The Presidential Green Chemistry Challenge Awards Program:

Summary of 2007 Award Entries and Recipients

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Introduction

The Presidential Green Chemistry Challenge Awards Program is a competitive incentive to create environmentally preferable chemicals and chemical processes. Each year the United States Environmental Protection Agency (U.S. EPA) celebrates innovative, award-winning technologies developed by high-quality nominees. The year 2007 marks the 12th year of the program.

The national policy established by the 1990 Pollution Prevention Act is aimed at reducing pollution at its source whenever feasible. By applying scientific solutions to real-world environmental problems, the Green Chemistry Challenge has significantly reduced the hazards associated with designing, manufacturing, and using chemicals.

Through a voluntary U.S. EPA Design for the Environment partnership with the chemical industry and professional scientific community, this annual award program seeks to discover, highlight, and honor green chemistry.

An independent panel of technical experts convened by the American Chemical Society judged the entries for the 2007 awards. The judges used criteria that included health and environmental benefits, scientific innovation, and industrial applicability. Five of the more than 90 entries were nationally recognized on June 26, 2007, at an awards ceremony in Washington, D.C. This compilation summarizes the entries submitted for the 2007 awards. These technologies are meant to succeed in the marketplace as well: each illustrates the technical feasibility, marketability, and profitability of green chemistry.

For further information about the Presidential Green Chemistry Challenge and U.S. EPA's Green Chemistry Program, go to www.epa.gov/greenchemistry.

NOTE: The summaries provided in this document were obtained from the entries received for the 2007 Presidential Green Chemistry Challenge Awards. U.S. EPA edited the descriptions for space, stylistic consistency, and clarity, but they were not written or officially endorsed by the Agency. The summaries are intended only to highlight a fraction of the information contained in the nominated projects. These summaries were not used in the judging process. Judging was conducted on all information contained in the entries received. Claims made in these summaries have not been verified by U.S. EPA.

Academic Award

Hydrogen-Mediated Carbon–Carbon Bond Formation

Professor Michael J. Krische, Department of Chemistry and Biochemistry, University of Texas at Austin

Innovation and Benefits

A fundamental aspect of chemistry involves creating chemical bonds between carbon atoms. Chemical processes commonly used to make such bonds usually also generate significant amounts of waste. Professor Krische developed a broad new class of chemical reactions that make bonds between carbon atoms using hydrogen and metal catalysts. This new class of reactions can be used to convert simple chemicals into complex substances, such as pharmaceuticals, pesticides, and other important chemicals, with minimal waste.

Reductions mediated by hydrogen, termed "hydrogenations", rank among the most widely used catalytic methods employed industrially. They are generally used to form carbon–hydrogen (C–H) bonds. Professor Michael J. Krische and his coworkers at the University of Texas at Austin have developed a new class of hydrogenation reactions that form carbon–carbon (C–C) bonds. In these metal-catalyzed reactions, two or more organic molecules combine with hydrogen gas to create a single, more complex product. Because all atoms present in the starting building-block molecules appear in the final product, Professor Krische's reactions do not generate any byproducts or wastes. Hence, Professor Krische's C–C bond-forming hydrogenations eliminate pollution at its source.

Prior to Professor Krische's work, hydrogen-mediated C–C bond formations were limited almost exclusively to the use of carbon monoxide in reactions such as alkene hydroformylation (1938) and the Fischer-Tropsch reaction (1923). These prototypical hydrogen-mediated C–C bond formations are practiced industrially on an enormous scale. Yet, despite the importance of these reactions, no one had engaged in systematic research to develop related C–C bond-forming hydrogenations. Only a small fraction of hydrogenation's potential as a method of C–C coupling had been realized, and the field lay fallow for nearly 70 years.

Professor Krische's hydrogen-mediated couplings circumvent the use of preformed organometallic reagents, such as Grignard and Gilman reagents, in carbonyl and imine addition reactions. Such organometallic reagents are highly reactive, typically moisture-sensitive, and sometimes pyrophoric, meaning that they combust when exposed to air. Professor Krische's coupling reactions take advantage of catalysts that avoid the hazards of traditional organometallic reagents. Further, using chiral hydrogenation catalysts, Professor Krische's couplings generate C–C bonds in a highly enantioselective fashion.

Catalytic hydrogenation has been known for over a century and has stood the test of time because of its efficiency, atom economy, and cost-effectiveness. By exploiting hydrogenation as a method of C–C bond formation, Professor Krische has added a broad, new dimension to one of chemistry's most fundamental catalytic processes. The C–C bond-forming hydrogenations developed by Professor Krische allow chemists to create complex organic molecules in a highly selective fashion, eliminating both hazardous starting materials and hazardous waste. Commercial application of this technology may eliminate vast quantities of hazardous chemicals. The resulting increases in plant and worker safety may enable industry to perform chemical transformations that were too dangerous using traditional reagents.

Small Business Award

NovaSterilis Inc.

Environmentally Benign Medical Sterilization Using Supercritical Carbon Dioxide

Innovation and Benefits

Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilization techniques use ethylene oxide or gamma radiation, which are toxic or have safety problems. NovaSterilis invented a technology that uses carbon dioxide and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor gamma radiation.

None of the common methods for medical sterilization is well-suited to sterilizing delicate biological materials. The sterility of these materials is critical. Distribution of contaminated donor tissues by tissue banks has resulted in serious infections and illnesses in transplant patients. The two most widely used sterilants (ethylene oxide and gamma radiation) also raise toxicity and safety concerns. Ethylene oxide is a mutagenic, carcinogenic, volatile, flammable, reactive gas. Residues of ethylene oxide remain in the sterilized material, increasing the risk of toxic side effects. Gamma radiation is highly penetrating and is lethal to all cells. Neither ethylene oxide nor gamma radiation can sterilize packaged biological products without eroding their physical integrity.

NovaSterilis, a privately held biotechnology company in Ithaca, NY, has successfully developed and commercialized a highly effective and environmentally benign technique for sterilizing delicate biological materials using supercritical carbon dioxide (CO_2). NovaSterilis licensed a patent for bacterial inactivation in biodegradable polymers that was issued to Professor Robert S. Langer and his team at the Massachusetts Institute of Technology. NovaSterilis then enhanced, expanded, and optimized the technology to kill bacterial endospores. Their supercritical CO_2 technology uses low temperature and cycles of moderate pressure along with a peroxide (peracetic acid) and small amounts of water. Their Nova 2200™ sterilizer consistently achieves rapid (less than 1 hour) and total inactivation of a wide range of microbes, including bacterial endospores. The mechanism of bacterial inactivation is not well-understood, but does not appear to involve bacterial cell lysis or wholesale degradation of bacterial proteins.

The new technology is compatible with sensitive biological materials and is effective for a wide range of important biomedical materials including: (a) musculoskeletal allograft tissue (e.g., human bone, tendons, dermis, and heart valves) for transplantation; (b) biodegradable polymers and related materials used in medical devices, instruments, and drugs; (c) drug delivery systems; and (d) whole-cell vaccines that retain high antigenicity. Besides being a green chemical technology, supercritical CO_2 sterilization achieves "terminal" sterilization, that is, sterilization of the final packaged product. Terminal sterilization provides greater assurance of sterility than traditional methods of aseptic processing. Sterilization of double-bagged tissue allows tissue banks to ship terminally sterilized musculoskeletal tissues in packages that can be opened in operating rooms by surgical teams immediately prior to use. NovaSterilis's patented technology addresses the market need in tissue banks as well as other needs in the biomedical, biologics, medical device, pharmaceutical, and vaccine industries. By the end of 2006, NovaSterilis had sold several units to tissue banks.

Greener Synthetic Pathways Award

Development and Commercial Application of Environmentally Friendly Adhesives for Wood Composites

Professor Kaichang Li, Department of Wood Science and Engineering, Oregon State University; Columbia Forest Products; Hercules Incorporated

Innovation and Benefits

Adhesives used in manufacturing plywood and other wood composites often contain formaldehyde, which is toxic. Professor Kaichang Li of Oregon State University, Columbia Forest Products, and Hercules Incorporated developed an alternate adhesive made from soy flour. Their environmentally friendly adhesive is stronger than and cost-competitive with conventional adhesives. During 2006, Columbia used the new, soy-based adhesive to replace more than 47 million pounds of conventional formaldehyde-based adhesives.

Since the 1940s, the wood composites industry has been using synthetic adhesive resins to bind wood pieces into composites, such as plywood, particleboard, and fiberboard. The industry has been the predominate user of formaldehyde-based adhesives such as phenol–formaldehyde and urea–formaldehyde (UF) resins. Formaldehyde is a probable human carcinogen. The manufacture and use of wood composite panels bonded with formaldehyde-based resins release formaldehyde into the air, creating hazards for both workers and consumers.

Inspired by the superior properties of the protein that mussels use to adhere to rocks, Professor Li and his group at Oregon State University invented environmentally friendly wood adhesives based on abundant, renewable soy flour. Professor Li modified some of the amino acids in soy protein to resemble those of mussels' adhesive protein. Hercules Incorporated provided a critical curing agent and the expertise to apply it to commercial production of plywood.

Oregon State University, Columbia Forest Products (CFP), and Hercules have jointly commercialized soy-based adhesives to produce cost-competitive plywood and particleboard for interior uses. The soy-based adhesives do not contain formaldehyde or use formaldehyde as a raw material. They are environmentally friendly, cost-competitive with the UF resin in plywood, and superior to the UF resin in strength and water resistance. All CFP plywood plants now use soy-based adhesives, replacing more than 47 million pounds of the toxic UF resin in 2006 and reducing the emission of hazardous air pollutants (HAPs) from each CFP plant by 50 to 90 percent. This new CFP plywood is sold under the PureBond™ name. During 2007, CFP will replace UF at its particleboard plant. The company is also seeking arrangements with other manufacturers to further the adoption of this technology.

With this technology, those who make and use furniture, kitchen cabinetry, and other wood composite materials have a high-performing formaldehyde-free alternative. As a result, indoor air quality in homes and offices could improve significantly. This technology represents the first cost-competitive, environmentally friendly adhesive that can replace the toxic UF resin. The technology can greatly enhance the global competitiveness of U.S. wood composite companies. In addition, by creating a new market for soy flour, currently in over-supply, this technology provides economic benefits for soybean farmers.

Headwaters Technology Innovation

Greener Reaction Conditions Award

Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

Innovation and Benefits

Hydrogen peroxide is an environmentally friendly alternative to chlorine and chlorine-containing bleaches and oxidants. It is expensive, however, and its current manufacturing process involves the use of hazardous chemicals. Headwaters Technology Innovation (HTI) developed an advanced metal catalyst that makes hydrogen peroxide directly from hydrogen and oxygen, eliminates the use of hazardous chemicals, and produces water as the only byproduct. HTI has demonstrated their new technology and is partnering with Degussa AG to build plants to produce hydrogen peroxide.

Hydrogen peroxide (H_2O_2) is a clean, versatile, environmentally friendly oxidant that can substitute for environmentally harmful chlorinated oxidants in many manufacturing operations. However, the existing manufacturing process for H_2O_2 is complex, expensive, and energy-intensive. This process requires an anthraquinone working solution containing several toxic chemicals. The solution is reduced by hydrogen in the presence of a catalyst, forming anthrahydroquinone, which then reacts with oxygen to release H_2O_2. The H_2O_2 is removed from the solution with an energy-intensive stripping column and then concentrated by vacuum distillation. The bulk of the working solution is recycled, but the process generates a waste stream of undesirable quinone-derived byproducts that requires environmentally acceptable disposal.

Headwaters Technology Innovation (HTI) has produced a robust catalyst technology that enables the synthesis of H_2O_2 directly from hydrogen and oxygen. This breakthrough technology, called NxCat™, is a palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable byproducts. It produces H_2O_2 more efficiently, cutting both energy use and costs. It uses innocuous, renewable feedstocks and generates no toxic waste.

NxCat™ catalysts work because of their precisely controlled surface morphology. HTI has engineered a set of molecular templates and substrates that maintain control of the catalyst's crystal structure, particle size, composition, dispersion, and stability. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for H_2O_2 up to 100 percent.

The NxCat™ technology enables a simple, commercially viable H_2O_2 manufacturing process. In partnership with Degussa AG (a major H_2O_2 manufacturer), HTI successfully demonstrated the NxCat™ technology and, in 2006, completed construction of a demonstration plant. This demonstration plant will allow the partners to collect the data necessary to design a full-scale plant and begin commercial production in 2009. The NxCat™ process has the potential to cut the cost of H_2O_2 significantly, generating a more competitively priced supply of H_2O_2 and increasing its market acceptance as an industrial oxidant. Except for its historically higher price, H_2O_2 is an excellent substitute for the more frequently used—and far more deleterious—chlorinated oxidants. The NxCat™ technology has the benefit of producing an effective, environmentally preferable oxidant (H_2O_2) without the waste or high cost associated with the traditional process.

Designing Greener Chemicals Award

BiOH™ Polyols

Cargill, Incorporated

Innovation and Benefits

Foam cushioning used in furniture or bedding is made from polyurethane, a man-made material. One of the two chemical building blocks used to make polyurethane is a "polyol". Polyols are conventionally manufactured from petroleum products. Cargill's BiOH™ polyols are manufactured from renewable, biological sources such as vegetable oils. Foams made with BiOH™ polyols are comparable to foams made from conventional polyols. As a result, each million pounds of BiOH™ polyols saves nearly 700,000 pounds of crude oil. In addition, Cargill's process reduces total energy use by 23 percent and carbon dioxide emissions by 36 percent.

Polyols are key ingredients in flexible polyurethane foams, which are used in furniture and bedding. Historically, polyurethane has been made from petrochemical polyols. The idea of replacing these polyols with biobased polyols is not new, but the poor performance, color, quality, consistency, and odor of previous biobased polyols restricted them to limited markets. Previous biobased polyols also suffer from poor chemical reactivity, resulting in foam with inferior properties.

Cargill has successfully developed biobased polyols for several polyurethane applications, including flexible foams, which are the most technically challenging. Cargill makes BiOH™ polyols by converting the carbon–carbon double bonds in unsaturated vegetable oils to epoxide derivatives and then further converting these derivatives to polyols using mild temperature and ambient pressure. BiOH™ polyols provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams. These foams set a new standard for consistent quality with low odor and color. Foams containing BiOH™ polyols retain their white color longer without ultraviolet stabilizers. They also are superior to foams containing only petroleum-based polyols in standard tests. In large slabstock foams, such as those used in furniture and bedding, BiOH 5000 polyol provides a wide processing window, improved comfort factor, and reduced variations in density and load-bearing capacity. In molded foams such as automotive seating and headrests, BiOH 2100 polyol can enhance load-bearing or hardness properties relative to conventional polyols.

Use of BiOH™ polyols reduces the environmental footprint relative to today's conventional polyols for polyurethane production. BiOH™ polyols "harvest" carbon that plants remove from the air during photosynthesis. All of the carbon in BiOH™ polyols is recently fixed. In conventional polyols, the carbon is petroleum-based. Replacing petroleum-based polyols with BiOH™ polyols cuts total energy use by 23 percent including a 61-percent reduction in nonrenewable energy use, leading to a 36-percent reduction in carbon dioxide emissions. For each million pounds of BiOH™ polyol used in place of petroleum-based polyols, about 700,000 pounds (2,200 barrels) of crude oil are saved, thereby reducing the dependence on petroleum. BiOH™ polyols diversify the industry's supply options and help mitigate the effects of uncertainty and volatility of petroleum supply and pricing. Cargill is the first company to commercialize biobased polyols on a large scale in the flexible foam market. Formulators can now use biobased polyols in flexible foam without compromising product performance. That the top North American polyol users choose BiOH™ polyols is validation of Cargill's accomplishment.

Entries from Academia

Bromine-Free, TEMPO-Based Catalyst System for the Oxidation of Alcohols

Dr. Robert L. Augustine, Center for Applied Catalysis, Seton Hall University; The NutraSweet Corporation

The selective oxidation of alcohols to the corresponding carbonyls is one of the more important transformations in synthetic organic chemistry. A large number of oxidants have been reported in the literature, but most of them are based on transition metal oxides such as those of chromium and manganese. Because most of these oxidants and their reduced compounds are toxic, their use creates serious problems in handling and disposal, especially in large-scale commercial applications. A common alternative is the Anelli process, which replaces the metal oxides with NaOCl and TEMPO (2,2,6,6-tetramethylpiperidinyloxy). The Anelli reaction is carried out in a two-phase (CH_2Cl_2–H_2O) system using TEMPO as a catalyst and NaOCl as the oxidant. A co-catalyst, KBr, increases the reaction rate.

Dr. Augustine's oxidation procedure is an extension of the Anelli process. His new procedure replaces KBr with the more benign $Na_2B_4O_7$ (borax) and does not require any organic solvents. In the absence of organic solvents, the reactant alcohol comprises about 38 percent of the total reaction volume compared with only about 2.5 percent in the classic reaction using dichloromethane. This has positive cost, environmental, and process safety implications. A further advantage to the solvent-free reaction is the isolation of the product aldehyde by phase separation from the aqueous solution, which saves even more energy because there is no solvent to remove. Dr. Augustine's process can oxidize a number of primary alcohols, producing the corresponding aldehydes in very good to excellent yields. His process also oxidizes secondary alcohols to ketones in very good to excellent yields.

The Center for Applied Catalysis has been collaborating with the NutraSweet Corporation to scale up this reaction. NutraSweet is currently using Dr. Augustine's process to manufacture an aldehyde, 3,3-dimethylbutanal, on a commercial scale. This aldehyde is a feedstock for Neotame, which is an FDA-approved N-alkyl derivative of aspartame.

High-Performance Macromolecular Antioxidants for Materials: A Green Chemistry Approach

Dr. Ashok L. Cholli, Center for Advanced Materials, University of Massachusetts Lowell

NOTE: This project is the result of a partnership between Polnox Corporation and Dr. Ashok L. Cholli of the University of Massachusetts Lowell. The project was judged in both the small business and academic categories. The abstract appears in the small business section on page 34.

Professor Purnendu K. Dasgupta, Department of Chemistry and Biochemistry, The University of Texas at Arlington

A Green Analyzer for Arsenic in Drinking Water

Arsenic is an abundant element that is also a class A human carcinogen. Waterborne arsenic is a problem in drinking water worldwide and is typically of natural origin. In 2006, the U.S. EPA lowered the allowable As content of U.S. drinking water from 50 ppb to 10 ppb. U.S. EPA and U.S. Geological Survey (USGS) assessments show that approximately 32 million people in the United States drink water containing 2–50 ppb As. Making accurate measurements of arsenic in drinking water is critical to meeting the new standard. Presently the only techniques approved by the U.S. EPA are those that use atomic spectrometry.

Technology for affordable analysis of arsenic in the field is particularly needed in small water systems in the United States and in developing countries. The most common field analysis method is based on the over-100-year-old Gutzeit reaction chemistry. It uses toxic lead acetate, mercuric bromide ($HgBr_2$), and large amounts of sample to measure As levels near the 10 ppb limit. It also creates costly disposal problems.

Professor Dasgupta invented an affordable field analyzer (costing less than $2,500 for parts) that is unique, USGS-validated, small, robust, and fully automated. It uses an order-of-magnitude less sample, requires no toxic chemicals, and can measure As down to 0.05 ppm, rivaling atomic spectrometers that cost much more. The technology is based on the gas-phase chemiluminescence of arsine (AsH_3) and ozone. It uses sodium borohydride, sodium hydroxide, disodium ethylenediaminetetraacetic acid (Na_2EDTA), and sulfuric acid as reagents. The technology measures both As(III) and As(V) in 3 mL samples of water within 4–6 minutes. Because some water treatments only remove As(V), monitoring and remediation require highly sensitive techniques that can measure As(III) and As(V) separately. Professor Dasgupta filed patent applications in 2005 and 2006 for this technology.

Professor Arlin E. Gyberg, Augsburg College

A New, Heterogeneous, Fixed-Bed Catalyst for Continuous-Flow Biodiesel Production from Waste Fats and Oils

NOTE: This project is the result of a partnership between SarTec Corporation and Professor Arlin E. Gyberg of Augsburg College. The project was judged in both the small business and academic categories. The abstract appears in the small business section on 35.

Professor James E. Hutchison, Department of Chemistry and Director, Materials Science Institute, University of Oregon

Greener Production of Functionalized Nanoparticles

Professor Hutchison has applied the principles of green chemistry to the production of functionalized metal nanoparticles. Functionalized nanoparticles bring together the functionality of a molecular ligand shell and the novel properties of a nanoparticle core, resulting in a high degree of functionality in a nanoscale object. The unique properties of functionalized nanoparticles promise to enhance or revolutionize applications in a wide array of technological sectors including medical diagnostics and therapeutics, catalysis, electronic/optic materials, and environmental remediation.

Methods of producing functionalized nanoparticles are typically inefficient; they often require hazardous reagents. Professor Hutchison's team developed a novel synthesis of triphenylphosphine-stabilized gold nanoparticles that eliminates the need for hazardous reagents including diborane and benzene, reduces or eliminates organic solvents in both production and purification, and improves the overall safety of the process. At the same time, the synthesis is more efficient and economical. By addressing each of three steps

involved in producing functionalized nanoparticles (core synthesis, functionalization, and purification), Professor Hutchison has demonstrated that human health, environmental, and economic benefits can be realized. Further, his approach is general and can be readily extended to the production of other nanoparticle compositions.

The production of metal nanoparticles alone is forecast to reach 2 million metric tons by 2010. Given this anticipated growth, Professor Hutchison expects his approach to have a significant impact in realizing greener nanotechnology. Because his methods reduce the cost to produce functionalized nanomaterials, there is now commercial interest in them. In 2006, Dune Sciences LLC was formed to commercialize applications of nanoparticles in medical diagnostics and catalysis.

Development of Environmentally Benign Nonfouling Materials and Coatings for Marine Applications

Professor Shaoyi Jiang, Department of Chemical Engineering, University of Washington

Biofouling on ship hulls and other marine surfaces has become a global environmental and economic issue. The best antifouling coating is tributyltin- (TBT-) based paint, but it is being phased out because of environmental concern over its effects on nontarget marine organisms. Tin-free biocides such as copper particles or cuprous oxide are substituting for TBT in the current market, but these biocides are also harmful to the marine environment, and their application is very limited. Nontoxic, fouling-release coatings based on silicone also have very limited applications; they are only effective on vessels moving at high speeds (over 14 knots). However, fouling occurs most readily on static structures or ships moving slowly in seawater close to land.

Professor Jiang's vision is to develop nonfouling coatings to which marine microorganisms cannot attach, as the next generation of marine coatings. With support from the Office of Naval Research (ONR, U.S. Navy), Professor Jiang has demonstrated for the first time that coatings based on zwitterionic sulfobetaine (SB) and carboxybetaine (CB) are super-low-fouling. SB- and CB-based materials are biomimetic, nontoxic, very stable, easily handled, and low-cost. Professor Jiang has recently developed the first nontoxic, super-low-fouling, zwitterionic-based marine coatings. These coatings have outstanding performance against marine microorganisms in laboratory tests and effectively defer the settlement of microorganisms in field tests. Professor Jiang is currently integrating self-polishing via hydrolysis into his existing coatings in order to create the first environmentally benign, durable, effective, nonfouling paint products. He has filed three patents for his technology and is launching a startup company to commercialize it. In addition to marine coatings, these materials are very promising for biomedical applications and consumer products.

Application of Collagen Nanofibrils in Green Processing and Synthesis

Professor Gennaro J. Maffia, Department of Chemical Engineering, Widener University

A dilute milling process unravels collagen fibers from waste bovine hides (corium) into nanofibrils less than 100 nm in diameter. The molecular structure of the nanofibrils remains intact as the active surface area increases by several orders of magnitude. Collagen nanofibrils form dispersions in water and can retain water near their charged surface that is many times their own mass. When added to sludge or any material with suspended solids, collagen dispersions cause agglomeration, the formation of large clumps, and settling, all at a very rapid rate. Collagen nanofibrils are effective in the rapid agglomeration of fine solids in all types of sludge: industrial, water treatment, inert suspensions, and

kaolin. They have also shown promise in other environmental applications such aiding filtration, separation of pollutants from aqueous streams, selective fractionation of molecules, and oil droplet stabilization. Additional applications include cell culture, tissue engineering, and catalyst manufacture.

Professor Maffia also developed a "lost protein technology" to make porous metals using collagen nanofibrils. In this application, metal dust is blended with the nanofibril dispersion. The resulting material is molded into the desired shape, frozen, lyophilized, and then calcined to produce a porous metal. Professor Maffia is working with the Nanotechnology Institute and Synnovations, Inc. on applications for these porous metals.

Professor Maffia has focused on the production of collagen nanofibrils in ongoing research over the past 20 years. Over the past 5 years, he has shifted the starting material to ground bovine corium, a low-value byproduct of the meat-processing industry. Two patents have been issued for this technology. This technology received a Lindbergh Award in 2004 as an example of the balance between technological advancement and protection of the environment. Some small businesses (including Catalyx, Inc.) and government agencies are investigating the technology.

Professor Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

Diminishing Copper Catalyst Content in Atom Transfer Radical Polymerization (ATRP) in the Presence of Environmentally Friendly Reducing Agents

Atom transfer radical polymerization (ATRP) is a transition-metal-mediated, controlled polymerization process for radically polymerizable monomers that was discovered at Carnegie Mellon University (CMU) in 1995. Since 2002, ATRP has been licensed to 7 of the 15 corporations presently funding the research at CMU (PPG, Dionex, Ciba, Kaneka, Mitsubishi, WEP, and Encapson). Licensees have begun commercial production of high-performance, less toxic, safer materials, including sealants, dispersants, coatings, adhesives, lubricants, additives, and materials for electronic, biomedical, health, and beauty applications in the United States, Europe, and Japan.

Since the conception of ATRP, Professor Matyjaszewski has been working to make it a more environmentally benign process. During the last 3 years, he and his team at CMU developed new catalytic systems that allow a dramatic decrease in the concentration of transition metal, while preserving good control over polymerization and polymer architecture. The latest improvements are called activators generated by electron transfer (AGET, 2004), activators regenerated by electron transfer (ARGET, 2005), and initiators for continuous activator regeneration (ICAR, 2006). These methods allow the preparation, storage, and use of the most active ATRP catalysts in their oxidatively stable state as well as their direct use under standard industrial polymerization conditions. The recently discovered ARGET ATRP allows a reduction in the amount of copper catalyst from over 1,000 ppm to less than 10 ppm in the presence of environmentally friendly reducing agents such as FDA-approved tin(II) octanoate, sugars, and ascorbic acid (Vitamin C). AGET and ARGET ATRP provide routes to pure block copolymers. The new processes allow oxidatively stable catalyst precursors to be used in aqueous, homogeneous, dispersed (miniemulsion, inverse miniemulsion, microemulsion, emulsion, and suspension), and solventless bulk polymerizations. Professor Matyjaszewski's work is opening new routes for production of many advanced polymeric materials in a more environmentally benign, green way.

Regioregular Polythiophenes as a Platform for Organic Photovoltaic Technology

Professor Richard D. McCullough, Dean, Mellon College of Science, Carnegie Mellon University

Global sustainability relies on renewable energy; solar energy promises the greatest long-term solution. At $5 per watt, however, traditional silicon-based solar cells (photovoltaics) are too expensive to have serious impact. Further, the production of silicon solar cells requires toxic and explosive gases, corrosive liquids, and suspected carcinogens.

Professor Richard D. McCullough's fundamental discoveries have substantially enhanced the potential of plastic solar cells to mitigate global warming. Earlier, Professor McCullough synthesized nearly 100 percent regioregular polythiophenes (rr-PTs) with unprecedented conductivities and created an energy-efficient, comparatively inexpensive synthesis of pure rr-PTs. He can now synthesize rr-PTs in a process that dramatically reduces hazardous chemicals, consumes significantly less energy, is cheaper, and is scalable to industrially relevant levels (e.g., 100-kilogram batches).

The solubility of poly(3-hexylthiophene) enhanced by side-chain modifications enables it to be solution-processed and inkjet-printed onto various substrates, thus lowering production costs for organic solar cells. Professor McCullough's synthesis of poly-(3-hexylthiophene) is now the dominant technology for producing the most efficient polymer photovoltaics to date, with power conversion efficiencies of up to 5 percent.

In 2002, Professor McCullough cofounded Plextronics, a company committed to delivering revolutionary renewable energy products. These products include organic photovoltaics and organic light-emitting diode (OLED) displays based on Plexcore™, Professor McCullough's polythiophene technology. One of the products, Plexcore PV, is a p-type semiconductor with tunable energy and bandgap that will improve the efficiency of organic (or polymer) solar cells. It can be printed onto substrates, thus enabling large area, low-cost solar cell production that will drive the cost toward the commercially viable $1 per watt. Plexcore™ can be adapted to various applications, so Plextronics is well-positioned to develop markets such as OLEDs, displays, solid-state white lighting, and solar cells for integrated building photovoltaics. Plextronics began kilogram-scale, commercial production of poly(3-hexylthiophene) in 2003 and established a solar cell production facility in 2005.

Highly Efficient and Practical Monohydrolysis of Symmetric Diesters

Professor Satomi Niwayama, Department of Chemistry and Biochemistry, Texas Tech University

The development of environmentally friendly, cost-effective organic reactions is of central importance in academia and industry. Water is among the most environmentally friendly solvents because it generates no hazards during chemical conversion processes. Therefore, water-mediated organic reactions represent green chemistry. Water is also the least expensive solvent.

Desymmetrization of symmetric compounds is one of the most cost-effective synthetic reactions because symmetric compounds are typically commercially available at low cost or are produced easily from inexpensive precursors on a large scale. Desymmetrization of symmetric organic compounds mediated by water would be of tremendous synthetic value and would make a significant contribution to creating greener reaction processes.

Monohydrolysis of symmetric diesters produces half-esters, which are highly versatile building blocks in organic synthesis and have considerable commercial value. Because the two ester groups in the symmetric diesters are equivalent, however, it can be challenging to

distinguish the ester groups chemically. The most common method for effective monohydrolysis uses enzymes, which provide no basis for predicting the yield or enantioselectivity. Classical saponification usually affords only complex mixtures of dicarboxylic acids, the starting diesters, and a small amount of the half-esters, which are difficult to separate. As a result, saponification yields a large amount of undesirable, dirty waste.

Professor Niwayama discovered and has been developing a highly efficient and practical monohydrolysis of symmetric diesters. Her reaction is the first such selective, nonenzymatic monohydrolysis of a series of symmetric diesters. In this reaction, aqueous sodium hydroxide (NaOH) is added to a water–tetrahydrofuran (THF) suspension of a symmetric diester at 0 °C. The reaction rapidly produces pure half-esters in high- to near-quantitative yields without dirty waste. It uses only relatively simple apparatus, allowing large-scale production of half-esters and potential industrial applications. Professor Niwayama anticipates that this reaction will contribute to environmentally friendly green chemistry in industry and academia.

Professor Michael C. Pirrung, Department of Chemistry, University of California, Riverside

Environmentally Friendly Isonitrile-Based Syntheses

Professor Pirrung's technology has two main components. The first is the significant acceleration of isonitrile-based multicomponent reactions in water. The technology not only replaces organic solvents with water, but in some cases also promotes reactions that do not occur in organic solvents. This technology shows that water is superior to organic solvents for certain chemical processes. The simultaneous chemical processes that occur in multicomponent reactions also reduce the number of steps required to prepare useful products, decrease their production costs, and increase efficiency in both unit time productivity and absolute chemical yield. Professor Pirrung's multicomponent reactions are 100 percent atom economical: they do not generate any byproducts. Because the reaction products are frequently insoluble in water, this technology also significantly facilitates product isolation and eliminates traditional energy- or material-intensive purification procedures such as chromatography or distillation. The only initial drawbacks of the technology were (1) the highly offensive odors of the isonitriles that are essential to the most powerful and commonly used multicomponent reactions and (2) their problematic preparation.

The second component is Professor Pirrung's development of a much more environmentally friendly route to prepare isonitriles that also eliminates their stench. Traditional routes to isonitriles involve dehydration of formamides with phosgene. Phosgene is a highly toxic gas that was used as a chemical warfare agent; thus, there is strong resistance to using it in any chemical process. Other dehydrating agents used in its place are not as efficient. Professor Pirrung's alternate route treats readily available oxazoles with a strong base to form isonitriles, eliminating formamide dehydration. The resulting isonitrile esters exhibit uncompromised chemical reactivity and do not have offensive odors. This safer route to isonitriles allows them to replace carbon monoxide in some reactions. Professor Pirrung's technology should increase economy in the production of drug candidates, combinatorial libraries, and active pharmaceutical ingredients.

Enhancing the Efficacy of Totally Organic Wood Preservatives with Low-Cost, Benign Additives

Professors Tor P. Schultz and Darrel D. Nicholas, College of Forest Resources, Mississippi State University

Biocide treatment prevents the biodegradation of wood in outdoor exposures. Treated wood is both economical and sustainable, unlike its main competitors: plastic "lumber", steel, and concrete. Copper-rich preservatives are the current biocides for residential lumber, but these preservatives have environmental concerns. A few U.S. localities have restricted copper-treated wood, and increasing limitations are expected. Future preservatives will likely be totally organic; three European countries already mandate them. Organic biocides have two major problems: they cost more than metallic biocides, and they will themselves biodegrade over time, losing their effectiveness.

Professors Schultz and Nicholas found that combining butylated hydroxytoluene (BHT) with numerous commercial organic biocides significantly enhanced the efficacy of the biocides against wood-destroying fungi. (BHT is a low-cost, benign antioxidant approved for various uses including as a food additive.) Further, the addition of BHT significantly reduced depletion of an organic biocide in long-term, outdoor testing. Low-cost, benign, metal-complexing compounds also enhanced the efficacy of organic biocides in wood decay tests; adding BHT provided even greater enhancement.

Wood is also a hydroscopic material. Used outdoors, particularly as decking, wood swells during rainstorms and shrinks as it dries, causing undesirable warping, splitting, and growth of surface mold. Premium wood decking is treated with a water repellent made from petroleum-derived wax to minimize these dimensional changes. Professors Schultz and Nicholas have recently identified an inexpensive, safe, renewable, metal-complexing compound (tall-oil rosin) and have used it in a waterborne formulation for treating wood. Tall-oil rosin is a byproduct of the chemical pulping of southern pine trees. Initial decay tests combining this compound with several organic biocides showed enhanced efficacy. This compound also increases water repellency of wood and, thus, could replace current petroleum-based water repellents. Mississippi State University has licensed this technology to two international companies. Additional discussions on licensing are ongoing.

Biomimetic Reductive Processes

Professor Vadim A. Soloshonok and Dr. Hisanori Ueki, Department of Chemistry and Biochemistry, The University of Oklahoma

Biomimetic reductive processes via organic base-catalyzed 1,3-proton transfer are conceptually different from purely chemical processes. They replace a conventional, external reducing reagent with the relatively cheap reagent, benzylamine, or its derivatives, both as a source of nitrogen and as a reducing reagent. This allows the development of environmentally benign, metal-free, organocatalytic reductive processes. This technology has three significant advantages over other contemporary reductive methods. First, biomimetic transamination can be conducted under operationally convenient conditions at ambient temperatures in commercial-grade solvents, without any solvent, or thermally. It also has attractive economics and is applicable to large-scale production. Second, correct choice of the structural and electronic features of starting compounds allows transamination to occur with complete chemical yield and complete control over the stereochemical outcome. Finally, the organic base catalyst for the transamination can be used on a solid support that allows its complete recovery and reuse as well as the ultimate development of a synthetically and economically efficient continuous-flow process. The available purely chemical reductive methodology does not allow such a process.

The nominated biomimetic technology has already proven superior for several industrially important reductive processes. These include (1) reductive amination of carbonyl

compounds (aldehydes, ketones); (2) consecutive 1,3-proton-shift-dehydrohalogenation reactions that provide a general approach for the preparation of 2-aza-1,3-dienes (versatile intermediates in the syntheses of nitrogen heterocyclic compounds); (3) hydrodehalogenation of α-halogenated carbonyl compounds; (4) reduction of carboxylic acids to aldehydes; (5) reductive amination of carboxylic acids to amines; (6) enantioselective, organocatalytic, biomimetic, asymmetric, reductive amination of ketones and ketoacids to the corresponding amines and amino acids; and (7) ultimately efficient, continuous-flow, reductive processes using a column packed with an organic base catalyst (chiral or achiral) bound to a solid support. The American Cyanamid Company is currently using this technology for the large-scale synthesis of several amines containing trifluoromethyl groups.

Professor Bala Subramaniam, Center for Environmentally Beneficial Catalysis, Department of Chemical and Petroleum Engineering, University of Kansas

A Greener Hydroformylation Process

Industrial processes for the catalytic hydroformylation of higher olefins (> C_5) are hampered by limited syngas availability in the liquid phase and require rather harsh conditions (5–30 MPa, 150–300 °C) to activate and stabilize the catalyst. Further, recovering the catalyst requires much acid, alkali, and solvent, generating significant waste.

Used as reaction media, CO_2-expanded liquids help overcome these drawbacks. For example, partly replacing excess 1-octene (substrate) with dense CO_2 to create a CO_2-expanded liquid (CXL) phase in the homogeneous hydroformylation of 1-octene with a rhodium-based catalyst complex significantly increases both the hydroformylation rate and the selectivity toward the linear aldehyde. The increased rate and selectivity correlate with experimental results showing improved availability of the gaseous reactants in the CXL phase. The observed time of flight (TOF; ~300 h^{-1}), *n/i* ratio (>10), and aldehyde selectivity (~90%) at the optimum CO_2 content are either comparable to or better than values reported with other media and catalysts. The operating pressure (3.8 MPa) and temperature (60 °C) for the CXL process are significantly milder than those reported for industrial hydroformylation processes. Following the reaction, excess CO_2 easily precipitates the rhodium catalyst complex from the reaction mixture.

The CXL process is estimated to require approximately 50 percent of the capital cost and 80 percent of the production cost of the benchmark Exxon process. The cost savings from the lower operating pressures and temperatures in the CXL process are substantially more than the costs of the recompression and recycling of CO_2. The environmental E-factor (kg of waste generated per kg of desired product) for the CXL process is two- to three-fold less than that of the Exxon process. In addition, the overall toxicity index of the CXL process is approximately 40-fold lower than that of the Exxon process. In principle, the CXL process could tune selectivity in carbonylations, hydrogenations, and asymmetric hydroformylations to produce specialty chemicals and pharmaceuticals.

Professor Daniel Tao, The Department of Mining Engineering, University of Kentucky

Georgia-Pacific Mining Reagents that Improve Recovery, Reduce Wastes, and Conserve Water and Other Natural Resources

NOTE: This project is the result of a partnership between Georgia-Pacific Chemicals, LLC and Professor Daniel Tao of the University of Kentucky. The project was judged in both the academic and greener reaction conditions (Focus Area 2) categories. The abstract appears in the Industry and Government section on page 50.

Novel, One-Step, Chromate-Free Coatings Containing Anticorrosion Pigments to Replace Chromate Pretreatment and Pigments

Professor Wim J. van Ooij, Department of Chemical and Materials Engineering, University of Cincinnati

Paints and organic coatings are often used to protect metals and alloys from corrosion. The paint industry uses approximately 600,000 metric tons of chromates annually for chromate conversion coatings and as pigments. The "self-healing" property of chromates makes them difficult to replace. Hexavalent chromate, Cr(VI), has been identified as toxic and carcinogenic, however; it is subject to regulation by various government bodies. Chromate exposures cause a gamut of health problems including ulcers, irritation of the nasal mucosa, holes in the nasal septum, skin ulcers, allergic reactions, and nasal and lung cancer.

Paints are formulated with high-molecular-weight polymers for good anticorrosion properties. These polymers require solvents that are volatile organic compounds (VOCs). During curing and drying of the paint, these VOCs evaporate, posing an occupational safety hazard.

Professor van Ooij invented a one-step, low-VOC, anticorrosion primer system for use on metals, particularly aerospace aluminum alloys. The system can be applied directly to the metal, eliminating the chromate conversion coating. The novel primer is produced by mixing organofunctional bis-silanes with waterborne resins like acrylates (e.g., Maincote AE58 acrylic resin from Rohm & Haas), polyurethanes, or epoxies (like Daubond D9010 from Daubert Industries, Inc.). To mimic the self-healing properties of chromate pigments, Professor van Ooij developed a synergistic silane-polymer structure incorporating commercial pigments such as zinc phosphate. The pigments leach out of the paint layer very slowly and only when corrosion starts to develop. This novel primer eliminates chromates entirely, yet performs equally well. Further, it cures at elevated temperature or at room temperature, leading to tremendous cost savings.

Professor van Ooij is commercializing his primer system through a small business that he founded, ECOSIL Technologies LLC. Many companies including DuPont, PPG, Sherwin Williams, Hentzen Paints, and BASF have received samples and are about to launch more intensive cooperation with ECOSIL.

Passive Treatment of Metal-Contaminated Water

Professor Thomas Wildeman, Department of Chemistry and Geochemistry, Colorado School of Mines

A serious environmental consequence of the mining legacy in the United States is large flows of water laden with metals, usually known as acid mine drainage. These waters have concentrations of hazardous contaminants such as arsenic, cadmium, and lead that are harmful to human health and aquatic ecosystems. The typical treatment for these waters is to add industrial chemicals to precipitate the metals and then send the water through clarifying, settling, and filtering tanks. Such a labor- and material-intensive process is expensive; it is also impossible to use at the remote sites of many of the abandoned mines within western United States.

Passive treatment is a process for removing contaminant metals from water using natural materials such as wood chips, hay, manure, and limestone instead of industrial chemicals. The breakdown of these materials is catalyzed by natural bacterial consortia to produce sulfide, carbonate, and hydroxide ions that precipitate the contaminating metals. These precipitates are filtered from the water using natural, constructed, wetland structures that blend into the landscape, replacing capital-intensive settling and filtering structures. In summary, passive treatment not only looks green, but is chemically green.

Passive treatment was first successful at the Westfork Lead Mine in Missouri. Full-scale systems have been built for private clients at the Cannon Gold Mine in Wenatchee, Washington, the Haile Gold Mine in South Carolina, the Delamar Gold Mine in Oregon, and the MSF Nickel Mine in Brazil. The systems at all of these sites eliminated active precipitating chemicals, eliminated energy and material-intensive separation steps, and removed metal contaminants such as lead, cadmium, and arsenic, as well as zinc, copper, and mineral acidity from the water. Following these successes at private sites, the U.S. EPA recently adopted this technology at two places in the Ten Mile Creek Superfund Site near Helena, Montana.

Professor Xumu Zhang, Department of Chemistry, The Pennsylvania State University

Practical Asymmetric Catalytic Hydrogenation

Over 50 percent of the world's pharmaceuticals are single enantiomers; sales of chiral drugs were $159 billion in 2002. A growing challenge is to develop cost-effective, green chemical catalytic processes to make chiral molecules. Asymmetric chemocatalysis is one of the most competitive replacements for classic chiral resolutions, which generally require large volumes of solvents, chiral resolving agents, and even waste treatment of unwanted enantiomers. The cleanest and most cost-effective reductant available is hydrogen. Asymmetric hydrogenation accounts for over 70 percent of the current methods for commercial asymmetric chemocatalysis. Fundamental, innovative chemical methods are needed to develop these green chemical processes. Breakthroughs in this area will have broad applicability in industry.

Professor Zhang and his group have developed novel transition-metal-reduction catalysts for the practical synthesis of chiral alcohols, amines, acids, amino alcohols, diols, and α- and β-amino acids. They have investigated the fundamental factors controlling enantioselectivity and invented a toolbox of practical chiral ligands for the asymmetric hydrogenation of ketones, alkenes, imines, and aromatic compounds. They have observed high activity (up to 50,000 turnovers) and enantioselectivity (up to 99 percent enantiomeric excess) for the hydrogenation of some substrates. They have demonstrated the synthetic utility of asymmetric hydrogenation in the green chemical processes with challenging asymmetric transformations for important biologically active compounds such as Lipitor®, Cymbalta®, and carbopenem.

Professor Zhang's technology has numerous patents. He is commercializing it through Chiral Quest, Inc., which is providing his chiral technology to pharmaceutical and fine chemical companies including Phoenix, Pfizer, Merck, and Eli Lilly. Phoenix Chemicals Ltd. is currently manufacturing the Lipitor® side-chain using Chiral Quest's technology.

A Novel Phosphite Dehydrogenase Based NAD(P)H Regeneration Technology for Industrial Biocatalysis

Professors Huimin Zhao, Department of Chemical and Biomolecular Engineering; Wilfred A. van der Donk, Department of Chemistry; William W. Metcalf, Department of Microbiology, University of Illinois

Enzyme-catalyzed reactions that require stoichiometric amounts of reduced nicotinamide cofactors (NADH and NADPH) have great potential in industrial biocatalysis, but many are underutilized because the cofactors are very expensive. Preparative applications require regeneration of the cofactors in situ, usually by a second enzyme with high specificity for a sacrificial substrate. Professor Zhao and his collaborators Professors van der Donk and Metcalf have developed a novel technology to regenerate NAD(P)H that is based on phosphite dehydrogenase (PTDH). Their technology is more efficient than the most widely used technology based on formate/formate dehydrogenase (FDH).

Professor Zhao and his collaborators discovered and characterized a wild-type PTDH enzyme from *Pseudomonas stutzeri* that catalyzes the nearly irreversible oxidation of phosphite to phosphate with the concomitant reduction of $NAD(P)^+$ to NAD(P)H. Using rational design and directed evolution, they engineered a PTDH variant that exhibits drastically improved stability (its half-life of thermal inactivation at 45 °C is over 22,000-fold greater than that of the wild-type PTDH), activity (6-fold higher), and cofactor specificity (3.6-fold and 1,000-fold higher catalytic efficiencies for NAD^+ and $NADP^+$, respectively). Compared with FDH, PTDH has higher specific activity, a higher thermodynamic equilibrium constant ($K_{eq} = 1 \times 10^{11}$), and a broader pH-rate maximum. In addition, the phosphite substrate is inexpensive; both the substrate phosphite and the product phosphate are innocuous and act as a buffer, and phosphate can be removed readily by calcium precipitation if necessary.

The three professors used a membrane bioreactor to demonstrate the advantages of this mutant PTDH over FDH for cofactor regeneration in the industrially important synthesis of L-*tert*-leucine and xylitol. Their PTDH system has broad applicability in industrial synthesis of unnatural amino acids, polyols, chiral alcohols, and products labeled with deuterium or tritium. Recently, BASF (Germany) and BioCatalytics (Pasadena, CA) licensed their novel PTDH-based technology.

Entries from Small Businesses

Changing the Nature of Surfactants: Low-Molecular-Weight Proteins as Surfactant Synergists

Advanced BioCatalytics Corporation

In many chemical processes, surfactants and solvents enhance chemical reactions by reducing the surface energies of the reactions. The large markets that use surface-active agents include cleaners, agriculture, coatings, oil, fabric processing, and adhesives. The majority of raw materials used to produce surfactants and solvents are petroleum-based. Botanicals and other renewable, greener alternatives are available, but are confined to niche markets as their cost and performance have not met the needs of broader markets.

Advanced BioCatalytics developed Molecular Kinetics™, a technology based on a patented, low-molecular-weight protein system. That system, C.O.D.E.™, significantly reduces interfacial tension. Currently, Advanced BioCatalytics derives the C.O.D.E.™ proteins from the supernatant of a unique yeast fermentation process. The protein products are made in a food processing facility in a strategic partnership between Kikkoman Foods and Advanced BioCatalytics. C.O.D.E.™ can replace solvents in general-purpose cleaners, most of which are hazardous. It enhances surfactants, reducing their volumes significantly in cleaners and in numerous other chemical processes. For example, in a fabric processing test, C.O.D.E.™-based wetting agents reduced the amount of surfactant required by over 90 percent.

Demand for greener products is being fueled by the expanding public awareness of environmentally responsible chemicals and tightening regulatory requirements. C.O.D.E.™ proteins meet FDA guidelines for food contact, are safe for the user, and improve the environment in many ways. They could potentially replace millions of pounds of toxic chemicals, reducing air, water, and environmental pollutants. The features of C.O.D.E.™ provide chemical formulators with incentives that allow them to produce distinct, higher-margin products in commodity markets. Since 2004, Advanced BioCatalytics has commercialized four industrial and institutional products using C.O.D.E.™ proteins and is working with several companies to commercialize additional new products in 2007.

Uncoupling Biochemical Processes for Enhanced Biological Efficiency

Advanced BioCatalytics Corporation

Advanced BioCatalytics developed and patented naturally produced chemicals using a protein-based system called C.O.D.E.™. This led to a platform technology it calls Molecular Kinetics™, which uncouples oxidative phosphorylation in microbial metabolism such that the breakdown of organic compounds by microbes accelerates dramatically. The C.O.D.E.™ uncoupling factor signals microbes to view biofilms as nutrients and to digest them. C.O.D.E.™ products meet FDA guidelines for food contact, are approved by the National Science Foundation (NSF) for potable water use, are safe for the user, and improve the environment in many ways. In 2002, the company commercialized this technology as Accell®.

In industrial and municipal wastewater treatment facilities, Accell® can consistently reduce sludge production and its associated costs by 30 percent or more. In addition, the treatment plants operate more efficiently, with improved effluent quality, better sludge settling, increased plant throughput capacity, and the opportunity to reduce aeration costs by over 30 percent in some cases. Aeration is the greatest user of energy in these facilities. Using Accell® in its wastewater treatment plant saved one industrial customer $5 million

in capital equipment costs, reduced its operating costs, and saved over $200,000 per year in environmental surcharges.

The formation of biofilms in cooling systems contaminates heat exchange surfaces and fouls reverse osmosis filtration membranes drastically, corroding and degrading substrates and reducing energy efficiency. C.O.D.E.™ can reduce the toxic biocides typically used to control biofilm and biofouling by over 90 percent.

In seawater desalinization, the cost of energy to pump water through the membranes is the greatest operating expense. The process typically requires frequent cleaning cycles that can degrade the expensive membranes. C.O.D.E.™ treatment can save over 20 percent of energy use by reducing both operating pressures and cleaning cycles while increasing both throughput and salt rejection.

Amerikal Products Corporation

Genesis® BRIGL Wash

Genesis® BRIGL Wash is a biodegradable blanket and roller wash for offset printers. It has a volatile organic compound (VOC) content of 34.3 grams per liter and an ASTM D-92 flashpoint greater than 200 °F. It contains over 90 percent soy methyl ester (a U.S.-renewable resource), less than 8 percent VOC-exempt acetic acid methyl ester, proprietary antioxidants, and preservatives. It does not contain water or surfactants.

Genesis® BRIGL Wash offers a safer, more productive alternative to petroleum-based washes. It does not contain raw materials classified as SARA 313 chemicals or Hazardous Air Pollutants (HAPs). It offers a solution to printers who want to increase productivity without compromising the health and safety of their employees.

BRIGL is the only wash on the market that effectively cleans conventional, heat-set, ultraviolet, electronic-beam, and co-cure inks, so that printers can use only one wash for an entire pressroom instead of the usual four to nine solvents. More important, unlike other "green" blanket and roller washes, BRIGL is easily implemented into the print production environment. Since BRIGL's introduction in October 2006, over 50 full-time users have switched to it, and the list keeps growing.

Premier printers who took part in Amerikal's trial phase of BRIGL reported prolonged roller life, reduced overall consumption, a reduction in pressroom odors, and essentially no hazardous waste streams from blanket and roller washes. Printers also discovered that BRIGL could be used for manual and automatic wash-up procedures, reducing consumption by 50–70 percent compared with traditional washes and cutting overall costs.

With over 1,200 customers, Amerikal has used its vision, innovation, and initiative to redefine the standard for pressroom chemistry. Amerikal is the first and only pressroom chemical manufacturer dedicated solely to developing products that offset petroleum use; preserve natural resources; eliminate hazardous waste streams; and reduce global warming, energy costs, and pollution.

APTech Group, Inc.

A Greener Chemical Treatment for Cooling Tower Water

Chemical treatment of water in cooling towers is necessary to minimize microbiological growth and to eliminate corrosion and scaling. Liquid cooling tower products contain about 25 percent solids in water. Many of the active ingredients are insoluble in solutions at neutral pH, so manufacturers must add sodium hydroxide (NaOH), a highly caustic chemical, to increase the pH and stabilize the solution. NaOH typically accounts for about half of the solids in solution.

APTech Group developed a product in which only the active ingredients are mixed, heated, filled into jars, and then cooled into a solid product. The solid product contains sodium tolyltriazole, sodium salts of (1-hydroxyethylene) diphosphonic acid, sodium salts of 2-phosphonobutane-1,2,4-tricarboxylic acid, the partial sodium salt of acrylic acid terpolymer, VersaFlex™ One polymer (Alco Chemical), the sodium salt of hydroxyphosphonoacetic acid, and sodium chloride. It does not contain NaOH. The product is reconstituted with water into a very dilute solution (approximately 0.5 percent or less) onsite before use. This technology not only eliminates the discharge of NaOH into wastewater streams, but also eliminates the potential for spills of hazardous, highly concentrated chemicals that would have to be cleaned up by local personnel and could kill aquatic life if released into surface waters. It also eliminates the problems associated with disposal of the empty drums that had held the liquid chemicals. Solid chemicals can result in savings for the user. The use of solid chemicals can eliminate the transport of 309 million pounds of water and 38 million pounds of NaOH over U.S. highways annually, saving fuel and reducing the potential for spills.

Environmentally and Toxicologically Safe Firefighting Gel

Barricade International, Inc.

Liquid firefighting gel had its genesis in the 1990s, when John Bartlett, President of Barricade International, Inc., observed that used, disposable baby diapers survived a house fire in which even the appliances melted. The superabsorbent polymer and water content of the diapers prevented their combustion. Mr. Bartlett, a professional firefighter, realized that a superabsorbent polymer might change the way fires are fought. He then looked for liquid forms of the superabsorbent polymer that might be easily introduced into firefighting water to produce a fire retardant and suppressant gel.

In the late 1990s, Mr. Bartlett identified a printing paste thickener used in the textile industry that produced a thickened water gel that significantly improved fire extinguishing and prevention. Barricade's competitors now use that product, but it contains two components, petroleum distillate and nonylphenol ethoxylate (NPE), that have environmental and health concerns. Data have linked NPEs to endocrine disruption and mammalian reproductive concerns.

Barricade International, with E.T. Sortwell conducting R&D, has developed a product to match the firefighting properties of the existing gel without its environmental and health concerns. The product is Barricade II, a dispersion of superabsorbent polymer in food-grade vegetable oil (i.e., canola), sorbitan monooleate, and fumed silica. The superabsorbent polymer is typically a copolymer of acrylamide and acrylic acid derivatives such as salts. Barricade II is more effective at fire prevention than its NPE–petroleum distillate competitor. In aerial applications, Barricade costs only about half as much as traditional retardants and is effective at about 1/18 the application rates. The U.S. Forest Service has placed Barricade II on its Qualified Products List. A U.S. patent has been allowed, and Barricade International has begun full-scale commercial production of this product. California's Department of Forestry used Barricade II in aerial applications during the 2006 fire season with spectacular results.

Century Industrial Coatings Inc.

Nulo™ Technology: HAP-Free, Low-VOC, Water-Based, Air-Dry Coatings

The Nulo™ technology is a water-based coating developed to replace solvent-based paints in steel joist dip painting operations. The most transfer-efficient method to paint open-weave steel joists is by dipping the joists into vats filled with paint. Traditionally, the joist industry used solvent-based alkyd paints containing 3.5 pounds or more of volatile organic compounds (VOCs) per gallon. Conventional water-based paints have not been successful in dipping operations because of their high cost, poor film properties, and problems with their stability. Time and pH fluctuations cause these paints to thicken and can turn them into an unusable gelatinous mass in the dip tank.

Century Industrial Coatings developed Nulo™ as a new water-based paint that satisfies the joist industry's needs for reduced VOC emissions, stability in dip tanks, comparable cost, and product performance equal to that of solvent-based paints. Nulo™ paints contain no hazardous air pollutants (HAPs), have VOC levels of only 0.47 pounds per gallon, and have the appearance of solvent-based paints. The viscosity of Nulo™ paints is controlled with water, not volatile organic solvents. The benefits of using the Nulo™ paints to replace solvent-based paints include reduction of VOC emissions by 86 percent, elimination of HAP emissions, elimination of flammability and combustion problems, and reduced impact on human health and the environment.

Nulo™ dip primers have been in continuous commercial use since July 2003. Nulo™ primers have already replaced approximately 1 million gallons of solvent-based primers, eliminating about 2.89 million pounds of VOC releases to the atmosphere. Replacing solvent-based primers with Nulo™ primers in joist plants would eliminate an estimated 12.1 million pounds of VOC emissions each year. Century is in the process of expanding its technology to other painting processes and industry sectors.

Changing World Technologies, Inc.

Waste to Renewable Diesel

Changing World Technologies, Inc. (CWT) has successfully developed and patented an energy-efficient process that converts organic waste into diesel oil. Their Thermal Conversion Process (TCP) is capable of breaking down waste material using water, heat, and pressure. The process can use a broad range of wastes including animal carcasses and byproducts; fats, greases, and oils; and municipal and industrial wastes including plastics, metals, and recycled automobiles. It does not require exotic chemicals or catalysts, and it includes screening and grinding of waste; depolymerization at 290 °F and 80 psi; hydrolysis at extreme temperature and pressure (480 °F and 600 psi); and separation of the oil, water, and solid products. Because the process relies on waste, which is typically generated near areas of high energy demand, the company will be able to supply its renewable diesel locally without having to use costly and constrained energy infrastructure.

TCP is being demonstrated in a commercial environment. In December 1999, CWT opened a pilot plant at the Philadelphia Naval Business Center with the support of the Gas Technology Institute. CWT began construction of its Carthage, MI facility in 2002, produced its first gallon of renewable diesel in 2004, and commissioned the plant in February 2005 as a joint venture with ConAgra Foods, Inc. The company is currently selling its renewable diesel for use in industrial boilers. The efficacy, efficiency, and other key qualities of TCP have been reviewed and validated by a number of independent authoritative organizations such as the Brookhaven National Laboratory, the Massachusetts Institute of

Technology, the U.S. Department of Energy, and the Vehicle Recycling Partnership. CWT believes it is the first company to successfully demonstrate the ability to commercialize the process of converting waste to oil in an energy-efficient manner.

Chiral Quest, Inc.

Practical Asymmetric Catalytic Hydrogenation

NOTE: This project is the result of a partnership between Chiral Quest, Inc. and its founder, Professor Xumu Zhang of The Pennsylvania State University. The project was judged in both the academic and small business categories. The abstract appears in the academic section on 18.

Codexis, Inc.

Greening Atorvastatin Manufacture: Replacing a Wasteful, Cryogenic Borohydride Reduction with a Green-by-Design, More Economical, Biocatalytic Reduction Enabled by Directed Evolution

Atorvastatin calcium is the active pharmaceutical ingredient in Pfizer's cholesterol-lowering drug Lipitor®. The key advanced chiral intermediate in the manufacture of atorvastatin is *t*-butyl (4*R*,6*R*)-6-cyanomethyl-2,2-dimethyl-1,3-dioxane-4-acetate (ATS-8 or TBIN). It is the first isolated intermediate comprising both of atorvastatin's chiral centers. Pfizer's traditional ATS-8 process uses a sodium borohydride ($NaBH_4$) reduction of the corresponding (5*R*)-hydroxy-3-ketoester (ATS-6 or HK) under cryogenic conditions to give, after quenching, the (3*R*,5*R*)-dihydroxyester (ATS-7 or diol). The ATS-6 is first converted in situ to a diastereodirecting boron chelate by treatment with hazardous diethylmethoxyborane that is reacted with $NaBH_4$ at below 85 °C to further promote diastereoselectivity. After the reaction, the borane reagent is regenerated and recovered by repeated methanol quenches and vacuum distillations. Nonetheless, several percent of the undesired (3*S*) diastereomer is formed. Subsequently, the ATS-7 diol, an oil, is protected as its acetonide, ATS-8, whose diastereopurity is upgraded by crystallization, with concomitant product loss.

The nominated technology represents a greener, more economical process for reducing ATS-6 to stereopure ATS-7. It uses a ketoreductase biocatalyst specifically evolved to reduce ATS-6 with perfect diastereoselectivity under greener reaction conditions (300 g/L in water at ambient temperature and pressure) in conjunction with a previously evolved, process-tolerant, glucose dehydrogenase biocatalyst that returns the oxidized cofactor ($NADP^+$) to its reduced state (NADPH). The Codexis technology eliminates the use of hazardous boron reagents, reduces solvent use by 85 percent, reduces waste by 60 percent, lowers energy use dramatically, and provides a higher yield of ATS-7 with greater stereopurity. Even without crystallization, both ATS-7 diol from this reaction and ATS-8 produced from it are more diastereopure than the atorvastatin in Lipitor®. Codexis's biocatalytic process is now in commercial use to supply high-quality ATS-8 to generic atorvastatin manufacturers on a multi-ton scale at shutdown prices.

Crosslink

Corrosion-Resistance without Chromium: On-Demand Release of Environmentally Safe, Non-Chromium Corrosion Inhibitors from Electroactive Polymer Coatings

Currently, the prevalent primers and pretreatments used to inhibit corrosion of aluminum alloys for the aerospace industry contain hexavalent chromium, Cr(VI). These primers are extremely effective, but their manufacturers are under significant pressure to eliminate Cr(VI) from them. Employees exposed to Cr(VI) have increased risk of developing serious adverse health effects including lung cancer, asthma, and damage to nasal passages and skin. In addition, these standard coating systems release Cr(VI) to the environment throughout their useful life. Federal, State, and local agencies have issued regulations that limit or prohibit the use of materials containing chromium.

Crosslink has developed a commercially available, environmentally and worker-friendly coating to replace Cr(VI)-containing paint primers for protecting aluminum alloys in aerospace applications. Their novel coating is based on electroactive organic polymers (EAPs). EAPs possess two unique properties: the ability to conduct electricity through an organic polymer and the ability to bind and expel molecules or ions in response to an applied electrochemical potential. Local electrochemical reactions that occur on the surface of a metal during corrosion trigger a change in an EAP's redox state. Crosslink has synthesized EAPs with corrosion inhibitors (molecules or ions) as dopants. In Crosslink's protection system, the onset of corrosion forms a local galvanic couple that triggers release of the inhibitor from the EAP. Released inhibitor molecules then diffuse to the corroding site and inhibit the anodic or cathodic reaction. In this sense, these coatings are "smart": they release the inhibitor only when corrosion occurs. A nontoxic inhibitor, 2,5-dimercapto-1,3,4-thiadiazole, forms the basis of one new chromium-free primer. Incorporation of Crosslink's EAP system into paint systems such as epoxy and polyurethane could eliminate the need for chromium-based primer coatings and their associated environmental and safety risks. Crosslink has identified a business partner to commercialize its technology during 2007.

Cutting Edge Formulations, Inc.

Nature's Avenger™ Organic Herbicide: A Highly Effective, Nontoxic, Organic Alternative to Synthetic and Natural Herbicides

Nature's Avenger™ Organic Herbicide (NAO) is a safe, highly biodegradable, effective, nonselective, post-emergent herbicide that has been approved by the U.S. EPA for organic agriculture production. NAO's active ingredient, *d*-limonene, is the primary component of citrus oil and is found naturally in more than 300 herbs, edible plants, and fruits. Citrus oil is a strong degreasing agent that is commonly used in soaps, detergents, commercial cleaners, deodorizers, shampoos, and mouthwashes. It is also used as a flavoring agent. This natural degreaser strips away the waxy cuticle from weeds, subsequently dehydrating and killing them.

Earlier work demonstrated that *d*-limonene by itself is a relatively weak herbicide. Work by Cutting Edge showed that increasing the pH enhances the herbicidal efficacy significantly. A mixture of proprietary inert ingredients also contributes to activity such that NAO is comparable in activity to Roundup® and paraquat, both of which are synthetic, nonorganic herbicides.

In the absence of an effective organic herbicide, organic growers tend to control weeds primarily with mechanical tillage and hand labor, at a cost of approximately $1,000 per acre. The availability of an easy-to-use, effective, cost-effective organic herbicide to control weeds could revolutionize how organic growers manage their weeds. Using mechanical tillage along with NAO in areas that cannot be mechanically tilled would bring the organic grower cost of NAO into a range of $45–80 per acre, which is within the range of what traditional, nonorganic growers pay for weed control. In consumer and professional markets, the availability of a safer, more efficacious, organic herbicide gives the homeowner and professional users an important alternative.

Green Chemistry for Industrial Coatings

Ecology Coatings

The conventional industrial coating process is pollution-, time-, space- and energy-intensive. In a departure from both solvent-based traditional coatings and newer powder coatings that require substantial heat to cure, Ecology Coatings's LiquidN™ coatings are sprayable, 100 percent solids formulations that cross-link to form a durable barrier when exposed to ultraviolet light. They offer abrasion resistance, moisture resistance, and durability equal to or better than that of conventional waterborne, solvent-based, or powder coatings. The LiquidN™ coatings can be precision-sprayed at ambient temperatures, enabling them to integrate easily into existing finishing processes. Requiring only a few seconds of light exposure to cure, these pioneering coatings reduce time up to 99 percent, energy use up to 75 percent, and space on the manufacturing line up to 80 percent. These solvent-free coatings also virtually eliminate emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), in turn reducing associated regulatory burdens.

In addition to presenting Ecology Coatings with clear economic and environmental advantages over conventional industrial coatings, LiquidN™ coatings have unique characteristics that enable them to serve an entirely new spectrum of applications. Because the coatings contain no liquid and do not require heat to cure, they are particularly well-suited for consumer electronics and other sensitive products. Unlike existing coatings that are generally limited to one or two applications, LiquidN™ coatings are suitable for plastics, metals, composites, paper, biodegradable materials, and more. Ecology Coatings's innovative coatings technology is capable of propelling the coatings market, an integral piece of the U.S. manufacturing industry, into America's greener future. Ecology Coatings has licensed its technology to DuPont Performance Coatings and Red Spot, which is a leader in the field of UV-curable coatings.

Liquid Seal and Nonhazardous Cleaner Eliminate Odor, Health, and Maintenance Problems Stifling the Acceptance and Implementation of Waterless Urinals

Environmentally Sensitive Solutions, Inc.

The Kohler Company approached Environmentally Sensitive Solutions, Inc. (ESS) to develop the chemistry for a new waterless urinal in a joint project. Waterless urinals have existed for years, but their high maintenance requirements and lack of effective odor and exposure controls have limited their large-scale adoption. ESS was to develop a superior liquid seal and nonhazardous cleaner that would be an environmentally friendly combination, both more effective than current waterless urinal designs and safer than traditional, caustic urinal cleaners.

The ESS unique liquid seal eliminates the odor that is problematic in traditional waterless urinals. The patent-pending liquid seal is a formulated vegetable-oil-based, biodegradable product that floats on the urine in the trap. This liquid seal is formulated to prevent sewer gases and urine odors from emanating from the waterless urinal while allowing urine through. Even when subjected to turbulence, the liquid seal repairs itself quickly, preventing hazardous gases and undesirable odors from escaping. The liquid seal chemistry also eliminates the need for the hazardous urinal pucks used as supplemental odor control in an estimated 90 percent of flush urinals. These *p*-dichlorobenzene-based pucks have been proven harmful to human health and the environment.

The ESS waterless urinal cleaner is neutral, noncorrosive, and surfactant-based; it eliminates the hazards of traditional cleaners. For daily cleaning, the ESS cleaner is compatible with the liquid seal and does not adversely affect the performance of the liquid seal.

The keys to waterless urinal acceptance and implementation are the complete odor control and low maintenance that only these green chemistries can provide. Each waterless urinal has the potential to save up to 40,000 gallons of water per year. Kohler has implemented the ESS liquid seal and cleaner in the global launch of its *Steward*™ collection of waterless urinals.

EverTech LLC

Everdex-Enhanced Alowood

Deforestation of old-growth forests and rainforests is of growing concern given the far-ranging debates today on climate change. Consumers, however, still want the look of exotic hardwoods in products such as flooring and furniture. Alowood offers an environmentally friendly alternative: the opportunity to get an exotic look and performance using fast-growing plantation softwoods as the base wood impregnated with an innovative green chemistry, the Everdex formulation.

Everdex is a polymeric formulation made from urea, glyoxal, and starch in water; it does not contain any formaldehyde. Softwoods, particularly sustainably grown, plantation softwoods, are immersed in dilute solutions of Everdex and subjected to a vacuum and pressure treatment to impregnate them with Everdex. Next, the impregnated wood is heated, causing the starch polymer to cross-link with the wood cellulose through the urea-glyoxal groups. This creates Alowood, a denser, harder, more workable wood product akin to a natural hardwood.

EverTech is currently selling Everdex-enhanced Alowood to the building industry segment as an alternative to natural hardwood. This innovative product is making a significant positive environmental impact in that every piece of Alowood sold replaces a piece of hardwood lumber or exotic wood that can remain a part of the ecosystem. Alowood made from plantation wood grown in about 30 years is preferable to exotic hardwoods that often take hundreds of years to grow.

Exelus, Inc.

ExSact – A "Green" Gasoline Technology

Alkylate is a clean, high-octane, blending component of gasoline made primarily by alkylating isobutane with butenes. Alkylate is an ideal replacement for MTBE (methyl *t*-butyl ether) in reformulated gasoline. It has a low vapor pressure, a high octane value, and is not water-soluble. Most U.S. refineries produce alkylate. The current technology for alkylation, however, requires either hydrofluoric acid (HF) or concentrated sulfuric acid as the catalyst. These liquid acid catalysts pose many problems. HF is deadly, causing severe burns and tissue damage. It also tends to form stable aerosols, so that an accidental release

can create a lethal cloud. The 50 HF units in the United States threaten as many as 15.6 million people living nearby. Sulfuric acid is somewhat safer, but its use creates a byproduct mixture of hydrocarbons and sulfuric acid that must be disposed of or regenerated. Sulfuric acid units use considerable amounts of the acid as catalyst, requiring the transport and storage of large amounts of this acid.

ExSact solves these problems by replacing dangerous liquid acids with a noncorrosive, environmentally friendly, solid acid. This breakthrough catalyst is safe enough to be held in hand and is benign in the open environment. Previous solid acid catalysts have not been commercially successful because they tend to deactivate rapidly by coking during alkylation. Exelus has engineered every aspect of its new catalyst to reduce coke formation. It has optimized both the distribution and strength of the acid sites and has chosen a pore structure that creates the proper reaction environment near the active sites. Its ExSact technology represents the first commercially viable solid acid alkylation process in the world. Exelus has successfully demonstrated the ExSact technology in a 1,000-hour pilot program and has licensed its technology to a European refiner. The first commercial plant is expected to start up in early 2008.

ExSyM – The Next Generation of Styrene Monomer Technology

Exelus, Inc.

Styrene monomer is a large-volume commodity chemical with a current global demand of about 25 million metric tons per year. The current technology is over 70 years old. It relies on the dehydrogenation of ethylbenzene, which is a highly endothermic and thermodynamically limited reaction. Styrene production consumes about 10 times more energy than does the production of most other industrial chemicals and is a major contributor to methane emissions.

Exelus is developing ExSyM (Exelus Styrene Monomer Technology), a technology to produce styrene monomer directly by the alkylation of the toluene side-chain with methanol. Others have studied this route for over 30 years, but they could not overcome the high rate of methanol decomposition and low yields of styrene that have prevented its commercialization.

Exelus has invented a new zeolite catalyst technology and made other breakthroughs that, for the first time, permit commercially viable reaction yields of 80 percent. The technology uses a simple fixed-bed process. Substituting toluene and methanol for the traditional process feedstocks (benzene and ethylene) leads to a 30-percent reduction in operating costs. This new technology also reduces the reaction temperature by over 200 °C, resulting in much lower capital costs than conventional plants.

Perhaps the single biggest benefit to society, however, is a massive reduction in energy use. This process would save up to 186 trillion British thermal units per year (Btu/yr) in the United States alone, cutting CO_2 emissions by 4.34 billion kg per year. These savings represent over 5 percent of the U.S. greenhouse gas reductions stipulated by the Kyoto Protocol. In addition, the hydrogen byproduct of the reaction can be used as fuel to produce all of the heat of reaction and most of the distillation energy for the process without generating any CO_2. Exelus has demonstrated its technology at the bench scale and expects to begin pilot plant tests in mid-2007.

Fungi Perfecti, LLC

Mycopesticides and Mycoattractants

Certain mold fungi, called entomopathogenic fungi, kill insects and use their carcasses as platforms for disseminating spores. With limited success, the pesticide industry has attempted to deploy entomopathogenic fungal spores to kill pests such as termites and ants. The spores of entomopathogenic fungi repel many of these insects, however, and insects have natural defenses against them. Soldier insects guarding the nest keep spore-contaminated foragers from entering in order to protect the queen and the colony from infection.

Fungi Perfecti has developed methods to deploy the presporulating mycelia of the entomopathogenic fungi *Metarhizium* and *Beauveria* as natural agents to attract and kill termites and ants. The novelty of this technology is the discovery by Fungi Perfecti that ants, termites, and flies are attracted to entomopathogenic fungi in their mycelial state, prior to sporulation. Fungi Perfecti isolated fungi from naturally infected insects and then cultured the fungi selectively to create strains that delay spore production for several weeks. The presporulating mycelia emit powerful attractants, trail-following elicitors, and feeding stimulants, which draw select pests to a chosen site, from where they spread the infectious fungi throughout the targeted nest and ultimately to the queen. In choice tests, termites prefer the presporulating mycelium of *Metarhizium anisopliae* to wood as food. The infected colony, upon sporulation, repels subsequent insect invasions.

This mycotechnology is economical and scaleable; it uses current cell culture methods. It has been awarded two patents, with more pending. Tests at Texas A & M University and the U.S. Department of Agriculture show this technology works against Formosan termites, eastern subterranean termites, and fire ants. Subsequent tests show positive results in controlling carpenter ants and fungus gnats. This discovery may well replace toxic pesticides and lead to novel methods for controlling insect pests worldwide, protecting the environment, people, and other organisms.

GreenBlue (Green Blue Institute)

CleanGredients™: Systems-Based Information Technology for Green Chemistry

CleanGredients™ is an online database of environmental fate, toxicology, and other data on cleaning product ingredients. CleanGredients™ uses a peer-reviewed framework to evaluate and compare chemicals within functional classes. It enables manufacturers to showcase ingredients with lower inherent environmental or human health hazards. It also enables formulators to identify ingredients for environmentally preferable products easily.

CleanGredients™ facilitates the ongoing development and implementation of green chemistry in the cleaning products industry. It has the potential to expand into other industry sectors. CleanGredients™ grew out of recommendations of the Unified Green Cleaning Alliance and a partnership between GreenBlue and the U.S. EPA's Design for the Environment (DfE) Program. The steering and technical advisory committees for the Alliance drew members from leading organizations in industry, government, and the non-profit sector. The committees established the overall format and identified the specific attributes for the CleanGredients™ database. Interested participants, now numbering around 600, serve as peer reviewers.

CleanGredients™ presents carefully selected information on chemical raw materials including performance properties, environmental fate, human and environmental health, safety, and sustainability in a format that helps formulators easily identify candidate ingredients for environmentally preferable product formulations. CleanGredients™ lists only

chemicals that have been characterized adequately and meet key human and environmental characteristics. Formulators can search the database by general ingredient information and physical properties to identify suitable candidate ingredients for particular applications. The first CleanGredients™ module (surfactants) was launched in 2006. Within 2 months, 11 raw material suppliers and 50 formulators had subscribed to list ingredients or access information. Modules for solvents, chelating agents, and other product classes are under development.

The Use of Green Unikleen in Oil Spill Clean-Up, Both on Land and in Water

IPAX Cleanogel, Inc.

IPAX's flagship product, Green Unikleen, will improve oil spill clean-up, both on land and at sea. Green Unikleen is a biodegradable, nontoxic, concentrated cleaner and degreaser that can be used with any manual or mechanical cleaning equipment. It is water-soluble and has no volatile organic compounds (VOCs). Its formula includes sodium silicate, Biosoft S-100, Neodole 23-5 (Shell Oil; includes a mixture of $C_{12\text{-}13}$ alcohol ethoxylates), a tetrasodium salt, and Surco SXS (40–42 percent sodium xylene sulfonate and up to 2 percent sodium sulfate in water).

Green Unikleen has been used extensively for washing automotive parts; it replaces VOC solvents and reduces hazardous waste. IPAX has research results demonstrating that Green Unikleen is an improvement over current technologies to clean up oil spills on land. Green Unikleen is able both to return oil-saturated soil back to a state that will support plant growth and to allow recovery of the oil for its original use. Together with added biosupplementation, Green Unikleen can reduce residual petroleum in treated soil to 0.1 percent, the maximum concentration allowed for agriculture.

For oil spills at sea, Green Unikleen has been shown to be a very effective dispersing agent as well as a fire-preventive and -extinguishing additive. Green Unikleen breaks oil spills into small droplets, forming a thin emulsion that disperses in the water column. In dispersed form, the oil is subject to natural degradation by marine microorganisms. Green Unikleen can be effective in dispersing most liquid oils and liquid water-in-oil emulsions with viscosities below about 2,000 centistokes. In a fire-extinguishing demonstration, Green Unikleen and water (1:10) required less than 2 minutes to extinguish a fire of benzene, diesel fuel, and crude oil that had been allowed to heat up to over 2,000 degrees before treatment. Green Unikleen is available commercially, and IPAX has applied for a patent for its technology.

New Green Technology for Eliminating Hydrogen Sulfide in Aqueous Systems, Especially Petroleum Industry Systems

The LATA Group, Inc.

The occurrence of hydrogen sulfide (H_2S) in aqueous systems is a major concern of many industries. This concern is especially acute in the international oil and gas industry. H_2S constitutes a serious health, environmental, and economic problem in virtually all major oil and gas production operations. Massive global reservoirs and water systems are now heavily contaminated with corrosive, poisonous H_2S and harmful iron sulfide precipitates that plug pipelines, impeding oil and gas production.

The source of H_2S is the reduction of soluble sulfate (SO_4) in the water by indigenous, aerobic, sulfate-reducing bacteria (SRB). To combat H_2S formation, the industry has used

biocides such as glutaraldehyde, acrolein, formaldehyde, quaternary amines, and chlorine extensively. However, SRB are becoming resistant to them, necessitating the use of increasingly toxic and dangerous biocides.

LATA's biocompetitive exclusion (BCX) technology is designed to attack SRB. The BCX process is initiated and sustained by patented, environmentally friendly formulas named Max-Well 2000 that contain a combination of inorganic nitrate and nitrite. These formulas target and directly manipulate the indigenous microflora of hydrocarbon-bearing reservoirs and a wide variety of surface injection and produced water systems. Low concentrations of Max-Well 2000 act as alternate electron acceptors for indigenous, nitrate-reducing bacteria (NRB) so that they subsequently flourish and out-compete SRB for essential growth nutrients. The nitrite component is toxic to SRB and also reacts chemically with existing H_2S to form soluble, nonhazardous SO_4. The end result of the growth of beneficial NRB populations is the production of nonhazardous nitrogen gas, elimination of existing H_2S in the system, and continuous blocking of new H_2S and iron sulfide production. One successful field project with a major oil company is leading to treatment expansions in the United States and elsewhere. Another ongoing field trial with a major oil company is destroying and controlling H_2S in an oil and gas reservoir.

MYCELX Technologies Corporation

Novel Device for Removing Mercury from Produced Water and Vapor Streams

Significant amounts of mercury can be present in the vapor and produced water generated by offshore drilling operations. Mercury in produced water associates itself with various impurities in the water in the form of organometallic, colloidal, ionic, and metallic species and as dissolved solids and gases. The broad range of organic and inorganic constituents in these streams makes treatment difficult. Treatments such as sulfide-impregnated carbon- or carbamate-based media that rely on a single stage to remove all mercury have been field-tested with poor results including organic fouling of the treatment media.

The novel MYCELX device uses a three-stage approach. Each upstream stage removes components that would otherwise tend to foul the subsequent stage. Stage 1 uses solubility and weak interactions. Stage 1 filtration media are impregnated with a curable viscoelastic rheology modifier, MYCELX HRM™, which is the reaction product of drying and semi-drying oils with isobutyl methacrylate. These media exhibit high affinity for colloidal mercury and insoluble organic compounds, binding them into a cohesive mass. Stage 2 uses Lewis acid-base reactions. In stage 2, a mixture of natural zeolite, MYCELX-impregnated carbon, and granular activated carbon exhibits high affinity for ionic and organically bound mercury and for soluble organic compounds, causing them to precipitate. The final stage uses redox potential. This stage incorporates a matrix of braided copper wire electroplated with precious metals into an anisotropic electroless reduction module that isolates and extracts elemental mercury.

Tests of the three-stage unit with mercury-laden (63.6 ppm) produced water from the field were successful at bringing the mercury levels below 0.5 ppb without a decrease in performance efficiency because of fouling. This device eliminates worker exposure to toxic compounds such as dimethyl mercury. It also eliminates mercury discharges into the oceans and atmosphere. MYCELX did pilot performance tests and applied for a patent for this technology in 2006.

Greener Chemistry for Nitrate Analysis: Enzymatic Reduction Method

The Nitrate Elimination Company, Inc.

The Nitrate Elimination Company, Inc. (NECi) is pioneering the migration of enzyme-based analytical methods from research and biomedical labs into the mainstream analytical chemistry community. Biotechnology enables the engineering of enzymes into dependable analytical reagents. NECi has adapted a plant enzyme, nitrate reductase, for use in nitrate analysis. NECi's recombinant nitrate reductase has made the company's enzymatic reduction method for nitrate analysis robust and practical. The enzyme is produced in commercial quantities with consistent performance properties at affordable cost.

Nitrate is a primary analyte under the Safe Drinking Water and Clean Water Acts. The U.S. EPA-certified method for nitrate analysis in drinking water and wastewater is based on cadmium metal reduction of nitrate to nitrite and conversion of the nitrite to a colored compound using Greiss reagents. Cadmium is hazardous to handle and ends up as toxic, persistent waste after use of this method.

In the new technology, NECi's recombinant nitrate reductase (NaR) and the natural reducing agent β-nicotinamide adenine dinucleotide in its reduced form (NADH) replace the first step of the cadmium reduction method. The enzymatic method is sustainable, greener, and safe to handle; it generates only minimal amounts of biodegradable waste. The enzymatic method has been validated by comparison to the cadmium method. It is ideally suited for the newer robotic analyzers, called discrete analyzers, which are beginning to be used for water analysis in the United States and the rest of the world. Between 2004 and 2006, NECi commercialized two Superior Stock Nitrate Reductases (YNaR1 and AtNaR2) for automated nitrate analysis using continuous flow analysis and discrete analyzers. Currently, NECi is submitting its NaR-based nitrate analysis methods to Standard Methods and the U.S. EPA for certification as alternatives for nitrate analysis in drinking water and wastewater.

PreKote® Surface Pretreatment: Replacing Hexavalent Chromium with an Environmentally Safe Solution

Pantheon Chemical

Hexavalent chromium (Cr(VI)) is the industry standard for corrosion protection on aluminum substrates prior to painting, but it is also toxic and hazardous. Discontinuing its use is a U.S. EPA pollution prevention priority through the 1993 Executive Order 12856. Cr(VI) is also on the European End of Life Vehicles (ELV) Directive of nonallowable materials. Most recently, in May 2006, the Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit (PEL) for Cr(VI) by 52 percent in the aerospace industry.

In 1994, Pantheon Chemical began an extensive research program to find an environmentally safe replacement for chromium pretreatments, also called chromium conversion coatings. Pantheon designed PreKote® on the molecular level from environmentally safe chemicals to clean and promote paint adhesion to substrates to be coated. PreKote® has a neutral formula that is not based on metals. It eliminates the need for an acid precoating treatment. Its corrosion inhibitors are not persistent, and its surfactants are biodegradable and environmentally friendly. Unlike other pretreatments, PreKote® is suitable for use on ferrous and nonferrous metals, anodized and phosphated surfaces, many plastics, and composite materials.

After years of extensive laboratory and field testing using highly advanced techniques of surface analysis and molecular modeling, Pantheon introduced PreKote® to the U.S. market as an efficient, green substitute for chromium pretreatments. In 2003, the United States Air Force (USAF) approved and implemented the use of PreKote® as a replacement for chromium pretreatments of aluminum substrates. Subsequently, leaders in the commercial aerospace market conducted extensive testing and implemented PreKote® for its safety, performance, and economic benefits. PreKote® technology provides superior performance while it improves environmental and worker safety by eliminating heavy metal waste streams and replacing toxic acids and solvents. It also decreases operational costs significantly by simplifying pretreatment procedures.

Penn Specialty Chemicals, Inc.

2-Methyltetrahydrofuran: A Green and Cost-Effective Alternative to Alkyl Ethers and Chlorinated Solvents

2-Methyltetrahydrofuran (MeTHF) is a green, cost-saving alternative to oil-derived solvents such as tetrahydrofuran (THF), dichloromethane, and diethyl ether. MeTHF is derived from furfural, which is produced from naturally occurring pentoses in agricultural waste like corncobs or bagasse (sugar cane). Penn Specialty Chemicals developed a cutting-edge liquid-phase hydrogenation process to synthesize MeTHF in two steps from furfural via 2-methylfuran. Penn Specialty Chemicals also optimized this technology to allow the large-scale commercialization of MeTHF.

MeTHF has a solid science and innovation foundation, provides important human health and environmental benefits, and has a track record of broad applicability. The marketing of MeTHF is based on a strong internal R&D program. The science behind MeTHF has been validated by scientific publications, a prestigious international innovation nomination, and its commercial success in the market.

MeTHF is a very versatile reaction solvent and is much more stable than THF under acidic and basic conditions. Because it is more stable, it is suitable for carrying out a wide combination of reactions successively in one pot without solvent degradation. MeTHF is also superior to mixtures of THF and toluene as an extraction solvent. These properties of MeTHF reduce overall solvent use.

MeTHF has important human health and environmental benefits. MeTHF is manufactured from green feedstocks. As a unique substitute for diethyl ether, MeTHF reduces the potential for fire and explosion. MeTHF also reduces the contamination of process effluent waters because, unlike THF, MeTHF is not water-soluble. Moreover, MeTHF can easily be recycled at reduced energy consumption, even in small-scale production.

In 2006, Penn Specialty Chemicals opened a dedicated plant in Memphis, TN to manufacture MeTHF. As a result, MeTHF now has a multimillion-dollar emerging market with a significant impact across industries, applications, and products.

Polnox Corporation

High-Performance Macromolecular Antioxidants for Materials: A Green Chemistry Approach

Industrial antioxidants are an increasingly important and fast-growing market. The antioxidant market generates annual sales of approximately $2.1 billion, based mainly on low-molecular-weight products with limited thermal stability, relatively low material protection, and higher material diffusion rates.

Polnox Corporation is in the process of introducing seven high-performance macromolecular antioxidants that it synthesizes from FDA-approved phenol antioxidants in a one-step process using biocatalysts and biomimetic catalysts. Polnox invented a new biotechnology-based methodology for synthesizing its macromolecular antioxidants. The starting materials for the Polnox macromolecular antioxidants include butylated hydroxyanisole, *tert*-butylhydroquinone, and propyl gallate. The Polnox antioxidants have shown superior oxidative resistance (1- to 30-fold) and higher thermal stability compared with current low-molecular-weight antioxidants. The antioxidants demonstrate superior performance in a wide range of materials and applications including but not limited to plastics and elastomers, lubricants, fuels, oil, cooking oil, food and food packaging, and beverage and other industries. They are cost-effective, safe to use, and have a superior price-to-performance ratio. Acute oral toxicity (LD_{50}) tests for these materials are at the same level as other FDA-approved antioxidants already used in food.

Dr. Cholli and his team at the University of Massachusetts Lowell originally discovered the technology. In January 2004, Dr. Cholli formed Polnox Corporation to commercialize his antioxidants. Polnox has filed for 40 patents and has also demonstrated production feasibility by scale-up to the multi-kilogram (mini-pilot plant) scale batches for two of its seven core antioxidants. Polnox completed beta site tests in 2006 and is planning to commercialize one or more of its antioxidants during 2007.

SarTec Corporation

A New, Heterogeneous, Fixed-Bed Catalyst for Continuous-Flow Biodiesel Production from Waste Fats and Oils

Fossil fuels have detrimental effects on the environment: they release sequestered carbon compounds and other pollutants into the atmosphere. Biobased fuels such as biodiesel are more environmentally friendly because their use recycles carbon through renewable biomass, and they burn cleaner than fossil fuels. Current manufacturing processes for biodiesel require high-quality, high-purity virgin oils, mostly soy oil. The price of high-quality oil accounts for over 80 percent of the price of biodiesel. As a result, the biodiesel industry is not commercially viable at present without government support.

Working with Professor Arlin E. Gyberg at Augsburg College, SarTec has developed a technology to produce biodiesel in a fixed-bed, flow-through reactor that could change how the industry produces this renewable fuel. The key to this new reactor is a highly efficient, heterogeneous catalyst that efficiently and economically converts inexpensive plant oils and animal fats to biodiesel. The catalyst contains modified porous microspheres based on zirconia (zirconium dioxide).

In addition to the environmental advantages of biofuel over fossil fuels, SarTec's process offers several advantages over the current biodiesel production method: (1) the production process uses less energy overall; (2) the process uses cheap feedstocks such as waste grease and animal tallow as well as a variety of plant oils; (3) the zirconia-based catalyst is contained in a fixed-bed reactor, eliminating the current need to add catalyst to the reaction mixture continuously, which, in turn, reduces the amount of waste produced; and (4) the new technology eliminates unwanted side reactions that produce soaps from free fatty acids, thereby reducing the amount of hazardous waste. During 2006, SarTec applied for a patent for this technology, and it also produced biodiesel with a lab-scale reactor using a variety of feedstocks including waste frying grease. The company is currently working to scale up its technology for large-scale biodiesel production.

Specialty Fertilizer Products

Biodegradable, Water-Soluble, Anionic Polymers Prepared in an Environmentally Benign Process Enhance Nutrition Efficiency, Reduce Waste, and Reduce Runoff of Phosphorus

Historically, phosphorous fertilization of crops has created a problem. Once phosphorous is applied to the soil, reactions with various cations including calcium, magnesium, aluminum, and iron fix 75–95 percent of the phosphorus, reducing its efficiency as a nutrient. As a result, farmers must use excess phosphorus to achieve high crop yields. Poor phosphorous efficiency has led to a buildup of residual phosphorous in soils, which has environmental consequences.

To overcome this problem, Specialty Fertilizer Products has designed a family of dicarboxylic copolymers that increase the efficiency of phosphorous fertilizers. The technology includes manufacturing several related, low-molecular-weight, itaconic–maleic copolymers and adding specific polymers to phosphorous fertilizers, which both enhances agricultural efficiency and reduces the environmental impact of fertilization.

Specialty Fertilizer uses a green process to synthesize its nontoxic, water-soluble, biodegradable polymers. The main component in these polymers (by weight) is itaconic acid, a monomer that is produced by fermentation of renewable agricultural products. Polymer synthesis occurs in water, with oxygen gas as the main byproduct. The process is highly atom-efficient and does not use organic solvents. The polymers biodegrade after use, so the environmental footprint of this technology is negligible.

The use of specific polymers derived from this process with granular and fluid phosphorous fertilizers greatly increases phosphorous availability in soils, resulting in greater absorption of phosphorous into growing plants. Benefits include reduced phosphate accumulation in soil and an average increase of 10–15 percent in crop biomass at minimal cost. Also, improved phosphorous uptake reduces phosphorous runoff and, therefore, contamination and eutrophication of waterways.

This technology also enables more biomass-derived fuel to be made with less environmental impact. By making phosphorus supply much more energy-efficient, far less fuel is consumed to grow more useful biomass and produce more plant-derived liquid fuels. Specialty Fertilizer sells these polymers under the trade name AVAIL™.

Steward Environmental Solutions, LLC

Development and Commercial Application of SAMMS™, a Novel Adsorbent for Reducing Mercury and Other Toxic Heavy Metals

SAMMS™ (self-assembled monolayers on mesoporous silica) was developed and commercialized to adsorb toxic metals such as mercury and to replace less-effective adsorbents such as activated carbon and ion exchange resins. SAMMS™ is a nanoporous adsorbent that forms strong chemical bonds with the target toxic material. It provides superior cost economics and adsorption capacity; it also reduces the volume of hazardous waste. It is currently being deployed in the chemical industry.

The original functionalization of SAMMS™ used toluene as the solvent. The resulting waste stream included water, methanol, toluene, and traces of mercaptan. It is impractical to separate the components of this mixture; therefore, it was usually disposed of as hazardous waste. This process was improved by substituting a green solvent, supercritical

carbon dioxide (sc CO_2), which allows complete silane deposition. With this patented process, SAMMS™ manufacturing is faster and more efficient. The sc CO_2 process also results in a higher-quality, defect-free silane monolayer with no residual silane in solution. When the reaction is complete, the only byproduct is the alcohol from the hydrolysis of the alkoxysilane. The CO_2 and the alcohol are readily separated and captured for recycling, eliminating the waste stream of excess reagents and solvent in the traditional synthesis. The SAMMS™ materials emerge from the reactor clean, dry, and ready for reuse. The combined impact of a green manufacturing process for SAMMS™ and the superior adsorption characteristics of SAMMS™ materials result in a long-term reduction in release of toxic metals into the environment.

The SAMMS™ technology and its commercialization represent collaboration between researchers at Pacific Northwest National Laboratory who did the original research and Steward Environmental Solutions, which licensed the technology and scaled up the manufacturing process. In 2006, Steward applied for two patents covering its green synthesis.

Alternative to Methyl Bromide to Overcome Nematode Damage to Crops and Concomitantly Enhance Yield, Crop Quality, and Abiotic and Biotic Tolerance

Stoller Enterprises Inc.

Worldwide, estimated annual losses of agricultural products to nematode damage total $100 billion. Currently, producers control nematodes by fumigating with methyl bromide, a highly toxic gas.

Stoller has developed products to replace methyl bromide for nematode control. These products include Root Feed™ and a host of others. Stoller products are a combination of some or all of three types of materials that occur naturally in plants: minerals, plant hormones, and small molecules. They are applied exogenously, preferably in water-efficient, drip irrigation systems. Stoller serendipitously discovered that these products not only enhance crop yield and quality (the original objective), but also strongly suppress damaging nematodes, resulting in much larger and more nutritious crops. Stoller has done extensive testing and intuitive modeling to determine which combination of ingredients among 20 minerals, dozens of plant hormones, and hundreds of small molecules is most effective. In 2006, Stoller tested a wide range of its products and noted universal effectiveness. In all cases, crop canopy increased, root mass increased, and nematodes were reduced to varying degrees, but always with very desirable yields and crop quality. Additional studies are in progress.

The emphasis of Stoller products is to improve the hormone balance in the crop plant and thereby enhance crop productivity and suppress pests. Stoller's hypothesis in nematode suppression is that by changing the auxin gradient in plants, Stoller products interfere with the ability of nematodes to form nematode-induced galls. A further mechanism may include the crop plant's cytochrome P450, which might be associated with or co-expressed with the auxin signal.

Stoller continues to work to elucidate the mode of action of its products on nematode suppression. It is currently selling its products in over 50 countries worldwide, and its products work on over 70 different crops under numerous climatic conditions.

Super Trap Inc.

GEL-COR®: A New, Environmentally Compatible, Bullet-Trapping Medium for Small-Arms Firing Ranges

In 2003, there were approximately 12,000 small-arms firing ranges in the United States. In 2001, the U.S. EPA estimated that approximately 6.4 million pounds of lead go onto these ranges each year. Containing and recovering lead and other heavy metals in a safe, environmentally acceptable manner is vital to controlling soil and groundwater pollution from ranges.

GEL-COR® is an engineered ballistic material designed to collect impacting bullets fired on small-arms training ranges in a safe, environmentally compatible way. It captures the spent bullets and contains the lead and other heavy metals that would otherwise escape into the environment. GEL-COR® is a mixture of recycled tire-tread rubber chunks, a hydrated superabsorbent polymer gel (a copolymer of acrylamide and potassium acrylate), and three salt additives (tricalcium phosphate, aluminum hydroxide, and calcium carbonate). This resilient mixture stops incoming bullets, captures them intact with few exceptions, and does not make any detectable metal dust. The gel-rubber mixture contains approximately 40 percent water by mass, which prevents it from sustaining a fire. The salt additives immobilize the lead and copper in the trapped bullets and keep them from leaching into the environment. Exposed lead surfaces react with the salts to form insoluble lead aluminum phosphate (plumbogummite), one of the safest, most stable lead compounds. Copper reacts to form an insoluble copper phosphate. The mixture maintains an alkaline pH, stabilizing the gel and minimizing the dissolution of the heavy metal salts. GEL-COR® is the first resilient medium that contains no toxic additives and will not burn, even if exposed to a source of ignition. GEL-COR® is an important step in ensuring that live-fire ranges are safer and more environmentally compatible.

Super Trap received two patents for this technology in 2006; it holds an exclusive license to the technology, developed under a Cooperative Research and Development Agreement with the U.S. Army.

Torchem LLC

Manufactured Firelogs Based on Whole Timber

Conventional manufactured firelogs offer lower emissions than cordwood. They are made of recycled materials such as sawdust bound together with petroleum wax from fossil fuel, which is a solid fuel additive. In the last few years, however, sharp increases in crude oil prices have greatly increased manufacturing costs for these conventional products.

Torchem has developed a natural alternative to conventional manufactured firelogs using cleaner-burning, inexpensive, bioderived materials. Torch firelogs are made from whole timber and crude glycerol by a simple timber treatment process. The timber is cut-off parts of plantation-grown trees that have only minimal commercial value as a feedstock for the paper industry. Because the timber is whole, Torchem can use a liquid fuel additive, glycerol. Crude glycerol is a low-value byproduct of biodiesel production. Torch firelogs offer an all-natural solution. They burn with emissions factors that are 50 percent lower than conventional manufactured fire logs, and they contain no fossil fuel components. In addition, they are available to consumers at a lower price than conventional manufactured firelogs.

Torchem LLC is a joint business venture between Torch Innovations and Chemco Inc., established to market the new Torch firelog for use in domestic fireplaces, stoves, and outdoors. After successful product testing, Torchem commissioned emissions profiles for its product in December 2006.

Olefins by High-Intensity Oxidation

Ethylene is the highest-volume, highest-value commodity chemical. Over 120 million tons are produced annually with a value of over $100 billion. The conventional path to ethylene is the energy-intensive steam cracking of ethane. This approach consumes approximately 500 trillion British thermal units per year (Btu/yr), the equivalent of over 80 million barrels of oil. Steam cracking also suffers from poor selectivity for ethylene, but is well-established and has favorable process economics.

Velocys is at the cutting edge of microchannel process technology, a platform with the potential to provide substantial cost and energy savings. With the support of the U.S. Department of Energy's Industrial Technologies Program, Velocys has been collaborating with Dow Chemical Company and Pacific Northwest National Laboratory. Velocys and its partners have developed a breakthrough process for producing ethylene. The process uses oxidative dehydrogenation in Velocys's proprietary microchannel process technology architecture, along with carefully controlled temperature and a catalyst adapted to the microchannel environment. This approach improves feedstock use and saves substantial energy. These benefits stem from the novel reaction path and the unique ability of microchannel devices to tailor reaction rates and temperatures. The process can provide higher selectivities, conversions, and throughputs than the conventional steam cracking process, which is equilibrium-limited. Dr. Terry Mazanec, Senior Technical Program Manager at Velocys, leads a multidisciplinary team that has demonstrated that microchannel oxidative dehydrogenation can achieve the economic targets set by Dow, the world's leading producer of ethylene.

The potential benefits of this novel, oxidative dehydrogenation route to ethylene are substantial. By 2020, Velocys's process could save 150 trillion Btu per year, eliminate more than eight million pounds per year of oxides of nitrogen (NO_X), and eliminate more than 10 million pounds per year of sulfur oxides (SO_X). Velocys has scheduled construction of its first commercial demonstration facility during 2007.

Entries from Industry and Government

Development of Water-Based Materials for Post-it® Super Sticky Notes

3M Office Supplies Division Laboratory

In the late 1980s, 3M developed a prototype of a new, enhanced Post-it® Notes product for use on vertical and hard-to-stick surfaces. This prototype used solvent-based adhesive formulations. At the same time, 3M launched an initiative to reduce volatile organic compound (VOC) emissions by 90 percent by the year 2000. Rather than install pollution control equipment to control the VOC emissions from the proposed manufacturing process for the new Post-it® Notes, 3M delayed introducing the product until it could develop a new, water-based adhesive formulation. 3M finally introduced Post-it® Super Sticky Notes in 2003.

The new water-based microsphere materials that 3M uses in its Post-it® Super Sticky Notes yield the desired performance, generate fewer air emissions, have a reduced environmental risk profile, and are less expensive to manufacture than the original, proposed, solvent-based formulations. The formulations are trade secrets, but they are based on acrylate polymers. They do not contain any fluorochemicals, alkylphenol ethoxylates, poly(vinyl chloride), phthalates, or heavy metals intentionally added or present as impurities above de minimus levels. The new formulations reduce annual VOC emissions by 33,400 pounds (with pollution controls) or 2,170,000 pounds (before pollution controls) and Toxic Release Inventory (TRI) emissions by 20,500 pounds (controlled) or 1,024,000 pounds (before control) compared with the projected emissions of the proposed, solvent-based process. The water-based system eliminates the need for a thermal oxidizer to control VOC emissions, reducing 3M's emissions of CO_2 from fuel combustion. It also increases worker safety and reduces the possibility of fire, chemical release, or explosion. The water-based system also generates significant cost savings.

3M's Post-it® Super Sticky Notes are an excellent example of the benefits of green chemistry and the importance of integrating 3M's core values into decision-making. Following its success with Post-it® Super Sticky Notes, 3M added water-based formulations to Post-it® Sticky Picture Paper for printing digital pictures and to other specialty applications in 2005.

AlkyClean®: The Safe Alkylation Technology for Producing Clean Gasoline

Albemarle Catalysts Company BV; ABB Lummus Global Inc.

Refinery alkylate is a clean gasoline component produced from light olefins (C_{3-5}) and isobutane. It consists of relatively harmless isoparaffins with low vapor pressures and very high octane numbers. Further, it eliminates environmentally unfriendly components such as aromatics (e.g., benzene), olefins, and sulfur and nitrogen compounds that are present in competing gasoline components. Alkylate is the preferred gasoline component to meet stricter environmental regulations.

Traditional alkylate production, currently about 30 billion gallons per year worldwide, requires hazardous processes catalyzed by liquid acids (HF or H_2SO_4). HF is extremely toxic: it can form aerosol clouds that can be lethal even more than 5 miles from their source. Sulfuric acid technologies are extremely corrosive. Worldwide, they generate 10–20 billion pounds per year of spent acid, which must be transported and regenerated.

For more than 40 years, academic and industrial researchers have searched for an economic, benign, solid acid catalyst technology to replace these liquid acid technologies.

The AlkyClean® process is an economically attractive and environmentally safe alternative that is now commercially available. AlkyClean® replaces the liquid acids with a novel, true solid acid zeolite catalyst in an innovative process. The zeolite-based formulation contains no halogens, has acid sites of optimum strength for alkylation, and exhibits the necessary activity, stability, and capacity for catalyst regeneration required for a successful process. Albemarle Catalysts of Houston, TX produced the zeolite catalyst, and ABB Lummus Global of Bloomfield, NJ designed and prepared a demonstration plant. This 10-barrel-per-day plant in Finland has been producing high-quality alkylate for more than 2 years using a refinery slipstream. During this time, the technology has been optimized for commercialization. Product quality is on par with existing technologies. The new process does not produce wastewater or sludge, and does not require any acid neutralization facilities or post-treatment of any kind.

Arch Treatment Technologies, Inc.

Wolman® AG Metal-Free Wood Preservative

Wolman® AG is the first organic preservative for pressure-treating wood used in decks, fences, and residential projects. The active ingredients are carbon-based and contain no metals. This is a long-envisioned breakthrough in wood preservation.

Wolman® AG preservative offers broad-spectrum protection against wood decay and termites yet does not contain copper, as do current alternatives. Just as an earlier transition replaced chromium and arsenate with copper in common wood preservatives, this advancement offers control of termites and fungal decay without copper. Instead, Wolman® AG takes advantage of the synergistic qualities of three organic biocides: propiconazole, tebuconazole, and imidacloprid, which have long histories of residential and agricultural use. They readily undergo bacterial degradation in soil and groundwater, becoming nonhazardous materials. As a result, Wolman® AG is intended for use on out-of-ground wood, which accounts for nearly 80 percent of all applications for pressure-treated wood.

Proven efficacious in field and lab tests, wood treated with Wolman® AG is recyclable after use as decking. It can be burned for energy in commercial incinerators in accordance with state and local laws. It is safe for landfills because any runoff is biodegradable. Wolman® AG contains the three biocides blended with emulsifiers to produce a concentrated aqueous formulation. The formulation has a pH of 7.5, close to that of water. It is not regulated as a hazardous material for land, water, or air transport. In addition, the amount of preservative needed is comparatively small, reducing total production and transportation requirements. The mammalian acute toxicity for Wolman® AG is 4,000 mg/kg, in contrast to that of copper-based alternatives, which have acute toxicities of 800 mg/kg or less. The price of Wolman® AG is comparable to or less than that of copper-based alternatives. In 2006, the product was first used at a customer's plant.

Arkema Inc.

Green Chemistry in the Manufacture of Thioglycolic Acid

Arkema Inc. has manufactured thioglycolic acid (TGA or mercaptoacetic acid) at its plant in Axis, AL for over 20 years. TGA is used as an industrial intermediate, a component of cosmetics, and a component of products to treat hides and leather. Arkema's traditional process included hydrogen sulfide (H_2S) as a feedstock. H_2S is a poisonous,

flammable, colorless gas that is regulated as an air pollutant, a water pollutant, and a hazardous waste. Because of its requirements for high-purity H_2S feedstock, Arkema was buying H_2S from a source in Canada and transporting over 4 million pounds of pressurized, liquid H_2S by railcar to Alabama each year.

Arkema developed and implemented a beneficial process change that replaced the H_2S in its manufacturing process with sodium hydrosulfide (NaSH). NaSH is safer for workers, is subject to fewer air, water, and waste regulations, is comparable to H_2S in price, and is readily available in consistently high purity. Further, changing to NaSH involved little or no change in facility air or wastewater permits or disposal methods for spent materials.

The substitution of NaSH solution for H_2S gas in the TGA process allowed the Alabama plant to eliminate the cross-country transportation of millions of pounds of an extremely hazardous and toxic chemical, reduce the risk of accidental release of a toxic chemical, and lessen risk management activities at the plant. The major advantages of this substitution were improved worker safety and a reduced risk of environmental releases. At the same time, Arkema realized higher production yields of 1 million pounds per year. In 2004, Arkema finished switching over to NaSH and made engineering modifications to increase its production capacity.

Reducing the Environmental, Health, and Safety Impact of Cooling Water Treatment Programs

Ashland Water Technologies

Typical conventional cooling water treatment programs require corrosion control, scale inhibition, and microbiological control. Among common water-treatment chemicals are potentially hazardous and toxic materials. Ashland Water Technologies developed a solution that significantly reduces the environmental, health, and safety impact of cooling water treatment programs without sacrificing performance. The unique combination of SONOXIDE ultrasonic treatment for microbiological control, ENVIROPLUS cooling water treatment products for corrosion and scale control, and the ULTRA-SERV solid chemical inventory management program delivers a high-performance, environmentally responsible program and enhances safety by eliminating the need for liquid chemicals.

ULTRA-SERV is a solid chemical feed system that reliably dissolves and delivers a solid, concentrated form of ENVIROPLUS corrosion and scale control product to recirculating cooling systems. The ENVIROPLUS series of cooling water treatment products includes a patented, complex, synergistic blend of multifunctional components that provide exceptional multimetal corrosion inhibition and scale control in alkaline cooling water systems. The blend includes polymeric antiscalants (biodegradable carboxylic antiscalants), phosphonocarboxylates, and other organic and inorganic components. ENVIROPLUS products reduce the environmental impact of treated water discharge because they are inherently biodegradable, contain no heavy metals, and contain very low phosphorous. This profile enables plants to comply with increasingly stringent discharge limitations and allows cooling towers to operate at higher cycles of concentration, thereby reducing water consumption.

SONOXIDE ultrasonic water treatment for microbiological control enhances health, safety, and environmental benefits even further. SONOXIDE ultrasonic treatment provides total-system microbiological control by applying low-power, high-frequency ultrasound. SONOXIDE treatment controls total bacteria and biofilm in recirculating cooling systems, virtually eliminating the need for chemical microbiocides. SONOXIDE is currently in use in over 500 cooling systems worldwide. Ashland introduced the newest component, ULTRA-SERV, in 2006.

Aspen Technology, Inc.

Correlating and Predicting Drug Molecule Solubility with a Nonrandom, Two-Liquid Segment Activity Coefficient Model

Quantitative knowledge of drug molecule solubility is essential for solvent selection, design, and optimization of synthesis and purification processes for active pharmaceutical ingredients (APIs). Lack of solubility information often leads to suboptimal design with respect to yield, productivity, cost, energy use, solvent consumption, and hazardous waste discharge in pharmaceutical manufacturing processes. Although powerful, automated solubility measurement tools are available, they remain time- and labor-intensive.

AspenTech researchers recently developed a novel, nonrandom, two-liquid segment activity coefficient model (NRTL-SAC) as a simple, practical molecular thermodynamic framework. NRTL-SAC characterizes drug molecular interactions in solution in terms of dimensionless hydrophobicity, hydrophilicity, polarity, and solvation. Using NRTL-SAC, chemists and engineers first measure the solubility of a drug in a few reference solvents to identify the molecular parameters of the drug. They then use the model to predict the drug's solubility in pure solvents and solvent mixtures. The model delivers robust solubility predictions with accuracy within ±50 percent or better. This level of accuracy is superior to that of all existing predictive models and is effective for solvent selection and API process design. AspenTech researchers also collaborated with major pharmaceutical companies to demonstrate the broad applicability of their model. The model has been integrated with Microsoft® Excel and process simulators in support of systematic and rational solvent selection, unit operation modeling, and design and optimization of pharmaceutical manufacturing processes.

NRTL-SAC represents a quantum step forward in predicting the solubility of drugs in solvents and mixed solvents. The NRTL-SAC technology offers a first-principles-based engineering solution, enabling chemists and engineers to design greener processes that deliver required drug purity and yield, minimize solvent use, generate less hazardous solvent waste, consume less energy, and decrease overall cost. AspenTech has been using NRTL-SAC in its products since 2005. Its collaborators include Eli Lilly, AstraZeneca, and Bristol-Myers Squibb.

BASF Corporation

A Non-HAP (Hazardous Air Pollutant) Coating for Extruded Aluminum

The market for coatings of extruded aluminum is dominated by spray-applied, solvent-containing coatings that are heat-cured and are typically used for window frames, door frames, and other building components. This market is estimated to be about 35,000 tons in the United States.

BASF has been supplying extrusion coatings to this market for many years. These coatings are based on hydroxy-functional polyester resins and typically contain about 25 percent solvents by weight. Of this traditional solvent blend, approximately 60 percent is Aromatic 100 (which includes ethyl benzene), 15 percent is xylene, 5 percent is Aromatic 150 (which includes naphthalene), and 5 percent is diethylene glycol monobutyl ether. In addition, the traditional blend contains 5 percent methyl ethyl ketone, which was previously classified as a hazardous air pollutant (HAP), but is no longer considered a HAP.

BASF developed a coating composition using a solvent blend without HAPs, which required the company to replace 90 percent of the solvents in the blend it had been using.

The new coating eliminates solvents that are known or suspected to cause serious health effects (such as cancer, reproductive effects, or birth defects) or adverse environmental effects. It replaces a product line formulated with five HAPs that accounted for 8–10 percent of the product as delivered. It eliminates xylene, diethylene glycol ethers, and several other materials. The new BASF coating meets the U.S. EPA's standard for being non-HAP as defined in the Miscellaneous Metal Parts and Products Surface Coating NESHAP. The new product has improved application efficiency and quality; it is cost-competitive, with a modest premium of only about $1 per gallon. At market projections, this product will reduce emissions of HAPs by about 500,000 pounds annually. BASF initiated commercial sales of its product in 2006 and is phasing out its previous technology.

Development and Commercialization of Biobased Resins and Toners

Battelle Memorial Institute

Over 400 million pounds of electrostatic dry toners based on petroleum-derived resins are consumed in the United States annually to make over 3 trillion copies in copiers and printers. Only a small fraction of this paper is recycled, however, because conventional toners are not designed for ready de-inking.

With early-stage funding from the Ohio Soybean Council (OSC), Battelle and Advanced Image Resources (AIR) formed a team to develop and market biobased resins and toners for office copiers and printers. A novel Battelle technology uses oil, protein, and carbohydrate from soybean and other crops as chemical feedstocks. Battelle has developed bioderived resins and toners from these feedstocks through innovative, cost-effective chemical modifications and processing. Battelle and AIR, the licensee of the technology, have coordinated to move from early-stage laboratory development to full-scale manufacturing and commercialization. Their efforts have resulted in a cost-competitive, highly marketable product that is compatible with current hardware and will provide users with seamless, environmentally friendly printing and copying.

The new technology also offers advantages in recycling waste office paper without sacrificing print quality. Improved de-inking of the fused ink from waste copy paper results in higher-quality recovered materials and streamlines the recycling process. Preliminary lifecycle analysis shows significant energy savings and reduced carbon dioxide emissions in the full-value chain from resin manufacture using biobased feedstocks, to toner production, and finally to recovery of secondary fibers from the office waste stream. At 25 percent market penetration, this technology could save 9.25 trillion British thermal units per year (Btu/yr) and eliminate over 360,000 tons of carbon dioxide emissions per year. Overall, soy toner provides a cost-effective, systems-oriented, environmentally benign solution to the growing problem of waste paper generated from copiers and printers. In 2006, AIR successfully scaled up production of the resin and toners for use in HP LaserJet 4250 Laser Printer cartridges.

Nexterra™ Carpet: Modified PET Carpet Backing

Beaulieu Group, LLC

Carpet tile backings have previously been made of polymers such as poly(vinyl chloride) (PVC), polyurethane, or mixtures of various thermoplastics that are derived from petrochemicals. The manufacture or disposal of some of these backing materials raises environmental concerns. Further, the energy required for the physical separation of the tile backing and the face fiber (usually by grinding or air elutriation) adds to the cost of recycling current tile backings. Physical separation also leads to impure component streams for recycling.

Beaulieu has developed a modified polyethylene terephthalate (PET) backing system that contains a much lower percentage of products derived from virgin petroleum, requires significantly less energy to produce, and offers new solutions to carpet tile recycling. Beaulieu had already been purchasing postconsumer PET bottles and converting them into carpet fiber. Now, however, Beaulieu is also converting plastic PET bottles into a pliable, flexible carpet tile backing system using a unique transesterification process (patent allowed). This process lowers both the molecular weight and the melting point of the polymer. Beaulieu's modified PET polymer allows the company to use postconsumer ground glass as a filler in their backing.

Altogether, their backing system contains 85 percent postconsumer materials and only 15 percent virgin petrochemicals by weight. Traditional carpet tiles contain approximately 50 percent virgin petrochemicals. The exclusive modified PET backing enables more cost-effective and energy-efficient recycling. The solubility of the polymer in polar solvents allows separation of the carpet tile backing from the face fiber (usually nylon 6 or 6,6). During recycling, Beaulieu uses a glycol monomer bath at 150–180 °C to dissolve the polymer, separating it and the glass from the insoluble face fiber.

Beaulieu launched Nexterra™ carpet tiles in May 2005. The company estimates its 2005 product sales at $1–5 million, and is expecting significant sales growth during 2006.

Benchmark Performance Group, Inc.

GreensKeeper® Polymer Slurries for Oil and Gas Well Stimulation

In December 2003, the major oil and gas pumping service companies (Benchmark's customers) entered into an agreement with the U.S. EPA to eliminate diesel fuel from hydraulic fracturing fluids injected into coalbed methane production wells. This agreement arose from U.S. EPA's concern that diesel-based slurries used for oil and gas well stimulation pose a risk to underground sources of drinking water. To respond to its customers, Benchmark evaluated many potential carriers as diesel substitutes, considering slurry quality, cost, performance, safety and regulatory concerns, toxicity, flammability, and environmental impacts. Benchmark used these nondiesel carriers to evaluate more than a thousand different suspension slurries.

In 2004, Benchmark introduced its GreensKeeper® line of environmentally friendly polymer slurries to replace diesel-based slurries. GreensKeeper® slurry products are the first ones available to the industry that are completely compliant with the requirements of the Safe Drinking Water Act. GreensKeeper® not only eliminates diesel but also contains no benzene, toluene, ethylbenzene, or xylene (BTEX), or any of the 126 Priority Pollutants identified by the U.S. EPA.

In addition to superior environmental performance, GreensKeeper® products offer exceptional slurry characteristics including stability for extended periods at temperatures of over 100 °F, pumpability under subzero (less than °F) conditions, and compatibility with all commonly used boron, titanium, and zirconium cross-linkers. Unlike diesel-based slurries, GreensKeeper® slurry products are nonflammable, thus reducing fire and explosion risk during production, transport, storage, and use. Unlike diesel, they are not DOT-regulated, thus eliminating the risks associated with transporting hazardous chemicals. Widespread acceptance of GreensKeeper® slurries was directly attributable to Benchmark's national distribution network and transportation capabilities. By December 2006, Benchmark had produced and sold over 10 million gallons of GreensKeeper® slurry to the oil and gas industry. After only 20 months, GreensKeeper® already represents 70 percent of Benchmark's monthly slurry sales volumes.

Irbesartan (Avapro®) Greenness Project

Bristol-Myers Squibb Company

Irbesartan, which is chemically synthesized, is an angiotensin II receptor antagonist used to treat hypertension and renal disease in type 2 diabetic patients. Although clinical trials had demonstrated the medical benefits of Irbesartan, the original synthetic process was difficult to manage from an environmental, health, and safety (EHS) perspective. The primary concerns included a potential runaway bromination reaction, severe skin and eye irritation from an intermediate product, and negative environmental effects of several organic solvents. Previously, Bristol-Myers Squibb (BMS) had mitigated some of the negative EHS impacts of the original synthesis, but the bromination in the first synthetic step remained a concern. This bromination created a nonbiodegradable byproduct that required incineration and, thereby, created a significant waste disposal problem.

To address that problem and further minimize EHS impacts, BMS modified the bromination and crystallization processes it uses in the synthesis and modified the recrystallization process for the active pharmaceutical ingredient. These modifications have increased yield, saved energy, reduced the use of hazardous materials, reduced waste, and improved workplace health and safety. Based on a projected 5-year production of Irbesartan, BMS expects to save over 680 metric tons of solid chemicals, over 40 million liters of solvents, and 4.4 million liters of water. Other projected benefits include a 325-ton reduction in solid waste requiring incineration and a savings of 24,400 megawatts of energy from recycling the two remaining process solvents.

Enzymes to Reduce Energy Use and Increase Recycling of Paper

Buckman Laboratories International, Inc.

Buzyme® from Buckman Laboratories is a novel enzymatic technology to modify the wood fibers used to manufacture paper. Buzyme® consists of a group of new cellulytic or hemicellulytic enzymes made by fermentation in bacteria or fungi. For each grade of paper, Buckman selects the enzyme that provides optimum results. This enzymatic treatment of the wood fiber reduces the amount of mechanical refining required to reach desired fiber properties. In various commercial applications in paper mills, this invention has given benefits such as increased use of recycled paper, reduced energy needed to produce paper, and improved quality of paper goods. This technology improves the strength of paper and paperboard, reducing the use of chemicals to improve strength. Less energy is needed to give the required strength to paper products. The technology is already in use successfully in about 10–15 paper machines in North America, producing tissue papers, napkins, corrugated boxes, and other grades of paper. One paper mill that makes dinner napkins was able to use recycled fiber exclusively and save $1 million that it had been spending for virgin wood pulp each year.

Buzyme® products make it possible to recycle more paper, produce paper more efficiently, and manufacture higher quality paper. Enzymes produce several benefits: enzyme biotechnology comes from renewable resources, is safe to use, and is itself completely recyclable. Use of these enzymes reduces requirements for chemicals derived from petroleum feedstocks. These enzymes are nontoxic to human health and the environment. They are produced by fermentation from readily available renewable resources. Although this technology has been studied in laboratories for some years, Buckman has recently found the keys to make it successful on a full-scale industrial basis.

Cytec Industries Inc.

Cytec Innovation Management System: Sustainable Development of New Products

Cytec Industries Inc., led by its Innovation Group, has established a process called the Cytec Innovation Management System (CIMS). This process guides development chemists and engineers in evaluating the safety, health, and environmental (SH&E) as well as economic aspects of products under development. Cytec chemists and engineers use the CIMS web-based process management software from the earliest stages of product development through commercialization and production. This process includes a series of stages and gates in which users assess aspects related to SH&E. CIMS requires varying degrees of data before it grants approval for subsequent stages. Cytec created the CIMS process by benchmarking best practices from other companies' New Product Development (NPD) processes, reviewing published NPD benchmarking studies, and surveying Cytec employees about earlier NPD processes. Cytec developed the SH&E questions after consultation with the American Institute of Chemical Engineers' Center for Sustainable Technology Practices.

CIMS puts in place common best-practice processes and tools that help drive commercialization by designing safe, energy-efficient, and environmentally sound products and processes. A critical component of CIMS is the Stage-Gate® process, which drives sustainable development. The Stage-Gate® process incorporates SH&E questions into the first stages of the new product development process, allowing researchers to evaluate the sustainability of a product early in the development process. Additional tools built into CIMS include Sustainable Futures models developed by the U.S. EPA and Cytec's Solvent Selection Guide that includes hazard information on 120 common solvents. Cytec incorporated the U.S. EPA tools for screening at the early stages of the process to drive commercialization of greener, safer, more environmentally friendly products. Cytec has implemented the CIMS process across functional areas and business units throughout the company.

Cytec Industries Inc.

Revolutionizing Energy-Curing Resins for Food Packaging Applications

Solvent-free, energy-curing technologies have recently emerged as mainstream technologies in printing human food packages. These technologies are energy-efficient processes that use accelerated electrons or UV photons to polymerize acrylate resins into a branched network of large polymers. In contrast to solvent- or water-based technologies, these solvent-free technologies do not require prolonged energy-intensive heating and drying cycles or expensive solvent abatement systems. Overall, radiation-curing systems save an estimated 85 percent of the energy required for traditional systems. In addition, these technologies can also improve production speed and print quality.

Following the principles of green chemistry and sustainability, Cytec Industries Inc. has developed a new range of low-extractable, low-odor (LEO) acrylate resins for use in energy-curing packaging inks and overprint varnishes. Renewable resources such as tall oil derivatives and glycerol account for 15 percent of the starting materials in the LEO product line. The LEO resins are characterized by enhanced size and complexity, lower migration from the packaging matrix, and frugal synthetic processes using nontoxic and preapproved building blocks. When formulated in inks, varnishes, or adhesives, these new acrylate resins are able to meet the most stringent regulatory safety requirements. In addition, Cytec has also developed testing protocols streamlined for the study of migration of

acrylates at the part-per-billion level to confirm minimal potential human exposure. Cytec launched the LEO project commercially in 2006. During that year, LEO resins eliminated 20 tons of waste, and Cytec anticipates even greater savings in the future.

Eastman Chemical Company

Optifilm Enhancer 400 – A Nonvolatile Coalescent for Formulating High-Performance, Reduced-VOC Architectural Coatings

Attainment of mandated ambient ozone standards continues to present great difficulties in urban areas of the United States, where both nitrogen oxides (NO_X) and anthropogenic volatile organic compounds (VOCs) are present at high levels in ground-level air pollution. State and local regulatory agencies have identified paints and coatings and, more specifically, architectural coatings as significant sources of VOCs. Consequently, these agencies have developed regulations limiting the amount of VOCs in architectural coating formulations. Currently, the strictest limits exist in California's South Coast Air Quality Management District.

Traditional waterborne latex architectural coatings for interior and exterior applications require additives referred to as coalescents or coalescing aids. These additives allow the latex particles in the coating resin to form a contiguous film after application and to provide the protective properties and appearance required of the coating. In the past, the typical coalescents have been VOCs, which have been implicated as contributors to the formation of ground-level ozone.

In response to the need to reduce VOCs in architectural coatings, Eastman Chemical Company has developed *Optifilm* Enhancer 400, a nonvolatile alternative to traditional coalescents. *Optifilm* Enhancer 400 allows paint manufacturers more flexibility to achieve the performance they require; it also reduces or eliminates the contribution of the coalescent to ozone formation. When tested neat by ASTM D2369, *Optifilm* Enhancer 400 is 99.3 percent nonvolatile; it has excellent efficiency to coalesce latex paints while maintaining a good balance of performance properties. *Optifilm* Enhancer 400 delivers excellent film integrity, touch-up properties, and scrub resistance, even in paints formulated to very low VOC contents. Paints using *Optifilm* 400 have also demonstrated good exterior durability after 3 years of exposure. *Optifilm* Enhancer 400 has been in use in commercially available architectural coatings since 2004.

Eli Lilly and Company

A Practical, Green Chemical Approach for Manufacturing an Investigational New Drug Candidate at Eli Lilly and Company

This nomination describes an innovative, environmentally friendly route for the commercial production of an active pharmaceutical ingredient (API) that is an investigational new drug candidate currently undergoing clinical trials. The improved route delivers the API in exceptionally high purity (over 99.9 percent), a significant accomplishment considering the potential for positional isomers for all five of its aromatic rings. The improved synthesis is based on a novel S_NAr methodology and a regioselective cycloaddition.

Eli Lilly and Company uses a metric called "e-factor" internally that is similar, but not identical to, Sheldon's E factor. Lilly's e-factor is the total mass of all raw materials, including water, used to produce each kilogram of API beginning from routinely available commercial starting materials. Despite the structural complexity of Eli Lilly's new

API, the new route has a net e-factor of 146 kilograms per kilogram API, an 84-percent reduction relative to the original process R&D route. Eli Lilly demonstrated the selected commercial route for the API on a pilot-plant scale during 2006 in Indianapolis, IN. Previously, the company had also developed two other synthetic routes at pilot-plant scale at their Indianapolis, IN and Mount Saint Guibert, Belgium facilities, respectively. Improvement of key green chemistry parameters across the evolution of these routes demonstrates the power of technical innovations and is testimonial to the importance of incorporating the 12 green chemistry principles into the design and definition of synthetic processes. Peak production volumes from tens to hundreds of metric tons are typical for APIs used for the same indications as Eli Lilly's investigational API. An e-factor improvement of 778 kilograms per kilogram of API in the new synthesis at peak production would provide savings in all materials of 17–170 million pounds per year. In 2006, Eli Lilly filed a patent application for its selected commercial route.

Emerson & Cuming

Tin- and Copper-Compatible Conductive Adhesive for Lead-Free Electronic Circuit Assembly

Tin–lead eutectic solder is currently the most common product used to attach electronic components on circuit boards. Lead, however, is a known toxin. Because lead can leach into the environment, the European Commission in its Waste Electrical and Electronic Equipment Directive enacted legislation in July 2006 mandating recycling of consumer electronics containing lead. This has prompted electronic circuit assemblers to seek an alternative attachment product. Conductive adhesives have also been used for years, but their use has been limited to attaching palladium–silver-, silver-, and gold-terminated components on both ceramic hybrid boards and flexible polyester circuits. Previous conductive adhesives were not stable on low-cost tin- and tin–lead-terminated components.

Emerson & Cuming's novel, patented chemistry allows it to achieve stable contact resistance and stable adhesion under damp-heat and high-temperature aging conditions with tin, tin–lead, and copper finishes. Compatibility with these finishes was not possible in the past. This compatibility was achieved by preventing galvanic corrosion on these less expensive, non-noble metal finishes. The incorporation of a corrosion inhibitor and a low-melting alloy into the adhesive formulation prevents oxidation on these finishes under extreme environmental conditions and leads to stable performance over time. About 40 major electronic circuit assembly companies currently purchase these Emerson & Cuming adhesives. These customers are from very demanding industry sectors including the automotive, medical, military, consumer electronics, and telecommunications sectors. Over the last 3 years, these adhesives have effectively eliminated the use of 12 metric tons of tin–lead eutectic solder. By 2010, this conductive adhesive technology will be replacing about 40 metric tons of solder per year.

Georgia-Pacific Chemicals, LLC

Georgia-Pacific Mining Reagents That Improve Recovery, Reduce Wastes, and Conserve Water and Other Natural Resources

Froth flotation is a method of purifying mined ores from the waste minerals and clays inherent in the ore bodies. Froth flotation exploits the difference in the surface hydrophobicity of an ore and a waste mineral or clay to separate and purify the ore. During this process, air is dispersed in the slurry that contains the ore and wastes, forming bubbles to

which the hydrophobic particles (ore) adhere. The hydrophobic particles are then carried with the bubbles into the froth layer whereas the hydrophilic particles (wastes) remain behind. Often termed slimes, the hydrophilic particles retain water. If they are carried along with the ore, they increase the energy required to dewater the product. In contrast, if too much of the ore remains in the slurry, it is disposed of with the waste or slimes.

Georgia-Pacific (GP) mining reagents improve the separation of ore from the associated waste, so less ore is wasted and less slime is recovered with the ore. The mining reagents act as depressors to help remove slimes and as coagulants to improve dewatering. As a result, significantly more water can be reused; the ore is easier to dry, and, therefore, resources, water, and energy are conserved.

Currently, in the United States, up to 30 percent of coal and 70 percent of potash are purified by flotation. Coal is a major source of energy, and approximately 53 percent of the electricity used in the United States is generated from the combustion of more than 1 billion tons of coal. Potash is commonly used as an agricultural fertilizer to supplement soluble potassium, which is one of the most essential elements required in large amounts for plants. This improved process helps to conserve natural resources including water, coal, potash, or other ores at the source as well as to reduce pollutants through increased energy efficiency at the mine site.

Nitamin Steady Delivery® Fertilizers for Improved Nitrogen Efficiency in Crops

Georgia-Pacific Chemicals, LLC

Worldwide, farmers apply approximately 82 million metric tons of nitrogen fertilizer, primarily urea, to cropland annually. Plants are often unable to take up all of the nitrogen released into the soil from urea hydrolysis and salt-based fertilizers such as ammonium nitrate, so the excess nitrogen leaches through the soil and contaminates nearby waterways. Agricultural nitrogen is a major contributor to the increasing nitrate levels in many waterways around the world. These excess nitrates create hypoxic areas in which the levels of dissolved oxygen are too low to support life.

Nitamin® fertilizers provide an economic solution to this problem by slowing the rate at which nitrogen becomes available to the plant. By reacting urea with ammonia and formaldehyde under specific conditions to form a blend of small urea-formaldehyde polymers and cyclic compounds, Georgia-Pacific can control the rate at which the nitrogen is released to plants. The primary Nitamin® fertilizer product releases nitrogen for approximately 90 days, corresponding well to the requirements of many crops. This controlled delivery allows the plant to use more of the applied nitrogen, resulting in reduced application rates and reduced leaching. Nitamin® fertilizer reduces the amount of nitrogen used by 25 percent (onions and tomatoes) to 55 percent (cabbage). In other studies with potatoes, onions, and tomatoes, Nitamin® fertilizer increased crop yields by 7–54 percent. Based on U.S. figures alone, even a 5 percent reduction in the amount of nitrogen applied to crops could eliminate the application of 810 million pounds of nitrogen annually. This improved efficiency of nitrogen use coupled with affordability is the highlight of this technology. Georgia-Pacific first commercialized its technology in January 2004. During 2005, universities and growers ran over 80 trials with different crops to verify the marketability of Nitamin® fertilizer. During spring 2006, Georgia-Pacific will commercialize a liquid Nitamin® fertilizer for use on vegetables.

Merck & Co., Inc.

Kilogram-Scale Purification of Pharmaceutical Candidates and Intermediates Using Preparative Supercritical Fluid Chromatography

Preparative chromatography is increasingly used in the pharmaceutical industry to purify kilogram quantities of developmental compounds for preclinical evaluation. Historically, the industry has carried out these separations by high-performance liquid chromatography (HPLC) using large amounts of petrochemical-derived organic solvents. Merck has recently demonstrated the possibility of performing these separations at the kilogram scale using subcritical or supercritical fluid chromatography (SFC), in which pressurized carbon dioxide (CO_2) replaces the hydrocarbon solvents often used in HPLC.

Using custom-designed preparative SFC equipment prepared in collaboration with several vendors, Merck has recently carried out the first kilogram-scale SFC enantioseparations of pharmaceutical intermediates in the pharmaceutical industry. Merck has reported its results in a recent publication (Welsh, C.J. et al., LC-GC, 2005, 16–29). In one example, enantioseparation of 2.5 kilograms of an intermediate was projected to require 36,000 liters of solvent by HPLC, but used only 900 liters by SFC. Although this example is extreme, a 10-fold decrease in solvent consumption is typical. Equally important, SFC also produces a corresponding decrease in solvent evaporation, leading to considerable savings in equipment, time, and energy. Further, preparative SFC is generally more productive than HPLC, especially for chiral separations. The SFC advantage can be extreme, as in the case where there was no suitable HPLC purification for a single stereoisomer of a drug candidate intermediate, yet SFC (5 cm i.d. column, 350 g/min, 830 L organic solvent) purified 1.7 kilograms easily in only 72 hours. During 2005, Merck demonstrated preparative SFC using a 15-ton CO_2 bulk tank and custom-built, 3-kilogram-per-minute CO_2 delivery system.

Merck has demonstrated that preparative SFC is not only a more environmentally friendly method for purifying developmental drugs and intermediates, it is simply better, with greater productivity and cost-effectiveness, both of which are important considerations for large-scale separations to support pharmaceutical manufacturing.

Merck & Co., Inc.

A New, Highly Efficient, Environmentally Responsible Synthesis of Laropiprant (MK-0524)

An environmentally responsible, highly efficient manufacturing process for laropiprant, Merck's phase III prostaglandin D_2 (DP) antagonist, has been achieved through significant scientific innovation. The combinations of laropiprant with niacin (MK-0524A) and with both niacin and simvastatin (MK-0524B) have shown promising efficacy for the treatment of atherosclerosis and are currently being evaluated in late-stage phase III clinical trials. An enzymatic route was developed to prepare over 25 kilograms of material for early clinical trials. With optimization, this route would have been a satisfactory manufacturing process. Merck chemists set out to reduce the environmental impact of the process significantly, however, by developing a new, highly efficient, asymmetric synthesis with green chemistry principles in mind. In realizing this goal, Merck researchers discovered two unprecedented transformations. The first was a novel extension to the classical Fischer indolization reaction to prepare indole ene acids in a one-step, highly convergent manner from readily available starting materials. The second was the development of a novel asymmetric catalytic hydrogenation of indole ene acids.

The new synthesis is convergent and highly atom-efficient, involves minimal extractions, distillations, or aqueous washes, and makes minimal use of protecting groups. By implementing its new manufacturing route, Merck reduced its overall aqueous and organic waste production by 90 percent and 65 percent, respectively, compared with the enzymatic route. The technology discovered by Merck is an excellent example of the positive impact of scientific innovation on reducing the environmental footprint of a chemical process. It also embodies the association between innovation in green chemistry and business benefits. Because Merck discovered and implemented the new route early in the development timeline, Merck will be able to realize the environmental and cost benefits of the highly efficient synthesis for the entire lifetime of this important new medicine.

TractionBack®: Alternative Green Adhesives for Textile Composites in Commercial Buildings

Milliken & Company

Poor indoor air quality is an important environmental health risk associated with building interiors. Traditional modular carpet installation requires adhesives and sealants that contain such volatile organic compounds (VOCs) as formaldehyde and 2-ethyl-1-hexanol. Carpet installation may also require surface preparation including sanding and removal of old adhesive, which degrades air quality further.

Milliken's TractionBack® anti-skid, adhesive-free backing is a thin coating formulation applied to the felt on the bottom of carpet tile. The formulation is an amorphous ethylene–propylene copolymer that is tackified with a hydrocarbon resin and tall-oil rosin, a biobased component. The raw materials in the formulation have almost no measurable VOCs in the solid state. TractionBack® for modular carpet eliminates the need for onsite adhesive applications and repairs traditionally required for new and replacement installations, thus eliminating related VOCs. Milliken estimates that TractionBack® eliminates the use of 400 tons of sealants and adhesives as well as 16,000 five-gallon containers of adhesive and sealant each year.

TractionBack® eliminates chemical pollutants such as adhesives, floor primers, sealants, and other VOCs; eliminates biological pollutants such as mold and bacteria; and reduces the particulate hazards of sanding and surface preparation. Additional environmental benefits include (1) energy reduction during production; (2) waste reduction during installation; (3) waste reduction to landfill by extending product life because individual tiles can be repositioned or replaced easily; (4) reduction of downtime for building spaces; (5) incorporation of biobased raw materials; and (6) removal of polyvinyl chloride (PVC), which has environmental issues related to its production, installation, and eventual disposal. TractionBack® uses fewer resources in both manufacturing and installation, reducing waste and eco-footprint. TractionBack® has been on the market since 2003. Milliken developed the current formulation for TractionBack® in 2005.

Commercialization of NXT Z®: An Ethanol-Free, Low-VOC, High-Performance Silane for Silica Tires

Momentive Performance Materials Inc.

Silica tires have experienced remarkable growth in the last decade because of their superior performance. Silica tires incorporate silane coupling agents to disperse the silica in the rubber matrix and reinforce the matrix, a key to reduced rolling resistance and other aspects of performance. Reducing rolling resistance can translate into improved vehicle fuel efficiency. Tire tread life relates to tire value and scrap rates, and traction is important for automotive safety.

Traditional silane coupling agents contain triethoxysilane moieties that hydrolyze to release ethanol. Tire manufacturing releases some of this ethanol, and tire companies must dispose of it at substantial cost. A significant amount of ethanol remains in the tire, however, and is released into the atmosphere while the tire is in use. Ethanol from silica tires can account for a measurable portion of the volatile organic compounds (VOCs) released by a vehicle. In California, the California Air Resources Board (CARB) enforces legislation that regulates background emissions of VOCs.

NXT Z® silane is a new coupling agent designed to improve the wear, traction, and rolling resistance of silica tires, without the ethanol emissions imparted by traditional silanes during tire manufacture and use. It builds on previous discoveries of blocked mercaptosilanes. NXT Z® silane contains both mercaptan and thiocarboxylate functionalities linked by high-boiling diols in place of the ethanol-derived alkoxy groups used in traditional silanes. The high-boiling diols have similar or faster hydrolysis rates than ethoxy groups, depending on whether they are bound to one or two silicon atoms. Once hydrolyzed, however, the high-boiling diols remain in the rubber compound, presumably bound to silica. NXT Z® silane also helps reduce manufacturing costs through hotter, harder, faster processing; single-step mixing; long-shelf-life silica compounds; and lower use levels. Several major tire companies tested NXT Z® for fast-track commercialization during 2006.

Momentive Performance Materials Inc.

Novel Superspreading Siliconized Surfactants

Silicone surfactants are a unique class of materials because of their high surface activity and easy-to-tune properties. The most common structures are poly(alkylene oxide)-substituted polydimethylsiloxanes, but these surfactants suffer from hydrolytic instability in alkaline or acidic environments.

Momentive's novel technology combines the reduced surface tension and low-use levels typical of silicone-based surfactants with the stability in acidic and alkaline environments that is more typical of hydrocarbon surfactants. Momentive's surfactants are stable in aqueous solutions from pH 2 to pH 12 without decomposition. These surfactants reduce the equilibrium surface tension of aqueous solutions to 21.5 mN/m at 0.1 weight percent, exhibit low critical micelle concentrations, and provide superspreading properties.

Momentive's pH-stable, siliconized surfactants provide benefits typically achieved only with fluorinated surfactants. In aqueous solutions, these materials approach the low surface tensions required for many current fluorosurfactant applications, and the silicon-containing portions provide friction reduction similar to that of the perfluorinated backbones. The acidic and basic stability of the new surfactants is similar to that of surfactants based on perfluorooctane sulfonate (PFOS). Momentive's materials can replace fluorosurfactants, which have come under scrutiny for their environmental persistence and bioaccumulation.

Silwet® Superspreader agricultural adjuvants represent another use of this technology. By helping water spread over and penetrate low-energy surfaces, superspreading surfactants help farmers conserve water while they control pests. Because they improve spray coverage, superspreaders allow lower rates of pesticide use. Because this novel class of superspreading adjuvants is pH-stable, the shelf life of pesticide formulations containing these surfactants is longer, and it is practical to package them in smaller containers, making their benefits available to the entire pesticide marketplace. Momentive has filed several patent applications for its pH-stable siliconized surfactants.

3D Trasar BioControl

Nalco Company

Microbes grow well in the warm, nutrient-rich waters of cooling systems. Unchecked, microbes coat the heat exchanger surfaces, impeding heat transfer and increasing energy costs. Biocides are added to control microbial activity. Although 99 percent of the microbial population resides on inaccessible surfaces in a cooling system, the industry could only monitor floating microbes. The result was either excessive biocide dosing (to preserve a margin for error) with subsequent discharge of biocides into natural waterways or insufficient biocide dosing. Either case increased energy use and public health concerns.

3D Trasar BioControl adds a fluorescent molecule, Resazurin, to the water in cooling systems. Microbial enzymes react with Resazurin and change its fluorescence: BioReporter (Resazurin) + microbial respiratory enzymes = BioProduct (Resorufin). Continuous monitoring of the fluorescence of both Resazurin and Resorufin allows instantaneous measurement of the total microbial activity in the system. Oxidizing biocide is added to the system only in response to increasing microbial activity. Oxidizing biocides also react with Resorufin and Resazurin, but do so at a much slower rate than do microbial enzymes. Fluorescent detection of the degradation of Resorufin by the oxidizing biocide is used to determine the precise endpoint for biocide addition.

With 3D Trasar BioControl, biomonitoring and control are continuous and comprehensive. Biocide is applied only when microbial activity is detected and before the population enters the log growth phase. As a result, oxidizing biocide use is reduced by 30–90 percent. Even a 30-percent reduction in oxidizing biocide worldwide could save 16 million pounds of biocide. 3D Trasar BioControl allows the most efficient use of biocide, ensures microbial control, reduces the formation of absorbable organic halide (AOX) from halogen-based oxidizing biocides, and reduces toxic discharge. During 2006, Nalco deployed over 1,400 new 3D BioControl units for a total of 3,000.

A New Corrosion Inhibitor Reduces the Environmental Impact of Industrially Treated Water

Nalco Company

Industrial water treatment systems suffer from the dual challenges of mineral scale fouling and ferrous metal corrosion. Scale and corrosion result in loss of flow, leaks, and general wasting that lead to plant shutdowns, high capital costs, and unplanned maintenance charges. To minimize the impact of these failures, chemical scale and corrosion inhibitors are added to the water in industrial cooling systems. Chemicals traditionally used as scale and corrosion inhibitors include phosphates, polyphosphates, phosphonates, and treatments based on zinc or molybdate. Concern for the environmental impact of metals and phosphates has led to increased oversight of the use of these materials. Broader implementation of discharge limitations is one means for reducing the impact of these chemicals on the environment, but it places industrial water users under greater burden to manage scale and corrosion in their water treatment systems.

Nalco developed a new inhibitor for cooling water applications, phosphinosuccinic oligomer (PSO), which has shown superior scale and corrosion protection. PSO also reduces or eliminates the need for zinc, molybdate, and compounds that decompose to phosphate. The scale inhibition of PSO has led to more efficient water use because cooling systems use less water when they can operate at higher mineral ion levels. PSO functions as a cathodic inhibitor. It has replaced molybdate and zinc successfully in traditional corrosion inhibition treatment programs while providing a high level of corrosion protection. The inhibitor is highly halogen-resistant. It does not revert to orthophosphate under normal conditions, allowing one to operate a cooling system with lower total phos-

phate levels compared with systems that use degradable polyphosphate. The cost and performance of PSO relative to traditional inhibitors have resulted in substantial reductions in the amount of zinc, molybdate, and phosphate used in water treatment. Between 2005 and 2006, Nalco increased its use of PSO by 77 percent.

The NutraSweet Corporation; Dr. Robert L. Augustine, Center for Applied Catalysis, Seton Hall University

Bromine-Free, TEMPO-Based Catalyst System for the Oxidation of Alcohols

NOTE: This project is the result of a partnership between Dr. Robert L. Augustine of the Center for Applied Catalysis at Seton Hall University and The NutraSweet Corporation. The project was judged in both the greener synthetic pathways (Focus Area 1) and academic categories. The abstract appears in the academic section on page 9.

Osmose, Inc.

MicroPro™ Technology in Wood Preservation

For over 75 years, water-borne preservatives have relied on solubilized ingredients to penetrate the wood being treated. Currently, approximately 85 percent of the pressure-treated wood in the United States is treated with amine–copper preservatives. The two most commonly used amine–copper preservatives require a solvent, monoethanolamine (MEA), to solubilize the copper component. MEA is a corrosive compound and a known kidney and liver toxin; it poses potential health and environmental hazards. It also facilitates the growth of mold on treated wood, reducing commercial acceptability.

Osmose, Inc. of Buffalo, NY developed MicroPro™, which uses micronized copper to penetrate wood, eliminating the use of any solvent. The copper particles in MicroPro™ are between 250 and 500 nm, allowing the preservative to penetrate the wood's cell structure uniformly. The particle size is small enough that the copper can be forced into the cellular structure areas of wood by pressure treatment, but large enough that it cannot readily move back out under normal pressure conditions. MicroPro™ has the potential to eliminate the use of 200 million pounds of MEA annually, equal to about half of the current MEA production. MicroPro™-treated wood leaches substantially less copper in service than does wood treated with current amine–copper systems. This reduces the environmental impact of copper from structures in aquatic and terrestrial environments by approximately 75 percent compared with the current systems.

MicroPro™ can be shipped at almost four-fold greater concentration than other current preservatives. The higher concentration of ingredients in MicroPro™ reduces the fuel energy required to deliver preservative to wood-treating plants by almost 75 percent, which reduces costs and overall environmental impact. In 2005, the U.S. EPA registered Smart Sense™ MicroPro™ as a pesticide. By November 2006, this product was being used by 18 wood-treatment plants in 9 states.

PPG Industries, Inc.

The Use of Chitosan in Paint Detackification

Automatic spray painting of automobiles, appliances, and other large articles is done in water-washed paint spray booths. The traditional, wet-paint spraying operations of automotive original equipment manufacturers (OEMs) transfer only 50–80 percent of the paint onto the vehicle; the remaining 20–50 percent is deposited in an air stream that is later purified in a circulating water curtain. Paint denaturants, also called "detackifiers", are added to the water curtain circulating in down-draft, water-washed, paint spray booths to render the oversprayed paint nonsticky. Paint detackifiers denature, coagulate, and flocculate the oversprayed paint in the water curtain, allowing it to settle out as sludge and be separated from the water. During 2005, the automotive industry used approximately 31 million pounds of detackifiers.

The current melamine–formaldehyde-based detackifiers contain small amounts of residual free formaldehyde, a known carcinogen. Alternative acrylic acid based paint detackifiers are derived from ethylene and propylene, which are produced during petroleum cracking and, therefore, require nonrenewable feedstocks and are subject to fluctuations in petroleum prices.

BC4200NP is a liquid, chitosan-based, paint denaturant technology that provides an alternative to both traditional melamine–formaldehyde and acrylic acid based denaturants. Chitosan is poly(glucosamine), a polysaccharide structurally similar to cellulose. It is made by deacetylating chitin from crab, lobster, and shrimp shells that are a waste product of food production. Because chitosan is less acidic than traditional products, it requires 87 percent less sodium hydroxide for pH control. It retards the growth of anaerobic organisms, so the circulating water requires less biocide. It also produces paint sludges that are more amenable to biodegradation than are traditional sludges. At optimal chitosan concentrations, BC4200NP is less costly or at least cost-neutral compared with traditional technologies. The Mitsubishi Motors facility in Normal, IL has been using it for over a year and a half with excellent results.

Tide Coldwater®: Energy Conservation through Residential Laundering Innovation and Commercialization

The Procter & Gamble Company

Procter & Gamble has recently commercialized a patented, breakthrough chemical innovation in environmentally friendly cleaning technology to provide superior cleaning and significant energy savings in low-temperature (60 °F) wash water. Over 7 million U.S. households have used Tide Coldwater® since its introduction in North America in January 2005.

Tide Coldwater® uses surfactant systems designed to be more hydrophobic than other detergents. The liquid detergent formula uses an optimized combination of alcohol ether sulfate, linear alkyl benzene sulfonate, and ethoxylated zwitterionic and alkyl amine surfactants. In combination with a builder/chelant to sequester metals, soil suspension systems, enzymes (protease and amylase), and brightener systems, this proprietary surfactant system delivers superior cleaning performance in cold water. The powder detergent formula is based on high-solubility alkyl sulfate, a proprietary branched surfactant. It also contains sodium nonanoyl oxybenzene sulfonate, a proprietary bleach activator, along with other additives in common with the liquid version.

In blind consumer tests, Tide Coldwater® provides superior cleaning in cold water relative to detergents formulated for warm and hot water. Without sacrificing performance in stain removal or whitening, consumers can save up to $63 per year in home energy costs, reducing greenhouse gas emissions from fossil-fueled power plants. Using a peer-reviewed model for residential energy use, Procter & Gamble estimates that Tide Coldwater® will reduce the fraction of residential energy used to heat water by up to 26–36 percent, with an associated reduction in carbon dioxide (CO_2) emissions of up to 1,259 pounds per household per year. The potential benefits of this innovation are significant: if everyone in the United States switched to cold water for laundry, the potential energy savings would be 70–90 billion kilowatt-hours per year, representing up to 3 percent of the nation's energy consumption. These savings are the equivalent of 26–34 million tons of CO_2 per year, representing over 8 percent of the CO_2 reduction target for the United States set in the Kyoto Protocol.

Rhein Chemie Corporation

Optimizing Renewable Resources in the Production of Polyurethane Systems and Plastics

Biobased products can help protect and preserve the environment. In addition, they can create a safer, healthier workplace, help cut air and water pollution, reduce the generation of hazardous waste, decrease the use of potentially toxic substances, and improve recycling opportunities. Soy-based polyols can substitute for petroleum-based polyols in polyurethanes, but the available acid groups in soy polyols can cause hydrolytic degradation and variable reactivity, leading to polyurethanes with inferior properties.

Rhein Chemie Corporation created soy-based polyol additives for the production of low-density, insulated spray foams for the industrial, commercial, and residential insulation markets. These particular soy-based systems use water as a blowing agent to replace chlorofluorocarbons (CFCs) and use flame retardants to reduce smoke effects as required for class 1 foams (the highest flame spread and smoke standard in the insulation industry). The combination of these Rhein Chemie technologies enables their insulation system to reduce depletion of the ozone layer effectively.

The Rhein Chemie insulation system comprises an ethoxylated soy polyol mixed with a common polyester, chain-extended with an isocyanate and modified with Rhein Chemie additives (such as Stabaxol P200 and Addocat 102) to form a "green" polymer. Stabaxol, a carbodiimide, scavenges the acid groups on the biopolyols and improves both the reactivity and the hydrolytic stability. Stabaxol also minimizes the deactivation of the catalysts by reacting out the acids that lead to variable reactivity.

Rhein Chemie pioneered the additive technology for soy-based polyol systems and toll manufactured the first commercial polyurethane systems for spray foams in the United States for industrial, commercial, and residential insulation. Rhein Chemie's soy-based polyol additives are effective, environmentally friendly alternatives to petroleum-based products and have been in commercial use in the United States for the past 5 years.

Severn Trent Services

Iron Oxide for Arsenic Removal from Drinking Water

The U.S. EPA's best available technologies for removing arsenic from drinking water include aluminum adsorption, ion exchange, reverse osmosis, and coagulation filtration. Adsorption technology is among the simplest approaches for removing metals, such as arsenic, from drinking water, but conventional adsorbents such as activated carbon or activated alumina have a limited capacity for arsenic.

Severn Trent Services worked with LANXESS Corporation to develop the proprietary Bayoxide® E33 media for efficient, effective adsorption of arsenic. Bayoxide® E33 consists of iron oxide hydroxide in the α-FeOOH form; it has a very high specific surface area and a high adsorption capacity for arsenic. Bayoxide® E33 is mechanically robust, is stable with a uniform grain size, has a low leaching potential, has good water distribution across the media minimizing pressure buildup, and is immediately effective in a start-stop process. Bayoxide® E33 can remove arsenic from groundwater to well below 4 micrograms per liter. In an adsorption system, SORB 33®, the Bayoxide® E33 media life expectancy depends on site-specific water quality and operating levels. The exhausted media is nonhazardous, passing the U.S. EPA's Toxicity Characteristic Leaching Procedure (TCLP) threshold requirements.

Bayoxide® E33 media achieves a three-fold reduction in waste. First, Bayoxide® E33 media is manufactured from iron sulfate, a waste product of the steel industry. Second, service wash water from routine backwashing of the Bayoxide® E33 media can be reclaimed

and returned to the plant inlet. Third, exhausted Bayoxide® E33 serves as a source of iron oxide for steel manufacturing processes, namely direct reduction iron (DRI) process and sintering plants, eliminating the disposal of Bayoxide® E33 into landfills.

The U.S. market for adsorptive arsenic removal media is estimated at over 6,000 metric tons per year, excluding residential applications. As of November 2006, Severn Trent Services had sold Bayoxide® E33 to municipalities in 35 States in the United States.

Dequest PB – Carboxymethyl Inulin: A Versatile Scale Inhibitor from the Roots of Chicory

Solutia Inc.

Fouling of surfaces by mineral salts is a major problem in water-bearing systems because scaling reduces the efficiency of heat transfer and interferes with the operational performance of industrial processes. Previous scale inhibitors were either products with poor biodegradability and moderate toxicity but good performance (e.g., polyacrylates) or biodegradable products with limited applicability (e.g., polyaspartates).

Carboxymethyl inulin (CMI) is based on inulin, an oligosaccharide harvested from the roots of chicory. Developed by Solutia and Cosun (The Netherlands), CMI provides a cost-effective, safe, and versatile alternative to traditional antiscalants. It combines good biodegradability with very low toxicity. It also has excellent scale inhibition performance for various types of scales, particularly sulfate scales. CMI can be used in many applications, but is especially well-suited for use in environmentally sensitive areas, such as offshore oil production. For example, CMI is used as a barium sulfate scale inhibitor in the Norwegian offshore oil drilling sector of the North Sea. CMI also is a suitable replacement for poorly biodegradable scale inhibitors in water and process water treatment, as well as in pulp and paper and sugar refining applications. In addition, the attributes of CMI make it a candidate as a laundry aid to prevent redeposition and as a builder component in household and industrial automatic dishwasher and laundry formulations. A CMI-based, phosphate-free automatic dishwashing tablet was launched on the European market in 2006.

In 2006, Solutia generated the first commercial sales of CMI in the United States under the trade name Dequest PB. At full market penetration, Dequest PB has the potential to replace 125 million pounds of polyacrylates currently used in U.S. and Canadian household and institutional laundry detergent formulations to prevent redeposition. Solutia and Cosun are currently developing a wider range of inulin-based products with different functionalities and performance characteristics.

Enzyme-Based Technology for Decontaminating Toxic Organophosphorus Compounds

U.S. Army, U.S. Army Edgewood Chemical Biological Center

Current field military or civilian decontaminants such as Decontaminating Solution 2, Super Tropical Bleach, and Sandia Foam are quite efficient against chemical and biological agents, but they are also toxic and corrosive. They are nonspecific oxidizing agents that must be used in stoichiometric amounts.

The U.S. Army Edgewood Chemical Biological Center (ECBC) has developed and patented a technology using enzymes to neutralize chemicals such as nerve agents and related pesticides. The technology consists of two enzymes in a dry granular form that can be added to water or water-based application systems (e.g., fire-fighting foams and sprays, aircraft deicing solutions, and aqueous degreasers). The enzymes quickly detoxify these

hazardous chemicals before they can contaminate wider areas. Because the enzymes are catalytic, only small quantities are required, greatly reducing transportation and storage requirements (by as much as 25- to 50-fold). The enzymes are also nontoxic, noncorrosive, and environmentally safe. Initially intended to decontaminate equipment, facilities, and large areas, these enzymes could potentially be used in shower systems to decontaminate personnel and casualties.

The specific bacterial enzymes are organophosphorus hydrolase (originally called parathion hydrolase) and organophosphorus acid anhydrolase (an X-Pro dipeptidase, EC 3.4.13.9). These two enzymes are effective against V- and G-type nerve agents, respectively. Genencor International, the premier manufacturer of industrial and specialty enzymes in the United States, is using its state-of-the-art fermentation manufacturing technology to produce the enzymes. Genencor has begun commercial production and now has industrial-scale quantities of the enzymes available under the trade name DEFENZ™. The enzymes will be sold to companies that produce and sell fire-fighting foams, sprays, and other potential matrices. These companies will formulate the enzymes into products for purchase by fire departments, HazMat groups, and other first-responders. Kidde Fire Fighting introduced the first such commercial product, All-Clear™, in August 2005.

U.S. Department of Energy, Argonne National Laboratory

Resin Wafer Technology

The U.S. Department of Energy has identified separations technology as one of the most significant cost barriers in process-intensive fields such as fossil energy consumption, water management, and CO_2 sequestration. Electrodeionization (EDI) is an electrical process that separates low-concentration, charged species from process streams. In conventional EDI, loose ion exchange resins are used to produce ultrapure water.

Resin wafer technology replaces loose resins and enables the extension of EDI well beyond its conventional applications. Resin wafers are fabricated from commercially available ion exchange resins and retain the chemical activity of their components. They can be molded into desired shapes using thermoplastics to provide structural integrity. The wafers can also incorporate such materials as biocatalysts, immobilization resins, electron conductivity nanoparticles, and fillers to control porosity.

Resin wafers offer several advantages: (1) controlled porosity, which makes stream flow more efficient; (2) enhanced ion conductivity, which reduces power consumption; and (3) reduced leakage, which both increases product recovery and cuts waste stream loss. Resin wafers also provide new functionalities not available with conventional EDI. These include direct immobilization of biocatalysts, which allows integrated bioconversion and separations; modification of wafer composition and format, which increases ion selectivity and direct pH control; and in situ catalysis. Resin wafers allow new processes in biobased chemical production, industrial water management, chemical production and purification, and, potentially, hydrogen production and CO_2 sequestration.

Resin wafer technology also offers significant environmental benefits. It reduces the cost of producing biobased chemicals, making them more competitive with petrochemicals. It decreases fresh water use and the release of wastewater. It reduces energy and chemical use during the production of organic acids, esters, and other chemicals. Finally, it can potentially enhance CO_2 sequestration from flue gases and hydrogen production from water. Resin wafer technology has been awarded 7 patents over the past 5 years.

Solventless Process for Making Tackifiers and Adhesives

U.S. Department of Energy, Argonne National Laboratory

Worldwide, over 2.5 million tons of pressure-sensitive adhesives (PSAs) are manufactured annually for use in many industries, including pulp and paper, electronics, wireless telecommunications, medical devices, cosmetic and personal hygiene, and others. PSAs are made by combining tackifier dispersions with latex dispersions. Tackifier dispersions are made either from low-temperature resins that melt at less than 100 °C or from resins that melt at higher temperatures. High-temperature resins are dissolved in organic solvents then heated to evaporate and recover excess solvent, resulting in some solvent emissions. Over time, any residual solvents in the adhesive also evaporate into the environment. Low-temperature resins are heated, melted, slowly added to hot water, and continuously stirred for over 4 hours to form an emulsion containing up to 50 weight-percent water. The emulsion is then transported to the site at which the adhesive is made. After the adhesive has been coated onto a substrate, radiant heating removes the excess water.

Argonne National Laboratory has developed a new process to make tackifier dispersions for PSAs. The Argonne process pulverizes the resin to an average particle size of less than 5 micrometers and then directly forms the dispersion in water, in just a few minutes, without dissolving the resin in solvents, melting it, or using excess water. The process does not require solvents or heat to process either high- or low-temperature resins. It also eliminates the need for transporting excess water. Argonne's process is cost-effective and energy-efficient. It reduces the cost of manufacturing water-based tackifier dispersions by over 35 percent and uses less than 25 percent of the energy required by conventional processes. As a result, it reduces greenhouse gas emissions.

Argonne has filed a patent application for this technology. Dyna-Tech Adhesives, Inc. has manufactured 500 pounds of resin with an average size of 2.5 micrometers for testing.

Green Primaries: Environmentally Friendly, Sensitive Explosives

U.S. Department of Energy, Los Alamos National Laboratory

Initiating devices use primary explosives (i.e., primaries) to detonate main charge explosives. The synthetic chemistry "holy-grail" in energetic materials has been the search for environmentally benign alternatives to replace toxic mercury fulminate, lead azide, and lead styphnate in primaries. Detrimental effects on the environment and personnel safety from primaries based on toxic mercury and lead have made their replacement essential.

Dr. Huynh at Los Alamos has created green primaries based on 5-nitrotetrazolato-N^2-metalates that contain iron or copper. These green primaries are coordination anions charge-compensated by environmentally benign cations. They combine superior explosive performance with greatly improved health and safety conditions during synthesis, manufacturing, and use. They have many national security and commercial applications.

The U.S. Department of Defense requires environmentally friendly primaries to meet six criteria. They must be insensitive to moisture and light, sensitive to initiation but not too sensitive to handle, thermally stable to at least 200 °C, chemically stable for extended periods, and devoid of toxic metals and perchlorate. Dr. Huynh's green primaries are the only primaries known to fulfill all six criteria. Green primaries give quantitative yields without purification or recrystallization, so they can be manufactured quickly with lower expenses for waste disposal.

The benefits of green primaries include safe, inexpensive manufacture and transport; elimination of mercury and lead contamination; great versatility in, and control over, initiating sensitivities and explosive performance; elimination of toxic waste; and release of

only innocuous byproducts upon detonation. The benign detonation byproducts prevent chronic lead exposure to civilians and military personnel. Green primaries are safely prepared in, and desensitized by, water or ethanol, so toxic fumes and solvents are eliminated during preparation. Green primaries eliminate the potential for accidental explosions, saving lives. Finally, they reduce costs for specialized safety equipment, transportation, and liability insurance.

Three patent applications have been filed; all three will be licensed exclusively so that commercialization can begin.

U.S. Department of Energy, Los Alamos National Laboratory

Ultrapure Carbon and Carbon–Nitride Nanomaterials Derived from Simple Pyrolyses of Nearly Chock-Full Nitrogen Compounds

Currently, carbon-based nanomaterials are manufactured primarily from residual oils or hydrocarbon precursors at extremely high temperatures and applied pressures. The toxic fumes and hazardous waste generated by these high-temperature, high-pressure reactions are detrimental to the environment and cause personal health risks.

Dr. Huynh has developed solventless pyrolytic conditions to prepare ultrapure carbon nanoparticles and diamond-hard carbon–nitride nano-architectures from novel high-nitrogen compounds, the so-called nearly chock-full nitrogen compounds. This requires simultaneous manipulation of melting points, heating patterns, and decomposition temperatures. Dr. Huynh's solid-state pyrolyses can be tuned controllably to produce nanomaterials of the size, shape, morphology, density, dimension, and nitrogen content required for a wide variety of applications. Some of these applications include next-generation computer chips, kinetic-energy penetrators with enhanced lethality, better insulation materials, tougher and harder cutting tools, high-sensitivity sensors, automobiles with greater fuel efficiency, aerospace components with enhanced performance characteristics, and longer-lasting medical implants. Unlike hydrocarbon feedstocks that contain primarily C–H and C=C bonds, these high-nitrogen compounds contain multiple C=N bonds and N=N linkages that make their thermal decompositions downhill processes owing to the extrusion of nitrogen gas as the only byproduct. Multiple N=N linkages make these high-nitrogen compounds nonvolatile and viscous, so they are easy to handle.

With Dr. Huynh's innovation, ultrapure carbon and carbon–nitride nanomaterials can be manufactured quantitatively with absolutely no hydrogen-incorporating byproducts. The manufacture of these carbon-based nanomaterials from high-nitrogen compounds is advantageous and cost-effective. This process abolishes specialized facilities and equipment, eliminates personal exposure to high-temperature and applied-pressure reaction conditions, eradicates lengthy preparation and complicated purification, and drastically reduces production costs associated with liability insurance and the removal of toxic fumes and hazardous waste. Essentially, Dr. Huynh has creatively applied high-nitrogen chemistry to solve environmental and nanotechnological problems. One patent has been granted for this technology; another is pending.

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