Frost strategy for synthesizing industrial chemicals using biocatalysis and renewable feedstocks is their synthesis of catechol. Approximately 21 million kg of catechol is produced globally each year. Catechol is an important chemical building block used to synthesize flavors (e.g., vanillin, eugenol, isoeugenol), pharmaceuticals (e.g., L-DOPA, adrenaline, papaverine), agrochemicals (e.g., carbofuran, propoxur), and polymerization inhibitors and antioxidants (e.g., 4-*t*-butylcatechol, veratrol). Although some catechol is distilled from coal tar, petroleum-derived benzene is the starting material for most catechol production. The Draths-Frost synthesis of catechol uses a single, genetically engineered microbe to catalyze the conversion of glucose into catechol, which accumulates extracellularly. As mentioned previously, plant-derived starch, hemicellulose, and cellulose can serve as the renewable feedstocks from which the glucose starting material is derived.

In contrast to the traditional syntheses of adipic acid and catechol, the Draths-Frost syntheses are based on the use of renewable feedstocks, carbohydrate starting materials, and microbial biocatalysis. As the world moves to national limits on carbon dioxide emissions, each molecule of a chemical made from a carbohydrate may well be counted as a credit due to the carbon dioxide that is fixed by plants to form the carbohydrate. Biocatalysis using intact microbes also allows the Draths-Frost syntheses to utilize water as a reaction solvent, near-ambient pressures, and temperatures that typically do not exceed human body temperature.

Small Business Award

PYROCOOL Technologies, Inc.

Technology for the Third Millennium: The Development and Commercial Introduction of an Environmentally Responsible Fire Extinguishment and Cooling Agent

Advances in chemical technology have greatly benefited firefighting in this century. From the limitation of having only local water supplies at their disposal, firefighters have been presented over the years with a wide variety of chemical agents, as additives or alternatives to water, to assist them. These advances in chemical extinguishment agents, however, have themselves created, in actual use, potential long-term environmental and health problems that tend to outweigh their firefighting benefits. PYROCOOL Technologies, Inc. developed PYROCOOL F.E.F. (Fire Extinguishing Foam) as an alternative formulation of highly biodegradable surfactants designed for use in very small quantities as a universal fire extinguishment and cooling agent.

Halon gases, hailed as a tremendous advance when introduced, have since proven to be particularly destructive to the ozone layer, having an ozone depletion potential (ODP) value of 10 to 16 times that of common refrigerants. Aqueous film-forming foams (AFFFs), developed by the U.S. Navy in the 1960s to combat pooled-surface, volatile hydrocarbon fires, release both toxic hydrofluoric acid and fluorocarbons when used. The fluorosurfactant compounds that make these agents so effective against certain types of fires render them resistant to microbial degradation, often leading to contamination of ground water supplies and failure of wastewater treatment systems.

In 1993, PYROCOOL Technologies initiated a project to create a fire extinguishment and cooling agent that would be effective in extinguishing fires and that would greatly reduce the potential long-term environmental and health problems associated with traditionally used products. To achieve this objective, PYROCOOL Technologies first determined that the product (when finally developed) would contain no glycol ethers or fluorosurfactants. In addition, it decided that the ultimate formulation must be an effective fire extinguishment and cooling agent at very low mixing ratios. PYROCOOL F.E.F. is a formulation of highly biodegradable nonionic surfactants, anionic surfactants, and amphoteric surfactants with a mixing ratio (with water) of 0.4 percent. In initial fire tests at the world's largest fire-testing facility in The Netherlands, PYROCOOL F.E.F. was demonstrated to be effective against a broad range of combustibles.

Since its development in 1993, PYROCOOL F.E.F. has been employed successfully against numerous fires both in America and abroad. PYROCOOL F.E.F. carries the distinction of extinguishing the last large oil tanker fire at sea (a fire estimated by Lloyd's of London to require 10 days to extinguish) on board the Nassia tanker in the Bosphorous Straits in just 12.5 minutes, saving 80 percent of the ship's cargo and preventing 78,000 tons of crude oil from spilling into the sea.

As demonstrated by the PYROCOOL F.E.F. technology, selective employment of rapidly biodegradable substances dramatically enhances the effectiveness of simple water, while eliminating the environmental and toxic impact of other traditionally used fire extinguishment agents. Because PYROCOOL F.E.F. is mixed with water at only 0.4 percent, an 87–93 percent reduction in product usage is realized compared to conventional extinguishment agents typically used at 3–6 percent. Fire affects all elements of industry and society and no one is immune from its dangers. PYROCOOL F.E.F. provides an innovative, highly effective, and green alternative for firefighters.

Alternative Synthetic Pathways Award

Flexsys America L.P.

Elimination of Chlorine in the Synthesis of 4-Aminodiphenylamine: A New Process That Utilizes Nucleophilic Aromatic Substitution for Hydrogen

The development of new environmentally favorable routes for the production of chemical intermediates and products is an area of considerable interest to the chemical processing industry. Recently, the use of chlorine in large-scale chemical syntheses has come under intense scrutiny. Solutia, Inc. (formerly Monsanto Chemical Company), one of the world's largest producers of chlorinated aromatics, has funded research over the years to explore alternative synthetic reactions for manufacturing processes that do not require the use of chlorine. It was clear that replacing chlorine in a process would require the discovery of new atomically efficient chemical reactions. Ultimately, it was Monsanto's goal to incorporate fundamentally new chemical reactions into innovative processes that would focus on the elimination of waste at the source. In view of these emerging requirements, Monsanto's Rubber Chemicals Division (now Flexsys), in collaboration with Monsanto Corporate Research, began to explore new routes to a variety of aromatic amines that would not rely on the use of halogenated intermediates or reagents. Of particular interest was the identification of novel synthetic strategies to 4-aminodiphenylamine (4-ADPA), a key intermediate in the Rubber Chemicals family of antidegradants. The total world volume of antidegradants based on 4-ADPA and related materials is approximately 300 million lb/yr, of which Flexsys is the world's largest producer. (Flexsys is a joint venture of Monsanto's and Akzo Nobel's rubber chemicals operations.)

Flexsys's current process to 4-ADPA is based on the chlorination of benzene. Since none of the chlorine used in the process ultimately resides in the final product, the pounds of waste generated in the process per pound of product produced from the process 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 that are difficult and expensive to treat. Furthermore, the process also requires the storage and handling of large quantities of chlorine gas. Flexsys found a solution to this problem in a class of reactions known as nucleophilic aromatic substitution of hydrogen (NASH). Through a series of experiments designed to probe the mechanism of NASH reactions, Flexsys realized a breakthrough in understanding this chemistry that has led to the development of a new process to 4-ADPA that utilizes the base-promoted, direct coupling of aniline and nitrobenzene.

The environmental benefits of this process are significant and include a dramatic reduction in waste generated. In comparison to the process traditionally used to synthesize 4-ADPA, the Flexsys process generates 74 percent less organic waste, 99 percent less inorganic waste, and 97 percent less wastewater. In global terms, if just 30 percent of the world's capacity to produce 4-ADPA and related materials were converted to the Flexsys process, 74 million lb/yr less chemical waste would be generated and 1.4 billion lb/yr less wastewater would be generated. The discovery of the new route to 4-ADPA and the elucidation of the mechanism of the reaction between aniline and nitrobenzene have been recognized throughout the scientific community as a breakthrough in the area of nucleophilic aromatic substitution chemistry.

This new process for the production of 4-ADPA has achieved the goal for which all green chemistry endeavors strive: the elimination of waste at the source via the discovery of new chemical reactions that can be implemented into innovative and environmentally safe chemical processes.

Alternative Solvents/ Reaction Conditions Award

Argonne National Laboratory

Novel Membrane-Based Process for Producing Lactate Esters—Nontoxic Replacements for Halogenated and Toxic Solvents

Argonne National Library (ANL) has developed a process based on selective membranes that permits low-cost synthesis of high-purity ethyl lactate and other lactate esters from carbohydrate feedstock. The process requires little energy input, is highly efficient and selective, and eliminates the large volumes of salt waste produced by conventional processes. ANL's novel process uses pervaporation membranes and catalysts. In the process, ammonium lactate is thermally and catalytically cracked to produce the acid, which, with the addition of alcohol, is converted to the ester. The selective membranes pass the ammonia and water with high efficiency while retaining the alcohol, acid, and ester. The ammonia is recovered and reused in the fermentation to make ammonium lactate, eliminating the formation of waste salt. The innovation overcomes major technical hurdles that had made current production processes for lactate esters technically and economically noncompetitive. The innovation will enable the replacement of toxic solvents widely used by industry and consumers, expand the use of renewable carbohydrate feedstocks, and reduce pollution and emissions.

Ethyl lactate has a good temperature performance range (boiling point: 154 °C, melting point: 40 °C), is compatible with both aqueous and organic systems, is easily biodegradable, and has been approved for food by the U.S. Food and Drug Administration. Lactate esters (primarily ethyl lactate) can replace most halogenated solvents (including ozone-depleting CFCs, carcinogenic methylene chloride, toxic ethylene glycol ethers, perchloroethylene, and chloroform) on a 1:1 basis. At current prices ($1.60–2.00/lb), the market for ethyl lactate is about 20 million lb/yr for a wide variety of specialty applications. The novel and efficient ANL membrane process will reduce the selling price of ethyl lactate to $0.85–1.00/lb and enable ethyl lactate to compete directly with petroleum-derived toxic solvents currently used. The favorable economics of the ANL membrane process, therefore, can lead to the widespread substitution of petroleum-derived toxic solvents by ethyl lactate in electronics manufacturing, paints and coatings, textiles, cleaners and degreasers, adhesives, printing, de-inking, and many other industrial, commercial, and household applications. More than 80 percent of the applications requiring the use of more than 3.8 million tons of solvents in the U.S. each year are suitable for reformulation with environmentally friendly lactate esters.

The ANL process has been patented for producing esters from all fermentation-derived organic acids and their salts. Organic acids and their esters, at the purity achieved by this process, offer great potential as intermediates for synthesizing polymers, biodegradable plastics, oxygenated chemicals (e.g., propylene glycol and acrylic acid), and specialty products. By improving purity and lowering costs, the ANL process promises to make fermentation-derived organic acids an economically viable alternative to many chemicals and products derived from petroleum feedstocks.

A U.S. patent on this technology has been allowed, and international patents have been filed. NTEC, Inc. has licensed the technology for lactate esters and provided the resources for a pilot-scale demonstration of the integrated process at ANL. The pilot-scale demonstration has produced a high-purity ethyl lactate product that meets or exceeds all the process performance objectives. A 10 million lb/yr demonstration plant is being planned for early 1999, followed by a 100 million lb/yr full-scale plant.

Designing Safer Chemicals Award

Rohm and Haas Company

Invention and Commercialization of a New Chemical Family of Insecticides Exemplified by CONFIRM™ Selective Caterpillar Control Agent and the Related Selective Insect Control Agents MACH 2™ and INTREPID™

The value of crops destroyed worldwide by insects exceeds tens of billions of dollars. Over the past fifty years, only a handful of classes of insecticides have been discovered to combat this destruction. Rohm and Haas Company has discovered a new class of chemistry, the diacylhydrazines, that offers farmers, consumers, and society a safer, effective technology for insect control in turf and a variety of agronomic crops. One member of this family, CONFIRM™, is a breakthrough in caterpillar control. It is chemically, biologically, and mechanistically novel. It effectively and selectively controls important caterpillar pests in agriculture without posing significant risk to the applicator, the consumer, or the ecosystem. It will replace many older, less effective, more hazardous insecticides and has been classified by the U.S. EPA as a reduced-risk pesticide.

CONFIRM™ controls target insects through an entirely new mode of action that is inherently safer than current insecticides. The product acts by strongly mimicking a natural substance found within the insect's body called 20-hydroxy ecdysone, which is the natural "trigger" that induces molting and regulates development in insects. Because of this "ecdysonoid" mode of action, CONFIRM™ powerfully disrupts the molting process in target insects, causing them to stop feeding shortly after exposure and to die soon thereafter.

Since 20-hydroxy ecdysone neither occurs nor has any biological function in most nonarthropods, CONFIRM™ is inherently safer than other insecticides to a wide range of nontarget organisms such as mammals, birds, earthworms, plants, and various aquatic organisms. CONFIRM™ is also remarkably safe to a wide range of key beneficial, predatory, and parasitic insects such as honeybees, lady beetles, parasitic wasps, predatory bugs, beetles, flies, and lacewings, as well as other predatory arthropods such as spiders and predatory mites. Because of this unusual level of safety, the use of these products will not create an outbreak of target or secondary pests due to destruction of key natural predators/parasites in the local ecosystem. This should reduce the need for repeat applications of additional insecticides and reduce the overall chemical load on both the target crop and the local environment.

CONFIRM™ has low toxicity to mammals by ingestion, inhalation, and topical application and has been shown to be completely non-oncogenic, nonmutagenic, and without adverse reproductive effects. Because of its high apparent safety and relatively low use rates, CONFIRM™ poses no significant hazard to the applicator or the food chain and does not present a significant spill hazard. CONFIRM™ has proven to be an outstanding tool for control of caterpillar pests in many integrated pest management (IPM) and resistance management situations. All of these attributes make CONFIRM™ among the safest, most selective, and most useful insect control agents ever discovered.

Academic Award

Professor Joseph M. DeSimone
University of North Carolina at Chapel Hill (UNC)
and North Carolina State University (NCSU)

Design and Application of Surfactants for Carbon Dioxide

It has been a dilemma of modern industrial technology that the solvents required to dissolve the environment's worst contaminants themselves have a contaminating effect. Now, new technologies for the design and application of surfactants for carbon dioxide (CO_2), developed at UNC, promise to resolve this dilemma.

Over 30 billion pounds of organic and halogenated solvents are used worldwide each year as solvents, processing aids, cleaning agents, and dispersants. Solvent-intensive industries are considering alternatives that can reduce or eliminate the negative impact that solvent emissions can have in the workplace and in the environment. CO_2 in a solution state has long been recognized as an ideal solvent, extractant, and separation aid. CO_2 solutions are nontoxic, nonflammable, safe to work with, energy-efficient, cost-effective, waste-minimizing, and reusable. Historically, the prime factor inhibiting the use of this solvent replacement has been the low solubility of most materials in CO_2, in both its liquid and supercritical (sc) states. With the discovery of CO_2 surfactant systems, Professor DeSimone and his students have dramatically advanced the solubility performance characteristics of CO_2 systems for several industries.

The design of broadly applicable surfactants for CO_2 relies on the identification of "CO_2-philic" materials from which to build amphiphiles. Although CO_2 in both its liquid and supercritical states dissolves many small molecules readily, it is a very poor solvent for many substances at easily accessible conditions ($T < 100$ °C and $P < 300$ bar). As an offshoot of Professor DeSimone's research program on polymer synthesis in CO_2, he and his researchers exploited the high solubility of a select few CO_2-philic polymeric segments to develop nonionic surfactants capable of dispersing high solids polymer latexes in both liquid and sc CO_2 phases. The design criteria they developed for surfactants, which were capable of stabilizing heterogeneous polymerizations in CO_2, have been expanded to include CO_2-insoluble compounds in general.

This development lays the foundation by which surfactant-modified CO_2 can be used to replace conventional (halogenated) organic solvent systems currently used in manufacturing and service industries such as precision cleaning, medical device fabrication, and garment care, as well as in the chemical manufacturing and coating industries.

Small Business Award

Legacy Systems, Inc.

Coldstrip™, A Revolutionary Organic Removal and Wet Cleaning Technology

For over 30 years, the removal of photoresists with Piranha solutions (sulfuric acid, hydrogen peroxide, or ashers) has been the standard in the semiconductor, flat panel display, and micromachining industries. Use of Piranha solutions has been associated with atmospheric, ground, and water pollution. Legacy Systems, Inc. (LSI) has developed a revolutionary wet processing technology, Coldstrip™, which removes photoresist and organic contaminants for the semiconductor, flat panel display, and micromachining industries. Coldstrip™ uses only water and oxygen as raw materials.

LSI's Coldstrip™ process is a chilled-ozone process that uses only oxygen and water as raw materials. The active product is ozone, which safely decomposes to oxygen in the presence of photoresist. Carbon dioxide, carbon monoxide, oxygen, and water are formed. There are *no* high temperatures, *no* hydrogen peroxide, and *no* nitric acid, all of which cause environmental issues.

The equipment required for the chilled-ozone process consists of a gas diffuser, an ozone generator, a recirculating pump, a water chiller, and a process vessel. The water solution remains clear and colorless throughout the entire process sequence. There are no particles or resist flakes shed from the wafer into the water; therefore, there are no requirements for particle filtration.

Using oxygen and water as raw materials replacing the Piranha solutions significantly benefits the environment. One benefit is the elimination of over 8,400 gallons of Piranha solutions used per year per silicon wet station and over 25,200 gallons used per year per flat panel display station. Additionally, the overall water consumption is reduced by over 3,355,800 gallons per year per silicon wafer wet station and over 5,033,700 gallons per year per flat panel display station. The corresponding water consumption in LSI's process is 4,200 gallons per year and there is no Piranha use.

In 1995, the U.S. Patent Office granted LSI Patent 5,464,480 covering this technology. The system has the lowest environmental impact of any wet-resist-strip process, eliminating the need for thousands of gallons of Piranha chemicals and millions of gallons of water a year.

Alternative Synthetic Pathways Award

BHC Company

BHC Company Ibuprofen Process

BHC Company has developed a new synthetic process to manufacture ibuprofen, a well-known nonsteroidal anti-inflammatory painkiller marketed under brand names such as Advil™ and Motrin™. Commercialized since 1992 in BHC's 3,500 metric-ton-per-year facility in Bishop, Texas, the new process has been cited as an industry model of environmental excellence in chemical processing technology. For its innovation, BHC was the recipient of the Kirkpatrick Achievement Award for "outstanding advances in chemical engineering technology" in 1993.

The new technology involves only three catalytic steps, with approximately 80 percent atom utilization (virtually 99 percent including the recovered byproduct acetic acid), and replaces technology with six stoichiometric steps and less than 40 percent atom utilization. The use of anhydrous hydrogen fluoride as both catalyst and solvent offers important advantages in reaction selectivity and waste reduction. As such, this chemistry is a model of source reduction, the method of waste minimization that tops U.S. EPA's waste management hierarchy. Virtually all starting materials are either converted to product or reclaimed byproduct or are completely recovered and recycled in the process. The generation of waste is practically eliminated.

The BHC ibuprofen process is an innovative, efficient technology that has revolutionized bulk pharmaceutical manufacturing. The process provides an elegant solution to a prevalent problem encountered in bulk pharmaceutical synthesis (i.e., how to avoid the large quantities of solvents and wastes associated with the traditional stoichiometric use of auxiliary chemicals for chemical conversions). Large volumes of aqueous wastes (salts) normally associated with such manufacturing are virtually eliminated. The anhydrous hydrogen fluoride catalyst/solvent is recovered and recycled with greater than 99.9 percent efficiency. No other solvent is needed in the process, simplifying product recovery and minimizing fugitive emissions. The nearly complete atom utilization of this streamlined process truly makes it a waste-minimizing, environmentally friendly technology.

Alternative Solvents/ Reaction Conditions Award

Imation

DryView™ Imaging Systems

Photothermography is an imaging technology whereby a latent image, created by exposing a sensitized emulsion to appropriate light energy, is processed by the application of thermal energy. Photothermographic films are easily imaged by laser diode imaging systems, with the resultant exposed film processed by passing it over a heat roll. A heat roll operating at 250 °F in contact with the film will produce diagnostic-quality images in approximately 15 seconds. Based on photothermography technology, Imation's DryView™ Imaging Systems use no wet chemistry, create no effluent, and require no additional postprocess steps, such as drying.

In contrast, silver halide photographic films are processed by being bathed in a chemical developer, soaked in a fix solution, washed with clean water, and finally dried. The developer and fix solutions contain toxic chemicals such as hydroquinone, silver, and acetic acid. In the wash cycle, these chemicals, along with silver compounds, are flushed from the film and become part of the waste stream. The resulting effluent amounts to billions of gallons of liquid waste each year.

Significant developments in photothermographic image quality have been achieved that allow it to compete successfully with silver halide technology. During 1996, Imation placed more than 1,500 DryView™ medical laser imagers, which represent 6 percent of the world's installed base. These units alone have eliminated the annual disposal of 192,000 gallons of developer, 330,000 gallons of fixer, and 54.5 million gallons of contaminated water into the waste stream. As future systems are placed, the reductions will be even more dramatic.

DryView™ technology is applicable to all industries that process panchromatic film products. The largest of these industries are medical radiography, printing, industrial radiography, and military reconnaissance. DryView™ is valued by these industries because it supports pollution prevention through source reduction.

Designing Safer Chemicals Award

Albright & Wilson Americas

THPS Biocides: A New Class of Antimicrobial Chemistry

Conventional biocides used to control the growth of bacteria, algae, and fungi in industrial cooling systems, oil fields, and process applications are highly toxic to humans and aquatic life and often persist in the environment, leading to long-term damage. To address this problem, a new and relatively benign class of biocides, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), has been discovered by Albright & Wilson Americas. THPS biocides represent a completely new class of antimicrobial chemistry that combines superior antimicrobial activity with a relatively benign toxicology profile. THPS's benefits include low toxicity, low recommended treatment level, rapid breakdown in the environment, and no bioaccumulation. When substituted for more toxic biocides, THPS biocides provide reduced risks to both human health and the environment.

THPS is so effective as a biocide that, in most cases, the recommended treatment level is below that which would be toxic to fish. In addition, THPS rapidly breaks down in the environment through hydrolysis, oxidation, photodegradation, and biodegradation. In many cases, it has already substantially broken down before the treated water enters the environment. The degradation products have been shown to possess a relatively benign toxicology profile. Furthermore, THPS does not bioaccumulate and, therefore, offers a much-reduced risk to higher life forms.

THPS biocides are aqueous solutions and do not contain volatile organic compounds (VOCs). Because THPS is halogen-free, it does not contribute to the formation of dioxin or absorbable organic halides (AOX). Because of its low overall toxicity and easier handling compared to alternative products, THPS provides an opportunity to reduce the risk of health and safety incidents.

THPS has been applied to a range of industrial water systems for the successful control of microorganisms. The United States industrial water treatment market for nonoxidizing biocides alone is 42 million lb/yr and growing at 6–8 percent annually. There are over 500,000 individual use sites in this industry category. Because of its excellent environmental profile, THPS has already been approved for use in environmentally sensitive areas around the world and is being used as a replacement for the higher risk alternatives.

Academic Award

Professor Mark Holtzapple
Texas A&M University

Conversion of Waste Biomass to Animal Feed, Chemicals, and Fuels

A family of technologies has been developed at Texas A&M University that converts waste biomass into animal feed, industrial chemicals, and fuels. Waste biomass includes such resources as municipal solid waste, sewage sludge, manure, and agricultural residues. Waste biomass is treated with lime to improve digestibility. Lime-treated agricultural residues (e.g., straw, stover, bagasse) may be used as ruminant animal feeds. Alternatively, the lime-treated biomass can be fed into a large anaerobic fermentor in which rumen microorganisms convert the biomass into volatile fatty acid (VFA) salts, such as calcium acetate, propionate, and butyrate. The VFA salts are concentrated and may be converted into chemicals or fuels via three routes. In one route, the VFA salts are acidified, releasing acetic, propionic, and butyric acids. In a second route, the VFA salts are thermally converted to ketones, such as acetone, methyl ethyl ketone, and diethyl ketone. In a third route, the ketones are hydrogenated to their corresponding alcohols such as isopropanol, isobutanol, and isopentanol.

The above technologies offer many benefits for human health and the environment. Lime-treated animal feed can replace feed corn, which is approximately 88 percent of corn production. Growing corn exacerbates soil erosion and requires intensive inputs of fertilizers, herbicides, and pesticides, all of which contaminate ground water.

Chemicals (e.g., organic acids and ketones) may be produced economically from waste biomass. Typically, waste biomass is landfilled or incinerated, which incurs a disposal cost and contributes to land or air pollution. Through the production of chemicals from biomass, nonrenewable resources, such as petroleum and natural gas, are conserved for later generations. Because 50 percent of U.S. petroleum consumption is now imported, displacing foreign oil will help reduce the U.S. trade deficit.

Fuels (e.g., alcohols) produced from waste biomass have the benefits cited above (i.e., reduced environmental impact from waste disposal and reduced trade deficit). In addition, oxygenated fuels derived from biomass are cleaner-burning and do not add net carbon dioxide to the environment, thereby reducing factors that contribute to global warming.

Small Business Award

Donlar Corporation

Production and Use of Thermal Polyaspartic Acid

Millions of pounds of anionic polymers are used each year in many industrial applications. Polyacrylic acid (PAC) is one important class of such polymers, but the disposal of PAC is problematic, because it is not biodegradable. An economically viable, effective, and biodegradable alternative to PAC is thermal polyaspartate (TPA).

Donlar Corporation invented two highly efficient processes to manufacture TPA for which patents have either been granted or allowed. The first process involves a dry and solid polymerization converting aspartic acid to polysuccinimide. No organic solvents are involved during the conversion and the only byproduct is water. The process is extremely efficient—a yield of more than 97 percent of polysuccinimide is routinely achieved. The second step in this process, the base hydrolysis of polysuccinimide to polyaspartate, is also extremely efficient and waste-free.

The second TPA production process involves using a catalyst during the polymerization, which allows a lower heating temperature to be used. The resulting product has improvements in performance characteristics, lower color, and biodegradability. The catalyst can be recovered from the process, thus minimizing waste.

Independent toxicity studies of commercially produced TPA have been conducted using mammalian and environmental models. Results indicate that TPA is nontoxic and environmentally safe. TPA biodegradability has also been tested by an independent lab using established Organization for Economic Cooperation and Development (OECD) methodology. Results indicate that TPA meets OECD guidelines for Intrinsic Biodegradability. PAC cannot be classified as biodegradable when tested under these same conditions.

Many end-uses of TPA have been discovered, such as in agriculture to improve fertilizer or nutrient management. TPA increases the efficiency of plant nutrient uptake, thereby increasing crop yields while protecting the ecology of agricultural lands. TPA can also be used for water treatment, as well as in the detergent, oil, and gas industries.

Alternative Synthetic Pathways Award

Monsanto Company

Catalytic Dehydrogenation of Diethanolamine

Disodium iminodiacetate (DSIDA) is a key intermediate in the production of Monsanto's Roundup® herbicide, an environmentally friendly, nonselective herbicide. Traditionally, Monsanto and others have manufactured DSIDA using the Strecker process requiring ammonia, formaldehyde, hydrochloric acid, and hydrogen cyanide. Hydrogen cyanide is acutely toxic and requires special handling to minimize risk to workers, the community, and the environment. Furthermore, the chemistry involves the exothermic generation of potentially unstable intermediates, and special care must be taken to preclude the possibility of a runaway reaction. The overall process also generates up to 1 kg of waste for every 7 kg of product, and this waste must be treated prior to safe disposal.

Monsanto has developed and implemented an alternative DSIDA process that relies on the copper-catalyzed dehydrogenation of diethanolamine. The raw materials have low volatility and are less toxic. Process operation is inherently safer, because the dehydrogenation reaction is endothermic and, therefore, does not present the danger of a runaway reaction. Moreover, this "zero-waste" route to DSIDA produces a product stream that, after filtration of the catalyst, is of such high quality that no purification or waste cut is necessary for subsequent use in the manufacture of Roundup®. The new technology represents a major breakthrough in the production of DSIDA, because it avoids the use of cyanide and formaldehyde, is safer to operate, produces higher overall yield, and has fewer process steps.

The metal-catalyzed conversion of aminoalcohols to amino acid salts has been known since 1945. Commercial application, however, was not known until Monsanto developed a series of proprietary catalysts that made the chemistry commercially feasible. Monsanto's patented improvements on metallic copper catalysts afford an active, easily recoverable, highly selective, and physically durable catalyst that has proven itself in large-scale use.

This catalysis technology also can be used in the production of other amino acids, such as glycine. Moreover, it is a general method for conversion of primary alcohols to carboxylic acid salts, and is potentially applicable to the preparation of many other agricultural, commodity, specialty, and pharmaceutical chemicals.

Alternative Solvents/ Reaction Conditions Award

The Dow Chemical Company

100 Percent Carbon Dioxide as a Blowing Agent for the Polystyrene Foam Sheet Packaging Market

In recent years the chlorofluorocarbon (CFC) blowing agents used to manufacture polystyrene foam sheet have been associated with environmental concerns such as ozone depletion, global warming, and ground-level smog. Due to these environmental concerns, The Dow Chemical Company has developed a novel process for the use of 100 percent carbon dioxide (CO_2). Polystyrene foam sheet is a useful packaging material offering a high stiffness-to-weight ratio, good thermal insulation value, moisture resistance, and recyclability. This combination of desirable properties has resulted in the growth of the polystyrene foam sheet market in the United States to over 700 million pounds in 1995. Current applications for polystyrene foam include thermoformed meat, poultry, and produce trays; fast food containers; egg cartons; and serviceware.

The use of 100 percent CO_2 offers optimal environmental performance because CO_2 does not deplete the ozone layer, does not contribute to ground-level smog, and will not contribute to global warming because CO_2 will be used from existing byproduct commercial and natural sources. The use of CO_2 byproduct from existing commercial and natural sources, such as ammonia plants and natural gas wells, will ensure that no net increase in global CO_2 results from the use of this technology. CO_2 is also nonflammable, providing increased worker safety. It is cost-effective and readily available in food-grade quality. CO_2 also is used in such common applications as soft drink carbonation and food chilling and freezing.

The use of Dow 100 percent CO_2 technology eliminates the use of 3.5 million lb/yr of hard CFC-12 and/or soft HCFC-22. This technology has been scaled from pilot-line to full-scale commercial facilities. Dow has made the technology available through a commercial license covering both patented and know-how technology. The U.S. Patent Office granted Dow two patents for this technology (5,250,577 and 5,266,605).

Designing Safer Chemicals Award

Rohm and Haas Company

Designing an Environmentally Safe Marine Antifoulant

Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry approximately $3 billion a year, largely due to increased fuel consumption to overcome hydrodynamic drag. Increased fuel consumption contributes to pollution, global warming, and acid rain.

The main compounds used worldwide to control fouling are the organotin antifoulants, such as tributyltin oxide (TBTO). While effective, they persist in the environment and cause toxic effects, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish. These harmful effects led to a U.S. EPA special review and to the Organotin Antifoulant Paint Control Act of 1988. This act mandated restrictions on the use of tin in the United States, and charged the U.S. EPA and the U.S. Navy with conducting research on alternatives to organotins.

Rohm and Haas Company searched for an environmentally safe alternative to organotin compounds. Compounds from the 3-isothialozone class were chosen as likely candidates and over 140 were screened for antifouling activity. The 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine™ antifoulant) was chosen as the candidate for commercial development.

Extensive environmental testing compared Sea-Nine™ antifoulant to TBTO, the current industry standard. Sea-Nine™ antifoulant degraded extremely rapidly with a half-life of one day in seawater and one hour in sediment. Tin bioaccumulated, with bioaccumulation factors as high as 10,000-fold, whereas Sea-Nine™ antifoulant's bioaccumulation was essentially zero. Both TBTO and Sea-Nine™ were acutely toxic to marine organisms, but TBTO had widespread chronic toxicity, whereas Sea-Nine™ antifoulant showed no chronic toxicity. Thus, the maximum allowable environmental concentration (MAEC) for Sea-Nine™ antifoulant was 0.63 parts per billion (ppb) whereas the MAEC for TBTO was 0.002 ppb.

Hundreds of ships have been painted with coatings containing Sea-Nine™ worldwide. Rohm and Haas Company obtained EPA registration for the use of Sea-Nine™ antifoulant, the first new antifoulant registration in over a decade.

Program Information

Additional information on the Presidential Green Chemistry Challenge program is available from:

- EPA's Pollution Prevention Clearinghouse at 202-566-0799 or e-mail ppic@epa.gov,
- Richard Engler of EPA at 202-564-8740 or engler.richard@epa.gov, and
- The Green Chemistry Web site at http://www.epa.gov/greenchemistry.

Disclaimer

Note: The summaries provided in this document were obtained from the entries received for the 1996–2002 Presidential Green Chemistry Challenge Awards. They were edited for space, stylistic consistency, and clarity, but they were neither written nor officially endorsed by EPA. These summaries represent only a fraction of the information that was provided in the entries received and, as such, are intended to highlight the nominated projects, not describe them fully. These summaries were not used in the judging process; judging was conducted on all information contained in the entries. Claims made in these summaries have not been verified by EPA.

Index