The Presidential Green Chemistry Challenge Awards Program:

Summary of 2008 Award Entries and Recipients

GREEN CHEMISTRY CHALLENGE

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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 (EPA) celebrates innovative, award-winning technologies developed by high-quality nominees. The year 2008 marks the 13^{th} year of the program. This compilation summarizes the entries submitted for the 2008 awards. Five of the more than 90 entries were nationally recognized on June 24, 2008, at an awards ceremony in Washington, D.C.

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 EPA Design for the Environment partnership with the chemical industry and professional scientific community, this annual awards 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 2008 awards. The judges used criteria that included health and environmental benefits, scientific innovation, and industrial applicability. These technologies are also meant to succeed in the marketplace: each illustrates the technical feasibility, marketability, and profitability of green chemistry.

For further information about the Presidential Green Chemistry Challenge and 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 2008 Presidential Green Chemistry Challenge Awards. 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 EPA

Academic Award

Green Chemistry for Preparing Boronic Esters

Professors Robert E. Maleczka, Jr. and Milton R. Smith, III, Michigan State University

Innovation and Benefits

One way to build complex molecules, such as pharmaceuticals and pesticides, is with a Suzuki "coupling" reaction. This versatile coupling reaction requires precursors with a carbon–boron bond. Making these precursors, however, typically requires harsh conditions and generates significant amounts of hazardous waste. Professors Maleczka and Smith developed a new catalytic method to make these compounds under mild conditions and with minimal waste and hazard. Their discovery allows the rapid, green manufacture of chemical building blocks, including some that had been commercially unavailable or environmentally unattractive.

"Coupling" reactions are one way to build valuable molecules, such as pharmaceuticals, pesticides and similar complex substances. Coupling reactions connect two smaller molecules, usually through a new carbon–carbon (C–C) bond. A particularly powerful coupling reaction is the Suzuki coupling, which uses a molecule containing a carbon–boron bond to make a larger molecule through a new C–C bond. In fact, the Suzuki coupling is a well-established, mild, versatile method for constructing C–C bonds and has been reported to be the third most common C–C bond-forming reaction used to prepare drug candidates.

Chemical compounds with a carbon–boron bond are often prepared from the corresponding halides by Grignard or lithiate formation followed by reaction with trialkyl borate esters and hydrolytic workup. Miyaura improved this reaction with a palladium catalyst, but even this new reaction requires a halide precursor.

Several years ago, Professors Milton R. Smith, III and Robert E. Maleczka, Jr. began collaborating to find a "halogen-free" way to prepare the aryl and heteroaryl boronic esters that are the key building blocks for Suzuki couplings. Their collaboration builds upon Smith's invention of the first thermal, catalytic arene carbon–hydrogen bond (C–H) activation/borylation reaction. This led to transformations using iridium catalysts that are efficient, have high yields, and are tolerant of a variety of functional groups (alkyl, halo-, carboxy, alkoxy-, amino, etc.). Sterics, not electronics dictate the regiochemistry of the reactions. As a consequence, 1,3-substituted arenes give only 5-boryl (i.e., *meta*-substituted) products, even when both the 1- and 3-substituents are ortho/para directing. Just as significantly, the reactions are inherently clean as they can often be run without solvent, and they occur with hydrogen being the only coproduct. The success of these reactions has led Miyaura, Ishiyama, Hartwig, and others to use them as well.

In brief, catalytic C–H activation/borylation allows the direct construction of aryl boronic esters from hydrocarbon feedstocks in a single step, without aryl halide intermediates, without the limitations of the normal rules of aromatic substitution chemistry, and without many common functional group restrictions. Moreover, due to its mildness, the borylation chemistry combines readily in situ with subsequent chemical reactions.

This technology allows rapid, low-impact preparations of chemical building blocks that currently are commercially unavailable or only accessible by protracted, costly, and environmentally unattractive routes. Indeed, most recently, Michigan State University licensed the nominated technology to BoroPharm, Inc., which is using these catalytic borylations to produce much of the company's product line. Thus, the nominated technology is proving to be practical green chemistry beyond the laboratory bench.

Small Business Award

SiGNa Chemistry, Inc.

New Stabilized Alkali Metals for Safer, Sustainable Syntheses

Innovation and Benefits

Alkali metals, such as sodium and lithium, are powerful tools in synthetic chemistry because they are highly reactive. However, unless they are handled very carefully, their reactivity also makes them both flammable and explosive. SiGNa Chemistry developed a way to stabilize these metals by encapsulating them within porous, sand-like powders, while maintaining their usefulness in synthetic reactions. The stabilized metals are much safer to store, transport, and handle. They may also be useful for removing sulfur from fuels, storing hydrogen, and remediating a variety of hazardous wastes.

Alkali metals have a strong propensity for donating electrons, which makes these metals especially reactive. That reactivity has enormous potential for speeding chemical reactions throughout science and industry, possibly including new pathways to clean energy and environmental remediation. Unfortunately, that same reactivity also makes them highly unstable and dangerous to store and handle. In addition, increased risk of supply-chain interruption and the expense of handling these metals have made them unattractive to the chemical industry. Industries from pharmaceutical to petroleum have developed alternative synthetic routes to avoid using alkali metals, but these alternates require additional reactants and reaction steps that lead to inefficient, wasteful manufacturing processes.

SiGNa Chemistry addresses these problems with its technology for nanoscale absorption of reactive alkali metals in porous metal oxides. These new materials are sand-like powders. SiGNa's materials eliminate the danger and associated costs of using reactive metals directly but retain the utility of the alkali metals. Far from their hazardous precursors, SiGNa's materials react controllably with predictable activation that can be adapted to a variety of industry needs. By enabling practical chemical shortcuts and continuous flow processes, the encapsulated alkali metals create efficiencies in storage, supply chain, manpower, and waste disposal.

For the pharmaceutical, petrochemical, and general synthesis industries, SiGNa's breakthrough eliminates the additional steps that these industries usually take to avoid using the alkali metals and produces the desired reaction in 80–90 percent less time. For the pharmaceutical industry in particular, the materials can accelerate drug discovery and manufacturing while bolstering worker safety.

Beyond greening conventional chemical syntheses, SiGNa's materials enable the development of entirely new areas of chemistry. In clean-energy applications, the company's stabilized alkali metals safely produce record levels of pure hydrogen gas for the nascent fuel cell sector. With yield levels that already exceed the U.S. Department of Energy's targets for 2015, SiGNa's materials constitute the most effective means for processing water into hydrogen. SiGNa's materials also allow alkali metals to be safely applied to environmental remediation of oil contamination and the destruction of PCBs and CFCs.

SiGNa's success in increasing process efficiencies, health, and environmental safety and in enabling new chemical technologies has helped it attract more than 50 major global pharmaceutical, chemical, and energy companies as customers.

Greener Synthetic Pathways Award

Development and Commercialization of Biobased Toners

Battelle

Innovation and Benefits

Laser printers and copiers use over 400 million pounds of toner each year in the United States. Traditional toners fuse so tightly to paper that they are difficult to remove from waste paper for recycling. They are also made from petroleum-based starting materials. Battelle and its partners, Advanced Image Resources and the Ohio Soybean Council, have developed a soy-based toner that performs as well as traditional ones, but is much easier to remove. The new toner technology can save significant amounts of energy and allow more paper fiber to be recycled.

More than 400 million pounds of electrostatic dry toners based on petroleum-derived resins are used in the United States annually to make more than 3 trillion copies in photocopiers and printers. Conventional toners are based on synthetic resins such as styrene acrylates and styrene butadiene. These conventional resins make it difficult to remove the toner during recycling, a process called de-inking. This makes paper recycling more difficult. Although others have developed de-inkable toners, none of the competing technologies has become commercial due to high costs and inadequate de-inking performance.

With early-stage funding from the Ohio Soybean Council, Battelle and Advanced Image Resources (AIR) formed a team to develop and market biobased resins and toners for office copiers and printers. This novel technology uses soy oil and protein along with carbohydrates from corn as chemical feedstocks. Battelle developed bioderived polyester, polyamide, and polyurethane resins and toners from these feedstocks through innovative, cost-effective chemical modifications and processing, with the de-inking process in mind. By incorporating chemical groups that are susceptible to degradation during the standard de-inking process, Battelle created new inks that are significantly easier to remove from the paper fiber. AIR then scaled up the process with proprietary catalysts and conditions to make the new resins.

The new technology offers significant 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 life-cycle analysis shows significant energy savings and reduced carbon dioxide (CO_2) emissions in the full value chain from resin manufacture using biobased feedstocks to toner production and, finally, to the recovery of secondary fibers from the office waste stream. At 25 percent market penetration in 2010, this technology could save 9.25 trillion British thermal units per year (Btu/yr) and eliminate over 360,000 tons of CO_2 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, the licensee of the technology, successfully scaled up production of the resin and toners for use in HP LaserJet 4250 Laser Printer cartridges. Battelle and AIR 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. The new toner will be sold under trade names BioRez® and Rezilution®. Once commercial, it will provide users with seamless, environmentally friendly printing and copying.

Greener Reaction Conditions Award

Nalco Company

3D TRASAR® Technology

Innovation and Benefits

Cooling water touches many facets of human life, including cooling for comfort in commercial buildings and cooling industrial processes. Cooling systems require added chemicals to control microbial growth, mineral deposits, and corrosion. Nalco developed 3D TRASAR® technology to monitor the condition of cooling water continuously and add appropriate chemicals only when needed, rather than on a fixed schedule. The technique saves water and energy, minimizes the use of water-treatment chemicals, and decreases environmental damage from discharged water.

Most commercial buildings, including offices, universities, hospitals, and stores, as well as many industrial processes, use cooling systems based on water. These cooling systems can consume vast quantities of water. Also, unless mineral scale and microbes are well-controlled, several problems can arise leading to increased water and energy consumption and negative environmental impacts.

Mineral scale, which consists mostly of carbonates of calcium and magnesium, forms on heat-exchange surfaces; this makes heat transfer inefficient and increases energy use. Similarly, microbial growth can lead to the formation of biofilms on heat-exchange surfaces, decreasing exchange efficiency. Conversely, high levels of biocide intended to prevent biofilm cause several adverse effects including increased corrosion of system components. Gradually, the integrity of the system becomes compromised, increasing the risk of system leaks. The material from these leaks, along with metal-containing byproducts of corrosion and the additional biocide, are ultimately discharged with the cooling water. Every time water is discharged, called "blowdown", pollutants are released in the wastewater, and fresh water is used to replace the blowdown. Traditionally, antiscalants and antimicrobials are added at regular intervals or, at best, after manual or indirect measurements show scale or microbial buildup.

In 2004, Nalco commercialized its 3D TRASAR® Cooling System Chemistry and Control technology. By detecting scaling tendency early, cooling systems with Nalco's technology can operate efficiently; in addition, they can use less water or use poor-quality water.

3D Scale Control, part of the 3D TRASAR® system, prevents the formation of mineral scale on surfaces, maintaining efficient heat transfer. The system monitors antiscalant levels using a fluorescent-tagged, scale-dispersant polymer and responds quickly when conditions favor scale formation. In addition, 3D Bio-control, also part of the 3D TRASAR® system, is the only online, real-time test for measuring planktonic and sessile bacteria. It uses resazurin, another fluorescent molecule, which changes its fluorescent signature when it interacts with respiring microbes. By adding an oxidizing biocide in response to microbial activity, 3D Bio-control generally reduces the use of biocide and also prevents biofilm from building up on surfaces, maintaining efficient heat transfer.

A proprietary corrosion monitor and a novel corrosion inhibitor, phosphino succinic oligomer, provide improved corrosion protection. In 2006, the 2,500 installations using the 3D TRASAR® system saved approximately 21 billion gallons of water. These installations have also significantly reduced the discharge of water-treatment chemicals to water-treatment plants or natural waterways.

Designing Greener Chemicals Award

Spinetoram: Enhancing a Natural Product for Insect Control

Dow AgroSciences

Innovation and Benefits

Spinosad biopesticide from Dow AgroSciences controls many insect pests on vegetables, but is not particularly effective against certain key pests of tree fruits. To solve this problem, Dow AgroSciences used an "artificial neural network" to identify analogous molecules that might be more effective against fruit-tree pests. They then developed a green chemical synthesis for the new insecticide, called spinetoram. Spinetoram retains the favorable environmental benefits of spinosad while replacing organophosphate pesticides for tree fruits, tree nuts, small fruits, and vegetables.

Spinosad biopesticide won the Presidential Green Chemistry Challenge Award for Designing Greener Chemicals in 1999. Spinosad, a combination of spinosyns A and D, is effective against insect pests on vegetables, but there have been few green chemistry alternatives for insect-pest control in tree fruits and tree nuts. Dow AgroSciences has now developed spinetoram, a significant advancement over spinosad that extends the success of spinosad to new crops.

The discovery of spinetoram involved the novel application of an artificial neural network (ANN) to the molecular design of insecticides. Dow AgroSciences researchers used an ANN to understand the quantitative structure-activity relationships of spinosyns and to predict analogues that would be more active. The result is spinetoram, a mixture of 3′-*O*-ethyl-5,6-dihydro spinosyn J and 3′-*O*-ethyl spinosyn L. Dow AgroSciences makes spinetoram from naturally occurring fermentation products spinosyns J and L by modifying them with a low-impact synthesis in which catalysts and most reagents and solvents are recycled. The biology and chemistry of spinetoram have been extensively researched; the results have been published in peer-reviewed scientific journals and presented at scientific meetings globally.

Spinetoram provides significant and immediate benefits to human health and the environment over existing insecticides. Azinphos-methyl and phosmet, two organophosphate insecticides, are widely used in pome fruits (such as apples and pears), stone fruits (such as cherries and peaches), and tree nuts (such as walnuts and pecans). The mammalian acute oral toxicity of spinetoram is more than 1,000 times lower than that of azinphos-methyl and 44 times lower than that of phosmet. The low toxicity of spinetoram reduces the risk of exposures throughout the supply chain: in manufacturing, transportation, and application and to the public.

Spinetoram has a lower environmental impact than do many current insecticides because both its use rate and its toxicity to non-target species are low. Spinetoram is effective at much lower rates than many competing insecticides. It is effective at use rates that are 10–34 times lower than azinphos-methyl and phosmet. Spinetoram is also less persistent in the environment compared with other traditional insecticides. In the United States alone, Dow AgroSciences expects spinetoram to eliminate about 1.8 million pounds of organophosphate insecticides applied to pome fruit, stone fruit, and tree nuts during its first five years of use. In 2007, EPA granted pesticide registrations to the spinetoram products Radiant™ and Delegate™, and Dow AgroSciences began commercial sales.

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. An alternative for the oxidation of alcohols is the Anelli process, which replaces the metal oxides with NaOCl and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The Anelli process uses a two-phase (CH_2Cl_2–H_2O) system with TEMPO as a catalyst, KBr as a co-catalyst, and NaOCl as the oxidant.

Dr. Augustine's oxidation procedure is a modification of the Anelli process. His procedure decreases TEMPO by a factor of eight and decreases the volume of buffer by 96 percent. It also replaces KBr with a very small amount of the more benign $Na_2B_4O_7$ (borax) and does not require 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 with dichloromethane as the solvent. This has positive advantages in environmental and process safety as well as cost. The procedure isolates the product aldehyde in excellent yield by phase separation from the aqueous solution, which saves energy. Dr. Augustine's procedure can oxidize a number of primary alcohols, producing the corresponding aldehydes in very good to excellent yields. His procedure also oxidizes secondary alcohols to ketones in very good to excellent yields.

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

The Mcgyan Process: A New, Heterogeneous, Fixed-Bed Catalyst Technology for Continuous-Flow Biodiesel Production from Waste Fats and Oils

Professor Arlin E. Gyberg, Augsburg College; SarTec Corporation

Fossil fuels have detrimental effects on the environment. 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 economically converts inexpensive plant oils and animal fats to biodiesel. The catalyst contains modified porous microspheres of zirconia, titania, or alumina.

In addition to the environmental advantages of biofuels over fossil fuels, SarTec's process offers several advantages over the current biodiesel production method: (1) SarTec's process uses less energy overall; (2) the process uses cheap feedstocks such as waste grease and 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 and reducing the amount of waste generated; and (4) the new technology eliminates unwanted side reactions that produce soaps from free fatty acids, thereby reducing the amount of hazardous waste.

During 2007, SarTec produced biodiesel from an ever-expanding list of feedstocks, including corn oil reclaimed from distiller's syrup, the byproduct of ethanol production. SarTec also constructed a pilot plant to prove scalability (ASTM-grade biodiesel is currently being produced at this facility) and began construction on a three-million-gallon-per-year facility that will use this technology.

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

Development of Environmentally Benign, Nonfouling Materials and Coatings for Marine Applications

Biofouling on ship hulls and other marine surfaces is a global environmental and economic problem. The majority of current marine coating products are antifouling coatings (i.e., coatings that release biocides to kill marine microorganisms). Because biocides are harmful to the marine environment, their applications are extremely limited. Nontoxic, fouling-release coatings based on silicone compounds are also available, but have not gained popularity and are only effective on vessels moving at high speeds (over 14 knots). Furthermore, these coatings require expensive material, application, and maintenance.

Professor Jiang has developed unique nonfouling coatings (i.e., coatings to which marine microorganisms cannot attach). Unlike antifouling coatings, his nonfouling coatings are nontoxic; they neither contain nor release biocides. Unlike fouling-release coatings, his coatings are highly resistant to attachment by marine microorganisms, even on stationary surfaces.

Professor Jiang's discovery of super-low-fouling zwitterionic materials based on sulfobetaine (SB) and carboxybetaine (CB) enabled his development of nonfouling marine coatings. SB and CB are highly effective, very stable, nontoxic, and low-cost. His "hydrophobic" zwitterionic precursors enabled Professor Jiang to develop self-polishing, durable coatings for long-term applications. The "hydrophobic" zwitterionic precursors have strong mechanical strength as coatings; in seawater, they hydrolyze to "hydrophilic" nonfouling zwitterionic groups at the outer-most layer of the coatings. Over the last three years, Professor Jiang and his group have developed three generations of SB- and CB-based nonfouling marine coatings. Both laboratory tests and field tests in Florida have been successful.

Among many technologies under development for marine coatings, Professor Jiang's nonfouling technology clearly stands out as the most promising. Its environmental and economic impacts are enormous. These SB- and CB-based materials are very promising for biomedical applications as well; Stericoat, an MIT spin-off business, is using the technology to prohibit microbial growth from attaching to medical devices. Professor Jiang has filed several patents for his technology.

Microwave Heating as an Enabling Tool for Greener Synthesis

Dr. Nicholas Leadbeater, Department of Chemistry, University of Connecticut

Dr. Leadbeater and his research group are using microwave heating to develop cleaner, greener synthetic routes to commodity chemicals, pharmaceuticals, and biofuels. Microwave heating can enhance the rate of reactions and, in many cases, improve product yields. He and his group have developed fast, easy, metal-catalyzed reactions that form C–C bonds; many of these reactions use water as a solvent. They can perform Suzuki and Heck couplings using sub-ppm quantities of simple palladium salts as catalysts and can also perform hydroxy- and alkoxycarbonylation reactions using near-stoichiometric quantities of carbon monoxide.

They have been working to scale up microwave-promoted chemistries and have investigated both batch and continuous-flow methods. They have developed a fast, easy route for preparing biodiesel with a commercially available microwave unit that works with both new and used oil and is energy-efficient. Their continuous-flow apparatus makes approximately two gallons of biodiesel per minute.

It is difficult to optimize reactions using microwave heating because monitoring the reaction progress generally requires stopping the microwave, allowing the reaction mixture to cool, and then analyzing it. Dr. Leadbeater's group has been using Raman spectroscopy to monitor microwave-promoted reactions in real time. They developed a prototype Raman unit in conjunction with CEM Microwave Technology and EnWave Optronics. With real-time monitoring, they can optimize reaction conditions and stop a reaction when it is complete, avoiding decomposition or byproduct formation. By using only the minimum energy required for a reaction, they save considerable energy over other microwave technologies. With the Raman apparatus, they are probing the kinetics of reactions and comparing microwave and conventional heating in much more detail than was possible previously.

Dr. Leadbeater and Professor Cynthia McGowan from Merrimack College have written a manual, "Clean, Fast Organic Chemistry: Microwave-Assisted Laboratory Experiments", for use in undergraduate chemistry laboratories.

Atom Transfer Radical Polymerization with a Low Concentration of Copper Catalyst in the Presence of Environmentally Friendly Reducing Agents

Professor Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

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 then, Professor Matyjaszewski has been working continually to make the process more environmentally benign.

During the last four 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 producing many advanced polymeric materials in a more environmentally benign, green way.

Since 2002, ATRP has been licensed to 8 of the 15 corporations presently funding the research at CMU (PPG, Dionex, Ciba, Kaneka, Mitsubishi, WEP, Lion, and Encapson). Licensees have begun commercial production of high-performance, less toxic, safer materials including sealants, dispersants, coatings, adhesives, lubricants, additives, pigment dispersants, and materials for electronic, biomedical, health, and beauty applications in the United States, Europe, and Japan.

Professor Ramani Narayan, Department of Chemical Engineering & Materials Science, Michigan State University; KTM Industries, Inc.

Biodegradable Starch Foams for Protective Packaging

The annual U.S. market for cushioning foam is approximately $800 million (Freedonia Group, 2003). This market segment is facing growing pressure from regulations and initiatives in market-based sustainability and carbon management. Plastic foam packaging, often made from polyethylene, is not biodegradable; because it is lightweight, bulky, and not profitable to recycle, it presents a major disposal problem. There is also growing pressure to reduce the carbon footprint of packaging by switching to biorenewable feedstocks. Previous biobased foams have been brittle, however, and unsuitable for protective packaging products.

Professor Narayan and KTM Industries have successfully designed and engineered biodegradable, starch-based biofoams using a one-step, reactive extrusion process. The resulting foams have the flexibility and reduced moisture sensitivity to be suitable for protective packaging. This technology uses water as the plasticizer and blowing agent along with starch polymer modifiers. Water and the shear during the extrusion process break the hydrogen bonds holding the starch molecules and release the polymer chains without significantly reducing their molecular weight. Nucleating agents and process aids allow control of cell structure and foam flexibility. Screw configurations and designer screw elements control the foaming process.

Some of their patented biodegradable, chemically modified plasticized starches (CMPS) include starch (amylase and amylopectin), maleic anhydride, or other dibasic acids as modifiers, plasticizers like glycerol, and a free-radical initiator; they have also developed a version of CMPS with nanoclays. In other work, Professor Narayan and KTM Industries have developed foams for foam sheet manufacture by grafting poly(butylene adipate-co-terephthalate) (PBAT) or maleated PBAT onto starch. In lifecycle assessments, these foams compare favorably with polyethylene foams in all eight environmental impact categories except eutrophication.

KTM Industries has successfully commercialized the biodegradable, starch-based biofoam technology under the trade name of GreenCell™ for packaging automotive parts, printers, and electronic parts.

Highly Efficient, 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. Desymmetrization of symmetric compounds is one of the most cost-effective synthetic reactions because symmetric compounds are typically available commercially at low cost or are produced easily from inexpensive precursors on a large scale. Desymmetrization of symmetric organic compounds mediated by water has the potential to be a greener reaction process of tremendous synthetic value.

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 produces 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 pioneered and has been developing a highly efficient, practical monohydrolysis of symmetric diesters. Her reaction is the first 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. The reaction can also occur without THF. It uses only relatively simple apparatus, allowing large-scale production of half-esters and potential industrial applications. Professor Niwayama has filed a provisional patent for this work. She anticipates that this reaction will contribute to environmentally friendly green chemistry in industry and academia.

Doped Semiconductor Nanocrystals as Heavy-Metal-Free Quantum Dots

Professor Xiaogang Peng, Department of Chemistry and Biochemistry, University of Arkansas; Nanomaterials and Nanofabrication Laboratories, LLC (NN-Labs)

Nearly all the colloidal fluorescent quantum dots being produced today with quality high enough for real-world applications contain toxic heavy metals such as cadmium, mercury, and lead. Although these quantum dots have better size-dependent electrical and optical properties than do bulk semiconductors, they are not used widely, due in part to the toxicity of their heavy metals.

Other researchers have studied doped nanocrystals as alternatives to heavy-metal-based quantum dots since the 1980s, but they have not discovered reaction schemes that achieve pure dopant emission at high fluorescence quantum yield. Often, a large portion of the nanocrystals were undoped, resulting in emission peaks from both the undoped and doped nanocrystals.

Professor Peng and NN-Labs have developed a breakthrough synthesis for doped quantum dots (D-dot™) that are free of heavy metals. Professor Peng developed quantum dots that replace the toxic dimethyl metal precursors with metal oxides. This technology produces doped semiconductor nanocrystals with pure dopant emission (over 99 percent) at fluorescence quantum yields greater than 80 percent. These doped quantum dots do not suffer the reabsorption self-quenching inherent in intrinsically emitting quantum dots, due to the large Stokes shift between the host absorption and dopant emission. In addition, these new high-quality, doped quantum dots have far greater thermal and photo stabilities than do conventional quantum dots. The superior quality of these new, heavy-metal-free, doped quantum dots will enable quantum dot applications to reach the commercial level without introducing toxins into the environment. These quantum dots are a suitable alternative in many applications from solid-state lighting to biomedical labeling.

Professor Peng has filed a patent for this technology. During 2007, NN-Labs launched its first two doped nanocrystal product lines, Yellow and Orange D-dots™. It is developing a full spectrum of D-dot™ emitters.

Professor Arthur Ragauskas, School of Chemistry and Biochemistry, Georgia Institute of Technology

Developing Lignocellulosic Biorefineries

Lignin typically represents 20–30 percent of plant biomass. Catalytic oxidative cracking of lignin is a crucial component of the efficient conversion of biomass resources to biofuels, biochemicals, and biomaterials. At present, however, the only use of lignin is as a low-value heating fuel.

Historically, oxidation reactions have required stoichiometric amounts of oxidizing reagents that have considerable drawbacks such as high cost, waste byproducts, and serious environmental disposal issues. The traditional oxidants include $KMnO_4$, MnO_2, CrO_3, and Br_2. In comparison, molecular oxygen is a superior oxidant that is abundant, costs less, and has a better safety and environmental profile. Researchers have directed concerted effort at developing systems that use various transition metals to catalyze aerobic alcohol oxidation, but many of these catalytic systems also require aromatic or halogenated hydrocarbon solvents that are volatile organic compounds (VOCs).

Professor Ragauskas is focusing on developing catalytic systems to replace previous VOC solvents with ionic liquids. The unique properties of ionic liquids include low volatility, high polarity, selective dissolving capacity, and reaction stability over a wide temperature range. These properties lead many to recognize ionic liquids as attractive, alternative, green reaction media. Professor Ragauskas has developed ionic liquid systems that are capable of solubilizing lignin. He and his group have discovered novel aerobic catalytic oxidative systems that can functionalize or fragment lignin. They have developed an oxidative chemistry based on ionic liquids that exhibits excellent selective catalytic properties, allows simple recovery of product, recycles its catalyst, uses O_2 as an ultimate oxidant, and does not generate hazardous heavy metal wastes. Professor Ragauskas's oxidative system makes a unique contribution to green chemistry, especially in applications relevant to converting lignin to biodiesel and biogasoline.

In 2007, Professor Ragauskas published his recent work in the Journal of Organic Chemistry and in Tetrahedron Letters.

Professors Shelby F. Thames and James W. Rawlins, School of Polymers and High Performance Materials, The University of Southern Mississippi

Development of Commercial-Grade Particleboards Based Solely on Soybean Protein Adhesive

Commercial particleboards use urea–formaldehyde resins as the adhesive to bind wood furnish. The occupational exposure to formaldehyde during particleboard production and the slow liberation of formaldehyde during the service life of particleboards pose serious health concerns due to formaldehyde's toxicity and carcinogenicity. Professors Thames and Rawlins have developed adhesives based on soybean protein that yield particleboards with performance properties comparable or superior to commercial particleboards. These particleboards are free of synthetic formaldehyde precursors and petroleum derivatives.

The adhesive synthesis involves mechanically blending commercial-grade soybean protein at 70 °C for 3½ hours with water and various raw materials. The process is energy-efficient and does not involve toxic chemicals. The adhesive blends easily with wood furnish at ratios similar to those used for commercial particleboards. The manufacture of particleboard with their new adhesive releases water as the primary volatile material, unlike the manufacture of commercial particleboards, which liberates water, methanol, and formaldehyde.

Professors Thames and Rawlins have developed a range of particleboards that meet American National Standards Institute (ANSI) performance specifications for M-1, M-2, M-3, and M-S grades. The particleboards based on their soybean protein adhesive are totally biodegradable, as validated by soil biodegradability and marine respirometry studies. These particleboards can be safely discarded in landfills or marine environments at the end of their useful lives. If one percent of the 2006 production of particleboard had been made with their new adhesive, 10 million pounds of soybean protein would have been used and 16 million pounds of urea–formaldehyde resin would have been eliminated.

Professors Thames and Rawlins have received two patents for their work in this area; a third patent is pending. Several pilot-scale trials at a particleboard manufacturing plant in Texas have validated the scalability and feasibility of commercializing this soybean protein adhesive.

Vegetable Oil Based Macromonomers in Emulsion Polymers for High-Performance, Zero-VOC Architectural Coatings

Professors Shelby F. Thames and James W. Rawlins, School of Polymers and High Performance Materials, The University of Southern Mississippi

Most waterborne coatings contain significant levels of volatile organic compounds (VOCs) as cosolvents to facilitate efficient film formation of high-glass-transition-temperature polymers. Vegetable oil based macromonomers (VOMMs) are a series of vegetable oil derivatives functionalized for efficient incorporation into emulsions by copolymerization with conventional monomers. The synergistic combination of vegetable oil derivatives and an acrylic backbone provides storage-stable, self-cross-linking systems for architectural and industrial coatings with reduced- or zero-VOC emissions. Professors Thames and Rawlins developed a series of VOMMs including soybean oil amide acrylate (SoyAA-1), a monomer that imparts flexibility to emulsion polymers and can replace butyl acrylate.

Professors Thames and Rawlins have successfully formulated emulsions synthesized with up to 80 percent by weight of SoyAA-1 into zero-VOC, waterborne architectural coatings that perform competitively against commercial zero-VOC coatings. They have also formulated SoyAA-1 into low-VOC, waterborne Navy Haze Gray (NHG) coatings as a potential replacement for current NHG coatings formulated with solvent-based, silicone-modified alkyds that contain high levels of VOCs (336 g/L). Their SoyAA-1-based NHG coatings contain very low levels of VOCs (less than 15 g/L), have fast drying rates, and meet military specifications MIL-PRF-24635C and MIL-PRF-24596A. Additional advantages include easy clean-up, reduced fire hazards, and low toxicity to Navy personnel. Their coatings have passed initial trials at the Naval Research Laboratory in Washington, DC and are scheduled for evaluation onboard naval ships to simulate and characterize the coatings in actual use.

If one percent of the 2006 production of flat, water-thinned coatings had incorporated 20 weight-percent of SoyAA-1, almost 300,000 pounds of soybean oil would have been used and 2.1 million pounds of VOC emissions would have been eliminated. Upon commercialization, VOMM technology will have the ability to transform the marketplace: the resulting high-value-added monomers, polymers, and finished products would reduce the VOC emissions of coatings significantly without affecting their performance.

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

Passive Treatment of Metal-Contaminated Water

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 the western United States.

Passive treatment is a process for removing contaminant metals from water using natural materials such as wood chips, sawdust, 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. Natural, constructed, wetland structures filter these precipitates from water. The process does not require continuous monitoring. It requires only periodic inspections and sampling, cutting annual operating costs in half. This method of treatment is more sustainable ecologically than are conventional, active-treatment systems. Passive treatment both looks green and is chemically green.

Passive treatment was first successful at the Westfork Lead Mine in Missouri; since then, full-scale systems have been built for several private clients. The systems at all of these sites eliminate active precipitating chemicals, eliminate energy and material-intensive separation steps, and remove metal contaminants such as lead, cadmium, and arsenic, as well as zinc, copper, and mineral acidity from the water. Following these successes, the EPA recently adopted this technology at two places in the Ten Mile Creek Superfund Site near Helena, MT for a savings of over $100,000 per year.

Entries from Small Businesses

Advanced BioCatalytics Corporation

Changing the Nature of Surfactants: Protein Synergists with Microbial Uncoupling

Advanced BioCatalytics (ABC) has combined low-molecular-weight proteins from yeast fermentation (i.e., yeast stress proteins) with synthetic surfactants and adjuvants to develop a family of products. These products are cost-effective, nontoxic, and fully biodegradable. They exhibit low surface tension (especially low interfacial tension), reduced critical micelle concentration, high wettability, and efficient penetration. Besides optimizing surface energies, ABC products activate natural bacterial metabolism by the partial, nonlethal, uncoupling of bio-oxidation from biosynthesis. This accelerates the bio-processing of organic contaminants to carbon dioxide, with lower accumulation of biomass. Increased nutrient uptake includes reduction of biochemical oxygen demand (BOD) in wastewaters due to digestion and prevention or reduction of biofilming (for example, in wastewaters, cross-flow membranes, and porous surfaces) to enhance cleaning efficiency.

The protein system directs natural microflora metabolism to convert hydrophobic contaminants such as grease and oil into additional surfactants, creating an autocatalytic effect. The key benefit is a significant decrease in the volume of surfactants, organic solvents, or chemicals required. For example, in coating hydrophobic diaper linings to achieve acceptable strike-through, the ABC product reduced the amount of surfactant by over 90 percent. By reducing BOD, ABC cleaners start digestion of organic nutrients at the point of use, greatly reducing the volume of both grease in sewer lines and sludge in wastewater treatment systems. These products also save a substantial amount of energy.

ABC products have many current and potential uses including enhanced oil recovery, degreasing, cleaning, wastewater sludge reduction, and control of odor and biofilm. Several cities currently use ABC's Clean 'N Green™ Cleaner/Odor Remover and major hospital chains have approved it for use. In 2007, ABC commercialized its Accell Clean™ for cleaning tanks of marine ships. The U.S. Coast Guard has approved Accell Clean™ for marine applications, as have numerous international ship lines.

The Adventus Group

EHC™ for a Greener Groundwater Treatment Technology

The patented EHC™ technology is a remediation product used for the in situ treatment of groundwater and saturated soil contaminated with persistent organic compounds. EHC™ is an injectable material composed of microscale zero-valent iron (ZVI) and food-grade organic carbon (solid or liquid) that ferments slowly to release fatty acids and nutrients in situ. The product supports rapid and complete destruction of chlorinated solvents, explosives, pesticides, and many other persistent compounds that may be present as contaminants in soil, sediment, and groundwater.

EHC™ works through a number of mechanisms: (1) direct abiotic reduction due to contact with the zero-valent iron; (2) enhanced thermodynamic conditions due to lowered redox potential; (3) indirect chemical reduction by reduced metals; and (4) biostimulation of dehalogenating bacteria down-gradient from injection locations.

Because it is, in part, a plant-based material, EHC™ can provide safe, renewable, cost-efficient, and effective remediation for many sites. Compared to some in situ chemical oxidation (ISCO) technologies, EHC™ is nonhazardous and much less disruptive of natural ecosystems. Compared to conventional organic substrates, ZVI and the complex carbon source in EHC™ minimize the production of potential fermentation end-products, such as methane. ZVI provides a substantial pH-buffering capacity, whereas conventional organic substrates can lead to aquifer acidification that adversely influences the natural attenuation mechanisms. EHC™ supports the complete dechlorination of trichloroethylene, tetrachloroethylene, and carbon tetrachloride without the accumulation of metabolites; this is a key factor differentiating EHC™ from competitive groundwater treatment technologies such as molasses, lactates, and vegetable oils. An EHC™ injection is typically required only once and is complete in one to two weeks with an active lifespan of three to five years in groundwater, minimizing its carbon footprint.

Since the first field-scale project in 2004, EHC™ has been used to treat approximately 100 locations around the globe.

ChK Group, Inc.

Nanophase Mn(VII) Oxide: Synthesis using Green Technology and Applications

The formation and stabilization of nanophase Mn(VII) oxide (i.e., NM7O) is central to the ChK Group's innovative technology. The starting material is a beige-colored mineral, hydrated Mn(II); upon addition of 1,4-phenylenediamine (PDA), it forms NM7O, which is violet-colored. The mechanism appears to be the oxidation of PDA to 1,4-benzoquinone in the presence of air, which then oxidizes the hydrated Mn(II) to NM7O. Scanning electron microscope (SEM) analysis shows a globular NM7O mass with particle sizes of 50–100 nm. Cyclic voltammetry and optical spectroscopy confirm the Mn^{7+} oxidation state.

NM7O is a safe product compared to harsh, toxic competing products. It is nonflammable and is safe for disposal in municipal landfills after use. NM7O is a super Lewis acid: it attacks compounds with lone pairs of electrons, such as cyclohexylamine and cyclohexanone. It removes odors by destroying amine compounds and converting thiol groups to disulfides. It also neutralizes surrogates for chemical warfare agents (CWAs) such as 2-chloroethyl ethyl sulfide (CEES, a mustard gas analog) and dimethyl methylphosphonate (DMMP, a sarin gas analog). In addition, it makes a good polish for silver.

ChK recently discovered that NM7O is good algaecide and bactericide; it does not, however, destroy aquatic fauna or flora. After reduction, the violet-colored NM7O changes to brown-black-colored, environmentally safe Mn(IV) oxide, allowing its use as an optical sensor. ChK has coated NM7O on and impregnated it into nonwoven and melt-blown fabrics. The treated fabrics can be incorporated into wipes and liners for consumer and industrial uses, clothing, and materials for military and homeland security uses.

The NM7O manufacturing process has received a U.S. patent; another patent is pending on its use to destroy CWAs; and ChK has filed provisional patents on NM7O-coated fabrics and the use of NM7O to destroy nuisance and pathogenic microorganisms. ChK has successfully manufactured clay-coated NM7O on a pilot scale.

Greening Atorvastatin Manufacture: Replacing a Wasteful, Cryogenic Borohydride Reduction with a Green-by-Design, Economic Biocatalytic Reduction

Codexis, Inc.

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 (i.e., ATS-8, also known as TBIN). It is the first isolated intermediate comprising both of atorvastatin's chiral alcohol centers. Pfizer's ATS-8 process uses a sodium borohydride ($NaBH_4$) reduction of the corresponding (5*R*)-hydroxy-3-ketoester (ATS-6, HK) enantiomer under cryogenic conditions to give, after quenching, the (3*R*,5*R*)-dihydroxyester (ATS-7, diol). The ATS-6 is converted in situ to a diastereodirecting boron chelate using hazardous diethylmethoxyborane, which is then reacted with $NaBH_4$ at or below -85 °C to further promote diastereoinduction. After reaction, the borane reagent is regenerated and recovered by repeated methanol quenches and vacuum distillations. Still, the diastereoinduction is inadequate, as several percent of the wrong (3*S*) diastereomer is formed. Subsequently, the ATS-7 diol, an oil, is protected as its acetonide, ATS-8, whose diastereopurity must be upgraded by crystallization, with concomitant product loss.

Codexis developed a greener, more economical process for reducing ATS-6 to diastereopure ATS-7. Codexis used advanced, recombination-based directed evolution to modify a ketoreductase biocatalyst so that it would reduce ATS-6 with perfect diastereoselectivity. This evolved ketoreductase exhibits high activity and stability. It works well at high substrate loading under greener, ambient, neutral aqueous conditions in conjunction with a previously evolved, process-tolerant, glucose dehydrogenase biocatalyst. It obviates 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 more stereopure ATS-7. Before any crystallization, the ATS-7 diol from this reaction and the ATS-8 produced from it are more diastereopure than the atorvastatin in Pfizer's Lipitor® pills. Codexis's biocatalytic process is already supplying over five metric tons per month of high-quality ATS-8 to generic atorvastatin manufacturers at shut-down prices compared to the captive production costs of Pfizer's original synthesis.

Greening Montelukast Manufacture: Replacing a Stoichiometric Chiral Boron Reagent with a Green-by-Design, Economical Biocatalytic Reduction Enabled by Directed Evolution

Codexis, Inc.

Methyl (*S*,*E*)-2-(3-(3-(2-(7-chloroquinolin-2-yl)vinyl)phenyl)-3-hydroxypropyl)-benzoate (MLK-III) is the key chiral intermediate in the manufacture of montelukast sodium, the active pharmaceutical ingredient in Merck's bronchodilator, Singulair®. The innovator's ketone reduction to this chiral alcohol requires at least 1.8 equivalents of the expensive, hazardous reductant (–)-β-chlorodiisopinocampheylborane ((–)-DIP-Cl) in tetrahydrofuran (THF) at -20 to -25 °C. After quenching, an extraction is required to remove spent borate salt waste. The reduction produces the *S*-alcohol in 97 percent enantiomeric excess (e.e.) and requires crystallization to give 99.5 percent e.e. in 87 percent isolated yield.

Codexis developed a green, more economical biocatalytic reduction to manufacture MLK-III with a ketoreductase biocatalyst evolved to reduce MLK-II, its ketone precursor. No naturally occurring or commercially available ketoreductase shows activity toward MLK-II. Codexis used a minimally active ketoreductase it had evolved previously and evolved it further to increase its activity and stability by over 2,000-fold, replacing one-third of the amino acids in its active site in the process.

The evolved ketoreductase produces MLK-III with essentially perfect enantioselectivity under greener reaction conditions: 100 g/L in isopropanol–water–toluene and 45 °C. Isopropanol is the reductant, which the ketoreductase uses to regenerate its catalytic cofactor NADPH, producing acetone as the coproduct. The process runs as a slurry-to-slurry conversion with product precipitation driving the reaction to completion. The precipitated chiral alcohol is of high chemical purity and exquisite stereopurity. (The distomer is undetectable.) Filtration and washing then recover MLK-III. The process replaces the hazardous boron reagent, greatly reduces organic solvent use, essentially eliminates inorganic salt waste, uses less energy, and provides a higher yield of MLK-III in higher stereopurity.

With its commercial manufacturing partner, Arch Pharmalabs, Codexis has scaled up the manufacture of MLK-III using this biocatalytic reduction and has provided samples of MLK-IV to manufacturers of generic montelukast. Codexis has scheduled commercial manufacture on the multi-ton scale in 2008.

Codexis, Inc.

Rapid Enablement of Green-by-Design Economic Processes for Chiral Alcohols by a Platform of Recombinant, Robust, Divergent Evolvants of a Single Ancestral Ketoreductase

Chiral secondary alcohols are intermediates in syntheses of numerous chiral active pharmaceutical ingredients (APIs). They are commonly produced from the corresponding ketones using hazardous boron-based reducing agents or asymmetric catalytic reduction. Typically, these reduction methods give imperfect stereoselectivity and require additional purification with concomitant losses in yield.

Biocatalytic reduction of ketones has long been recognized as an attractive greener alternative to hazardous reagents and energy- or mass-intensive processes for manufacturing chiral alcohols. This promise went largely unfulfilled, however, because available ketoreductase (KRED) biocatalysts had drawbacks including narrow substrate-specificity, low activity, poor in-process stability, inadequate stereoselectivity, and productivity-limiting product inhibition.

Codexis's widely applicable platform of pre-evolved, diverse KREDs from a common wild-type ancestor successfully meets industry's needs for greener processes for chiral alcohols both for launched active pharmaceutical ingredients and for new candidates under development. The Codex™ KRED Panel comprises 180 variants of one wild-type KRED that are pre-evolved for in-process thermal and solvent stability as well as efficient manufacture. The amino acid sequence of each variant is known. As a population, the variants contain combinatorial mutations that confer activity on a wide variety of ketones and selectivity to either alcohol stereoisomer. The variants are arrayed on microtiter plates for rapid screening to find the desired activity on a new ketone substrate and to obtain amino acid sequence versus activity data for further rapid evolution if needed. Codexis has evolved KREDs for activity on a wide structural variety of ketones, including some for which the wild-type ancestor showed no detectable activity and some in which the stereoselectivity of the evolved KRED is reversed from that of the natural enzyme.

Codexis has evolved ketoreductases to manufacture the chiral intermediates for a number of drugs. During 2007, Codexis launched its Codex™ KRED Panel as a development tool on a subscription basis; Merck is now using it successfully.

Elimination of Hexavalent Chromium Used in Hydraulic and Pneumatic Tubing

Commercial Fluid Power LLC

Chrome-plated rods and tubes are the backbone of hydraulic and pneumatic cylinders. Chrome plating produces an excellent wear surface, great lubricity, and good corrosion resistance. Chrome-plated cylinders are economical, time-tested, and readily available. The fluid power market relies heavily on chrome-plated tubes to manufacture pneumatic and hydraulic cylinders, but the hexavalent chromium (Cr(VI)) used in the plating process is carcinogenic.

Commercial Fluid Power is taking steps to help reduce the use of industrial hard chrome or engineered chrome in the fluid power market. Together with MACSTEEL's NitroSteel Division, Commercial Fluid Power has developed Nitro-tuff tubes, a product that replaces chrome-plated interior diameter (CPID) tubing and chrome-plated outside diameter (CPOD) tubing used to manufacture hydraulic and pneumatic cylinders. Nitro-tuff tubes are made by the ferritic nitro-carburizing of steel in ammonia and a carrier gas, followed by treatment with an oxidizing atmosphere to produce a thin, corrosion-resistant, black-colored surface film. A light polishing of the nitrided surface gives the product a more acceptable chrome-like surface that maintains its corrosion resistance. This improved appearance has opened new markets, especially in high-cycle cylinder applications such as shock absorbers.

The nitro-carburizing and oxidizing process can reduce the mechanical strength of the steel base material. Commercial Fluid Power and MACSTEEL selected a suitable base material, St52.3 SRA DOM, which maintains the mechanical strength of their tubing. This base material also exhibits better ductility under a severe side load. The two companies now recommend their chromium-free, St52.3 SRA DOM nitride-treated tubing for pneumatic cylinder applications.

Commercial Fluid Power will promote these environmental benefits actively during 2008. The journey for a safer more environmentally friendly replacement product at Commercial Fluid Power is ongoing.

Corrosion-Control Chemicals Based on Sustainable Resources

Cortec Corporation

Corrosion of metals is a natural process during which metals oxidize, returning to their natural state. Selected chemicals can prevent, control, and slow down the corrosion of metals. The chemistry of preventing, cleaning, and retarding corrosion differs for each task.

Cortec (<u>cor</u>rosion <u>tec</u>hnology) develops and provides products for corrosion control. Eight years ago, Cortec began a program to use chemicals derived from sustainable resources whenever possible in developing new products and changing old ones. For example, Cortec can use *d*-limonene as a replacement solvent and can replace a petroleum product with a vegetable oil.

Cortec now sells eleven corrosion control products based on soybean oil, canola oil, and castor oil, six based on gluconates, and one based on soy protein. It also sells three films with vapor corrosion inhibitor properties based on polylactic acid. Its most successful product uses gluconic acid derivatives from sugar beets as components of migratory corrosion inhibitors to protect the reinforcing steel (rebar) in concrete.

Cortec has received nine U.S. patents for its new systems. Most recently, Cortec published a paper on water-treatment products formulated from biodegradable raw materials.

Cutting Edge Formulations, Inc.

Nature's Avenger® Organic Herbicide: A Fast-Acting, Highly Effective, Organic Alternative to Synthetic and Natural Herbicides

Nature's Avenger® Organic Herbicide (NAO) is a GRAS (generally recognized as safe), highly biodegradable, extremely effective, nonselective, post-emergent herbicide that is approved by the EPA for organic agricultural production. Its active ingredient, *d*-limonene (citrus oil), is found naturally in more than 300 herbs, edible plants, and fruits. *d*-Limonene is used in many soaps, detergents, commercial cleaners, deodorizers, shampoos, and mouthwashes. It has proven to be a strong, natural, degreasing agent that acts by stripping away the waxy cuticle from weeds, subsequently dehydrating and killing them. *d*-Limonene is also a flavoring agent in many foods.

The volatility of *d*-limonene makes it a relatively weak herbicide. Cutting Edge Formulations (CEF) has spent considerable resources to develop proprietary emulsions that reduce the volatility of *d*-limonene substantially. Their emulsions ensure that *d*-limonene remains on plant surfaces longer and thus eradicates weeds more quickly. CEF research showed that increasing the pH significantly enhances the herbicidal efficacy. A mixture of proprietary inert ingredients also contributes to activity. NAO is comparable in effectiveness to glyphosate and paraquat, which are synthetic, non-organic herbicides. NAO also acts faster.

In consumer and professional markets, the availability of a safe, efficacious, organic herbicide provides an important alternative to both synthetic products and less-effective natural products. In the organic agricultural market, organic growers control weeds primarily with mechanical tillage and hand labor, which is extremely expensive at approximately $1,000 per acre. Combining mechanical tillage with NAO in areas that cannot be mechanically tilled would bring an organic grower's cost for NAO into a range of $45–80 per acre, which is within the range that traditional, non-organic growers pay for weed control. The availability of an easy-to-use, effective, cost-effective organic herbicide will revolutionize how organic growers control weeds.

During 2007, NAO received listing by the Organic Materials Review Institute (OMRI).

DuraBan International, Inc

Environmentally Friendly Antimicrobial Surface Treatment

DuraBan International has improved upon 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride (Si-QAC), an amino-functional silane developed originally by the Dow Chemical Company. Dow's product had antimicrobial activity, but was unstable and polymerized in water; it required methanol for stability as well as certified applicators.

DuraBan International developed the first water-stabilized Si-QAC that does not incorporate any chemical stabilizer and, thus, does not leach off treated surfaces. Unlike other antimicrobials that can leach toxic chemicals into the environment, DuraBan is virtually nontoxic. DuraBan does not release any toxic gases, volatile organic chemicals (VOCs), heavy metals, formaldehyde, or phenol. Either standing alone or built into products during manufacture, DuraBan's Si-QAC inhibits the growth of microbes (e.g., bacteria, mold, and mildew) that can cause stains, odors, and product deterioration.

Once applied, DuraBan bonds chemically to the product surface, creating a permanent antimicrobial barrier that destroys microorganisms upon contact by rupturing their cell membranes. DuraBan's proprietary, patented antimicrobial technologies deliver unmatched performance, durability, and efficacy through a unique formulation based on surface-modifying nanotechnology.

DuraBan products serve as powerful antimicrobial barriers for consumer, industrial, and medical products. This technology can be engineered into many surfaces and materials including coatings, polymers, textiles, lumber, plastic, and adhesives. DuraBan antimicrobials have never been shown to allow or cause microbial adaptation, resistance, mutation, diffusion, or migration. When incorporated into everyday products that often encounter bacteria, DuraBan can positively benefit the environment and prevent the spread of superbugs, including MRSA (methicillin-resistant *Staphylococcus aureus*) and VRE (vancomycin-resistant enterococcus). Henry Ford Hospital recently completed an extensive study in which DuraBan reduced MRSA and VRE contamination by over 85 percent compared to untreated surfaces. The hospital also found that clothing treated with DuraBan remained 94 percent effective after 50 washes.

Four of DuraBan's products are registered as pesticides by the EPA: MicrobeGuard, DuraBan I, DuraBan, and Mold Shield.

Enabling Technology for Methacrylic Acid Production using Isobutane as the Feedstock

EverNu Technology, LLC

Methacrylic acid (MAA) and its methyl ester, methyl methacrylate (MMA), are high-volume commodity chemicals that are building blocks for polymers used widely in the construction, automobile, appliance, and coating industries. Since the 1930s, the production of MAA and MMA in the United States has used the conventional acetone–cyanohydrin (ACH) process, whose feedstocks are acetone and highly toxic hydrogen cyanide (HCN). The production of one ton of MAA requires at least 0.31 ton of HCN along with 1.6 tons of concentrated sulfuric acid as both solvent and catalyst. It also generates 1.2 tons of ammonium bisulfate requiring disposal. In 2005 alone, the U.S. production of 1.82 billion pounds of MAA and MMA consumed at least 558 million pounds of HCN, used and regenerated about 2.88 billion pounds of concentrated sulfuric acid, generated and disposed of 2.16 billion pounds of ammonium bisulfate, and generated tens to hundreds of billion pounds of aqueous waste discharges.

EverNu has developed a patent-pending technology that uses proprietary, stable, metal oxide catalysts to produce MAA from isobutane and air as the only feedstocks. This technology has a significant economic benefit because isobutane costs only a fraction of the cost of acetone and HCN. It also saves tens of trillion Btu of energy per year because the partial oxidation of isobutane to MAA is an isothermic reaction. The environmental benefits are enormous. They include (1) completely eliminating the use of large quantities of HCN and sulfuric acid; (2) avoiding the generation and disposal of toxic, corrosive wastes from HCN and sulfuric acid; and (3) substituting the nontoxic feedstock isobutane, which is inherently much safer than HCN and sulfuric acid with regard to worker exposure and accident potential. Recent research indicates that isobutane can be obtained from renewable sources in the future.

Everdex-Enhanced Alowood

EverTech LLC

Deforestation of old-growth forests and rainforests is of growing concern given today's far-ranging debates on climate change. Although only 22 percent of the world's old growth forests remain intact, consumers still want the look of exotic hardwoods in products such as flooring and furniture.

Alowood offers an environmentally friendly alternative: an exotic look and performance using fast-growing plantation softwoods impregnated with the Everdex formulation, an innovative green chemistry. Everdex is a polymeric formulation made from urea, glyoxal, and starch in water along with environmentally friendly dyes and pigments; it does not contain any formaldehyde. Softwoods, particularly sustainably grown, plantation softwoods, are impregnated with dilute solutions of Everdex by a vacuum-pressure treatment. 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. During 2007, Alowood received GREENGUARD Indoor Air certification and class A fire retardant certification.

EverTech is currently selling Everdex-enhanced Alowood to the building industry as an alternative to natural hardwood. This innovative product is making a significant positive environmental impact: 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 10–20 years, is preferable to exotic hardwoods that often take hundreds of years to grow. In the time it takes a hardwood forest to rejuvenate, a softwood plantation of the same size could be harvested up to 100 times for use in Alowood. To date, over 2 million board feet of Alowood are on the market, saving over 10,000 hardwood trees.

G3 Technology Innovations, LLC

Surface Functionalized Nanomaterials: Significantly Reducing Fluorochemicals in Consumer Items

Fluorochemicals are used in many consumer products such as stain-resistant clothing, upholstery, carpets, paper, and non-stick coatings and paints. Certain fluorochemicals, however, persist in the environment, bioaccumulate, and have been deemed probable carcinogens by the EPA. Fluorochemical pollution from consumer products represents a significant environmental problem.

G3 Technology Innovations (G3*i*) has commercialized *SF*Nano™, a technology that reduces the use of fluorochemicals by at least a factor of eight. The technology mimics the natural water-repellant surfaces of those plants whose hierarchical surface roughness limits the contact angle of fluids. Water beads up and rolls off the leaves of many plants without wetting their surfaces. The G3*i* technology duplicates this effect, protecting consumer products including fabric, wood, paper, and stone from water damage through a simple coating process.

The G3*i* technology allows the facile surface functionalization of nanoparticles with groups of functional molecules. The technology uses common, colloidal silica nanoparticles that have been commercially available for over 60 years and are generally considered safe from an environmental perspective. Nanoparticles from these silica colloids, surface-modified with 5 nm zirconia particles, provide the scaffold to attach hydrophobic molecules (carboxylates or sulfonates). Amines are added to bond covalently to the substrate, such as a textile, and a small amount of fluorochemical is added to repel oil. When applied to a surface, the particles provide a micro- or nanoscopic roughness, like that of plant leaves. The hydrophobic molecules on the nanoparticle surfaces also repel water and dirt. The innovation has multiple human health and environmental benefits. It can be applied to a wide range of consumer items, providing an effective replacement for fluorochemicals or a means to reduce their use significantly.

Recently, Scientific Certification Systems certified this technology and its high performance at low fluorochemical loadings. G3*i* currently sells products based on its technology in the textiles market as GreenShield™.

H-O-H Chemicals, Inc.

Electrochemical Control of Mineral Deposition in Open Evaporative Cooling Water Systems: H-O-H Chemical's Green Machine

Cooling tower systems use hundreds of billions of gallons of water annually in the United States. These systems are subject to at least three significant challenges: mineral scaling, corrosion, and microbiological growth. Traditional chemical treatments to control deposits either (1) eliminate calcium carbonate by removing one of the scale-forming components (calcium by ion exchange or carbonate by adding acid) or (2) slow the rate of formation of calcium carbonate by treatment with other, less-hazardous chemicals. The latter treatment, however, uses 25–50 percent more water because it requires removing mineral-saturated water from the system and replacing it with fresh water.

The inspiration for a replacement technology was the fouling of cathodes by dissolved calcium salts that interferes with metal plating and water electrolysis operations. For H-O-H Chemicals, this classical nuisance suggested a mechanism to control troublesome deposition throughout large, real-world recirculating water systems.

Electrolysis of a meta-stable, supersaturated solution forms slow-to-precipitate, insoluble salts such as calcium carbonate. This technology may be employed to control deposit formation on heat exchange and other surfaces in systems such as industrial process water and evaporative cooling water loops. Hydroxyl ions formed at the cathode greatly accelerate the formation of calcium carbonate, such that the formation of ion clusters and crystalline calcium carbonate in the bulk phase cooling water is selectively diverted to the cathode. Properly engineered, side-stream electrolysis of recirculating cooling water can create a deposition gradient more than 1,000 times greater than anywhere else in a cooling system and, thereby, force deposition to occur within the electrolysis unit and nowhere else throughout an evaporative cooling water system. This technology also has implications for environmental and economic benefit. Potential water savings are substantial. Over 50 cooling systems in the United States now use electrolytic deposit control.

Inland Environmental Resources, Inc.

Environmentally Friendly, Antacid Formulations for Wastewater Treatment

For centuries, humans have used limestone and milk of magnesia (magnesium hydroxide) for medicinal antacid relief in their digestive systems. More recently, people have been using commercially formulated antacids that contain blends of metal hydroxides and metal carbonates. Despite these well-known medicinal benefits, no one thought until recently of using formulated antacid products for large-scale municipal and industrial wastewater treatment processes, which typically use hazardous alkaline chemicals such as caustic soda, lime, or soda ash.

Inland Environmental Resources, Inc. (IER) has invented antacid slurry formulations to treat wastewater on an industrial scale. These formulations use chemicals that are nonhazardous, environmentally friendly, and safe to handle. Each of IER's formulations (called Amalgam® products) contains a blend of hydroxides or carbonates of magnesium, aluminum, calcium, or potassium. Amalgam® products reduce phosphorous, total suspended solids (TSS), and biological oxygen demand (BOD) in wastewater, simultaneously boosting the pH of acidic wastewater streams. The reuse of Amalgam®-treated wastewater for land irrigation provides mineral nutrients to the soil, as opposed to the negative environmental impacts of irrigating crops with reclaimed water containing caustic or soda ash. Finally, Amalgam® formulations are less expensive to use than caustic soda, the industry standard.

With products that are much safer to handle, environmentally beneficial, better performing, and less expensive, IER has been growing very rapidly into the wastewater treatment market. Currently, IER is exploring other processes that require pH buffering as markets for its green chemical antacid formulations. It is developing new Amalgam® formulations to replace caustic soda in the recovery of chromium in the tanning process and to increase the yield of ethanol in the fuel ethanol industry. Since 2004, IER has constructed two manufacturing plants and a pilot plant. It has also filed a patent for its technology.

International Polyol Chemicals, Inc. (IPCI)

Production of Diverse Industrial Glycols from Renewable Six- and Five-Carbon Sugars and Glycerin, the Byproduct of Biodiesel Manufacture

The world market for glycols is approximately 20 million metric tons per year. The world's glycols are derived from natural gas or naphtha, except for those glycols derived from renewable feedstocks using a process developed by IPCI and its partners. The IPCI process converts C_5–C_6 monomer sugars continuously to alditols (e.g., glucose to sorbitol; fructose to mannitol) using a proprietary nickel-based catalyst in aqueous solution at pH above 10, pressure in the range of 2,000 psi, and 200 °C. A second hydrogenolysis step converts alditols continuously to glycols in excess hydrogen using a proprietary catalyst developed by Süd-Chemie Inc. The products include propylene glycol, ethylene glycol, and butanediol isomers. IPCI can shift its process to vary the products and allow market flexibility. Glycerin (C_3; a lower-valued byproduct of biodiesel production) can be directly subjected to hydrogenolysis, producing predominantly propylene glycol and ethylene glycol. Similarly, xylose and arabinose (C_5-sugars) can be hydrogenated to xylitol or arabinitol, respectively, and then converted to glycols. IPCI has also developed technology to separate close-boiling glycols using extractive and azeotropic distillation.

Overall conversions of sugars to glycols exceed 85 percent, which is about twice the yield of bioethanol from fermentation. Also, glycols are over twice as valuable as ethanol. One key product is 1,4-butanediol, the acetylene-based glycol used in engineering plastics and as an important precursor. Byproducts other than glycols are low-molecular-weight alcohols (ethanol, methanol, and propanol).

The IPCI process is inherently safer than other glycol manufacturing processes. Edible sugars are safe for the environment and humans. Water is the only solvent and both process catalysts and byproduct hydrogen are recyclable.

IPCI holds five sugar-to-glycol process patents and six glycol separation patents. Süd-Chemie holds two patents for the catalysts used in this process. Following completion of two smaller plants in the United States, a 200,000-metric-ton-per-year plant was completed in China in 2007.

Biodegradable Starch Foams for Protective Packaging

KTM Industries, Inc.; Professor Ramani Narayan, Department of Chemical Engineering & Materials Science, Michigan State University

NOTE: This project is the result of a partnership between Professor Ramani Narayan of Michigan State University and KTM Industries. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 12.

Microbial Production of Renewable Diesel Fuel

LS9, Inc.

Developing large-scale, sustainable replacements for petroleum is a national priority for environmental, political, and economic reasons. In 2007, the United States consumed 5.5 billion barrels of transportation fuel, increasing its reliance on foreign petroleum and releasing 2.5 billion tons of carbon dioxide and other pollutants into the atmosphere.

To realize the greatest potential for rapid, widespread adoption, a replacement fuel must be renewable, scalable, domestically derived, cost-competitive with petroleum, and compatible with the existing distribution and consumer infrastructure. LS9 has developed an efficient fermentation process to produce diesel fuel that meets these criteria. LS9 created metabolically engineered industrial microbes with a novel biosynthetic pathway: these microorganisms produce fatty esters and secrete them into the fermentation medium. The fatty esters are immiscible with the fermentation medium, obviating the need for distillation. LS9's biosynthetic pathway enables precise genetic control of the molecular composition and, hence, the performance characteristics of the resulting end products. LS9 can produce its biodiesel from diverse plant-based feedstocks. LS9 is now producing fuel that is superior to other plant-derived biodiesels in performance, yield, and cost.

Substituting LS9 diesel for petroleum-based diesel will reduce greenhouse gas emissions substantially; LS9 estimates that emissions from its diesel are as low as 20 percent of emissions from petroleum-based diesel. Unlike petroleum-based diesel, LS9's renewable diesel does not contain the environmental pollutants sulfur or manganese.

At current sugar prices, LS9 estimates that its diesel can compete with diesel made from $45-per-barrel petroleum without government subsidy. The LS9 technology anticipates bringing fundamental change to the biofuels landscape, setting the stage for rapid product adoption and widespread displacement of the petroleum-based diesel currently consumed by both households and industry. During 2007, LS9 filed several patent applications, demonstrated its technology in a 10-liter fermentor, and obtained over $20 million to finance further product development.

On-Site Generation of Mixed Oxidants as a Safe, Green Alternative to Chlorine Gas and Concentrated Bulk Bleach

MIOX Corporation

Although chlorine gas and bulk bleach have been used for 100 years to disinfect water and have saved countless lives in the process, these hazardous chemicals are now pervasive around the world. MIOX has developed on-site generation (OSG) of chlorine-based mixed oxidant solution (MOS) using low-cost salt brine (aqueous NaCl). This technology converts a brine solution electrolytically on-site and on-demand to produce MOS, which is a 0.4 or 0.8 percent chlorine-based disinfectant that is stored and metered at concentrations of less than one percent. This process is superior to bulk bleach and chlorine gas in safety, effectiveness, and cost. It eliminates the hazards associated with traditional technologies, reduces energy outputs, and inactivates water-borne pathogens immune to chlorine disinfection. Further, transporting salt rather than fresh bulk liquid bleach reduces the addition of carbon to the atmosphere by 3–6-fold. MIOX's technology is scalable from individual use to large cities. It offers significant chemical benefits including reducing the byproducts of chlorine disinfection, reducing disagreeable tastes and odors, reducing maintenance required by residual chlorine in water distribution systems, and eliminating biofilms. MIOX equipment produces a safe solution with capital payback periods of approximately three to five years.

MIOX's technology replaces hazardous chlorine gas and bulk sodium hypochlorite with OSG of MOS using sodium chloride, water, and electricity as the feedstocks. Salt is a harmless, renewable green chemical feedstock. More important, however, MOS is safer with regard to accident potential, has low operating costs, and produces treated water that is safer for humans because the MOS disinfectant kills microorganisms more effectively and produces fewer harmful chlorinated byproducts. The removal of biofilms from heat exchangers, piping systems, and other surfaces by MOS increases the efficiency of this equipment, which also reduces carbon footprints.

During 2007, MIOX launched RIO, its product line to generate industry-leading, on-site, on-demand disinfectant.

Nanomaterials and Nanofabrication Laboratories, LLC (NN-Labs); Professor Xiaogang Peng, Department of Chemistry and Biochemistry, University of Arkansas

Doped Semiconductor Nanocrystals as Heavy-Metal-Free Quantum Dots

NOTE: This project is the result of a partnership between Professor Xiaogang Peng of the University of Arkansas and Nanomaterials and Nanofabrication Laboratories, LLC. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 13.

Organic Recovery, LLC.

Biochemical Hydrolyzation of Organics in Food Wastes into a Liquid Fertilizer and Soil Amendment

Most agricultural growers use a variety of petrochemical fertilizers, pesticides, and fungicides. There is, however, growing concern that these chemicals in the air, soil, and groundwater are harming the health and safety of humans and wildlife.

Organic Recovery has developed a rapid, batch process to convert food waste into organic-based liquid fertilizers as a less-expensive, environmentally safe alternative to petrochemical fertilizers. The process uses a proprietary mixture of enzymes that may include xylanase, asparaginase, cellulase, urease, protease, lipase, and carbohydrase. The enzymes degrade the lignocellulosic cell walls, proteins, lipids, and starches present in the food wastes. Food-grade phosphoric acid or other acid is added to stop the enzymatic digestion before completion; this stabilizes the enzymes and nutrients in the concentrated fertilizer. For use, the fertilizer is mixed with water, adjusted to neutral pH, and applied to soil. The enzymes resume activity, breaking down proteins and releasing the nutrients and trace minerals that are locked up in the soil. The liquid fertilizer is biodegradable; applied to soils, it adds nutrient- and water-holding capacity. The biochemical hydrolyzation process requires significantly less effort and energy than other methods of recycling food and other organic wastes or producing petrochemical fertilizers.

Organic Recovery's process prevents the formation of carbon dioxide and methane; it is the only known way to sequester carbon from food waste. This technology can be used in communities needing to minimize carbon emissions, improve their recycling rate, and increase the capacity of their waste disposal facilities. The technology requires significantly less space than competing technologies. Because it is scaled to meet community needs, it keeps the procurement of feedstock and selling of the liquid fertilizer products local, further minimizing adverse impacts on the environment.

During 2007, Organic Recovery constructed a 60-ton-per-day, full-scale processing facility in Florida. It also filed for a patent on its technology.

Perchlorate-Free Pyrotechnic Composition for Military Training Munitions

Pyrotechnique by Grucci, Inc.

The U.S. Department of Defense uses many types of nonlethal training munitions on its installations and ranges. Two of the most widely used devices are M116A1 hand grenade simulators and M115A2 ground-burst simulators. Both simulators have traditionally employed a pyrotechnic composition based on potassium perchlorate and flaked aluminum, which react to produce the spectacular visual and auditory effects (i.e., flash and bang) required to prepare soldiers, sailors, airmen, and marines for combat.

Recently, there has been increasing awareness of the environmental and human health impacts of perchlorate compounds and concern for uses that release them into the environment. Perchlorate is both highly soluble in water and persistent; it has now been found in drinking water in at least 34 states.

Grucci, Inc. (the manufacturer of the simulators) joined a team of U.S. Army scientists and engineers to design a chemical composition that is less toxic, but still produces the same pyrotechnic effects. The team formulated, tested, and evaluated several perchlorate-free compositions. They used a unique environmental health assessment strategy to predict the toxicity and other hazards of the candidate compositions and to ensure that any potential environmental risks were reduced to an acceptable level.

The selected formulation consists of black powder and flaked aluminum. This composition has passed all qualification, hazard classification, and production testing, and the U.S. Army has approved its use in hand grenade and ground-burst simulators. In early 2008, Grucci will change all production of M115A2 and M116A1 simulators to this perchlorate-free, black powder based composition. This change will reduce the use of potassium perchlorate by approximately ten tons per year across the Department of Defense. Work is now underway to eliminate perchlorate from other munitions, including booby trap simulators, nonlethal stun grenades, and training rocket warheads.

The Mcgyan Process: A New, Heterogeneous, Fixed-Bed Catalyst Technology for Continuous-Flow Biodiesel Production from Waste Fats and Oils

SarTec Corporation; Professor Arlin E. Gyberg, Augsburg College

NOTE: This project is the result of a partnership between Professor Arlin E. Gyberg of Augsburg College and SarTec Corporation. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 9.

Specialty Fertilizer Products

Biodegradable, Water-Soluble Anionic Polymers, Prepared in an Environmentally Benign Process, Enhance the Efficiency of Phosphorus Use by Plants

Historically, fertilization of crops with phosphorous has been problematic. When phosphorous is applied to the soil, reactions with various cations including calcium, magnesium, aluminum, and iron fix 75–95 percent of the phosphorus. Because this leaves only 5–25 percent of the phosphorus available to crops, farmers must apply excess phosphorus. Erosion washes residual phosphorus into waterways, where it causes eutrophication.

Specialty Fertilizer Products (SFP) engineered and patented a family of dicarboxylic copolymers that increase the efficiency of phosphorous fertilizers and reduce the environmental impact of fertilization. The technology includes manufacturing low-molecular-weight itaconic–maleic copolymers for use with phosphorous fertilizers. The high negative charge of these polymers sequesters the cations that would otherwise fix the applied phosphorus. SFP sells these polymers under the trade name AVAIL®.

SFP uses a green process to synthesize its nontoxic, water-soluble, biodegradable polymers. Itaconic acid, the main component in these polymers by weight, 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. Using AVAIL® polymers with granular or fluid phosphorous fertilizers greatly increases phosphorous availability in soils, resulting in 80–90 percent of the phosphorous being available to crops. Benefits include reduced phosphate accumulation in soil, reduced phosphate runoff, and reduced contamination and eutrophication of waterways. AVAIL® produces an average increase of 10–15 percent in crop yields at minimal cost.

This technology lowers the environmental impact of biomass-derived fuel such as ethanol, butanol, and biodiesel. Because the phosphorus supply is much more energy-efficient, far less fuel is consumed to grow useful biomass and produce plant-derived liquid fuels. AVAIL® has been marketed in the United States and Canada since 2004. Currently, SFP is selling 40 million tons of AVAIL® per year internationally.

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 lead. SAMMS™ replaces commonly used adsorbents such as activated carbon and ion exchange resins whose manufacture and use are less environmentally friendly. SAMMS™ is a nanoporous adsorbent that forms strong chemical bonds with the target toxic material. It provides superior adsorption capacity and cost economics; it also reduces the volume of hazardous waste. Compared to activated carbon, SAMMS™ can reduce the volume of adsorbent waste by 30-fold.

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 in the traditional synthesis. The combination of a green manufacturing process for SAMMS™ and the superior adsorption characteristics of SAMMS™ materials results 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 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. SAMMS™ in powder form is now being used on liquid and mixed waste streams in the chemical, waste management, and petroleum industries.

Manufactured Firelogs Based on Whole Timber

Torch Technologies LLC

The market for conventional manufactured firelogs is 110 million logs per year. Conventional manufactured firelogs offer lower emissions than cordwood. They are typically made of recycled materials such as sawdust bound together with petroleum wax from fossil fuel, which is a solid fuel additive.

Torch Technologies has developed an alternative to conventional manufactured firelogs using cleaner-burning, inexpensive, bioderived materials that are waste streams from various industries. Torch firelogs are made from whole timber and crude glycerol by a simple timber treatment process. The timber is cutoff parts of plantation-grown trees that have only minimal commercial value as a feedstock for the paper industry. Because the timber is whole, Torch can use a liquid fuel additive, glycerol, which is a low-value byproduct of biodiesel production. Torch firelogs contain no fossil fuel components.

Torch firelogs are a sustainable fuel option. They are 20–40 percent less expensive to produce than conventional manufactured firelogs, depending on the raw materials. They burn with emissions that are 50 percent lower than conventional manufactured firelogs. Torch firelogs are structurally stronger than conventional manufactured firelogs, which makes them safer to burn and easier to package and transport (saving cost and energy). Their structure also allows consumers to burn multiple logs at one time, similar to a conventional cordwood fire, but with an extended burn time.

Torch Technologies 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. During 2007, the company continued development and raw material sourcing. It validated the combination of a wide range of waste streams from the logging, sawmilling, biodiesel, papermaking, and other industries.

Greening Insecticides and Parasiticides

TyraTech, Inc.

Synthetic chemicals are the current primary means of abating and controlling invertebrate pests, but these products are flawed due to the development of insect resistance, environmental concerns, and adverse health and environmental effects. Natural plant oils are safer and have various degrees of pesticidal activity, but historically have not been as effective as nor offered as broad a spectrum of control as products based on synthetic chemicals.

TyraTech is developing proprietary insecticide and parasiticide products that incorporate unique blends of natural active ingredients. TyraTech's proprietary development platform enables them to identify potent mixtures of plant oils that are active as insecticides and parasiticides. Their screening platform currently includes three chemoreceptors that they cloned into *Drosophila* cell lines: the tyramine neurotransmitter receptor (expressed solely in invertebrates) and two insect olfactory receptors. Compounds that bind to and activate these receptors have been shown to be powerful insecticides. With this platform, TyraTech can rapidly select blends of individual oils that have synergistic ability to activate multiple insect neurological and olfactory receptors.

TyraTech's products use natural, volatile oils as the main active ingredients, ensuring that toxic chemicals do not persist in the environment and also drastically limiting the potential for unintended adverse health effects for humans and other animals. By targeting multiple chemical receptors simultaneously with natural ingredients, TyraTech's products decrease the incidence of insect resistance that is characteristic of the synthetic chemical pesticides currently in use. Their products are highly effective and inherently safer than other current products.

TyraTech is targeting diverse pesticide markets including agricultural and horticultural applications, consumer and institutional markets, professional pest control, vector control, and human and animal healthcare applications. During 2007, TyraTech commercialized its first product, a ready-to-use broad spectrum Crawling Insect Spray for the institutional market.

Entries from Industry and Government

Replacement of Perfluorinated Alkyl Surfactants with Nonfluorinated Surfactants in Polymer Manufacturing

Arkema, Inc.

All manufacturers, including Arkema, had always used perfluorinated alkyl surfactants (PFOA) and related chemicals for emulsion polymerizations of fluorinated monomers, such as vinylidene fluoride. The high reactivity of the fluorinated monomers had led to the widely accepted belief that only perfluorinated surfactants are inert and stable enough to function in these polymerizations. PFOA and related chemicals are both persistent and widely distributed at low concentrations throughout the environment. In 2006, the EPA and major companies in the industry created the 2010/15 PFOA Stewardship Program to reduce and eventually eliminate emissions and product content of PFOA and related chemicals. Although other participating companies pursued containment, recycling, or substitution of alternative perfluorinated surfactants, Arkema targeted the complete elimination of fluorinated surfactants from its products.

Since 2002, Arkema has worked to eliminate perfluorinated alkyl surfactants from the manufacture of polyvinylidene fluoride (PVDF) resins. Arkema researchers first identified several hydrocarbon-based, nonfluorinated surfactants that worked well in the polymerization reaction. These surfactants have been used in consumer products such as shampoos and cleaning formulations; extensive data show that they are of low toxicity, do not bioaccumulate, and do not persist. Subsequently, an Arkema team identified fluorosurfactant-free polymerization conditions in the laboratory, optimized the reactions on a pilot scale, and successfully implemented the new processes at Arkema's commercial manufacturing site. Under optimized process conditions, these new surfactants allow the production of PVDF products with properties virtually identical to those of existing products.

Arkema is currently replacing its traditional approach with these new manufacturing processes for all 40 grades of its PVDF resins. During 2007, Arkema reduced its use of perfluorinated alkyl surfactants at its U.S. manufacturing site by roughly one-half. Its goals are 95 percent reduction by 2010 and complete elimination thereafter. This technology will reduce fluorinated surfactants in air emissions, wastewater discharges, and finished goods.

BioBased Tile™ with BioStride™ — A Revolutionary New Flooring Made with Rapidly Renewable Resources

Armstrong World Industries, Inc.

Historically, commercial flooring has been manufactured using binders derived from petroleum and fossil fuel feedstocks. These binders combine polyvinyl chloride (PVC), polyolefin, ethylene acrylic, or synthetic rubber with plasticizers, stabilizers, and processing aids. The binders hold together a filler matrix of limestone and pigment. Approximately one billion square feet of vinyl composition tile are installed in North America each year.

After two and half years of research and development, Armstrong is the first manufacturer in over 100 years to develop a new biobased polymer as a binder to make a new hard surface flooring product, BioBased Tile™ with BioStride™. The only other biobased, hard surface flooring products are natural rubber and linoleum. The latter, introduced by Armstrong in 1903, has linseed oil as its key binder ingredient.

BioStride™ is the breakthrough patent-pending polymer used in BioBased Tile™ with BioStride™, a new category of composition tile that provides enhanced environmental attributes, improved performance, a classic look, and affordability. The proprietary BioStride™ polyester contains ingredients from rapidly renewable, domestically grown corn, resulting in reduced reliance on petroleum and fossil fuels, and, therefore, a lower carbon footprint. Armstrong continues its efforts to increase the renewable content of BioStride™. With 13 percent biobased content by weight and 10 percent preconsumer recycled content, BioStride™ provides the same or better performance as traditional polymer binders based on PVC. Armstrong BioBased Tile™ contains 14 percent BioStride™, 75 percent locally mined limestone, 10 percent preconsumer recycled material, and one percent pigment. BioBased Tile™ includes 10 percent limestone fragments from quarries that would otherwise go to landfills.

Compared to vinyl composition tile, a 20,000 square foot installation of Armstrong BioBased Tile™ saves energy and natural resources equivalent to 72 gallons of petroleum. Armstrong completed the manufacturing scale-up of the BioStride™ polymer and began producing its BioBased Tile™ during 2007.

Ashland Inc.

GEOSET NEO®: Low Emission Technology for the Metal Casting Industry

Foundries in the metal casting industry typically use organic polymers, known as binders, on sand to produce a variety of cores and molds. Although these organic binders allow high productivity, they also emit volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Because the binders cause problems with worker health and safety, foundries must use expensive abatement equipment such as odor control filters and scrubbers. Inorganic binders can address these problems, but previous inorganic binders performed poorly, produced more core and mold scrap, and reduced productivity. Most were limited to nonferrous applications.

Ashland has developed a low-emission, inorganic binder technology for both ferrous and nonferrous applications in the metal casting industry. Their GEOSET NEO® (Negligible Emissions and Odor) inorganic binders are aluminosilicate gels that are water-based and heat-cured. They have excellent core and mold rigidity, good dimensional stability, and high hot strength. There is little concern for human exposure to VOCs or HAPs before, during, or after the casting process. GEOSET binders release virtually no nuisance odors during core or mold production. During the casting process, the decomposition products from GEOSET binders are water vapor and carbon dioxide (CO_2). As a result, foundries can both reduce or eliminate their costly abatement equipment and provide a cleaner atmosphere for employees and the environment nearby.

Ashland expects GEOSET NEO® binders to have a profound impact not only on foundries, but also on the environment. Substituting organic binders with inorganic binders can reduce a foundry's emissions by up to 90 percent and assist in compliance with environmental regulations. GEOSET can eliminate most nuisance odors and smoke that would otherwise drift into communities near a foundry. Due to the rising price of petroleum, inorganic binders are comparable in cost to organic binders. During 2006 and 2007, Ashland implemented and cultivated joint development programs with customers.

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

Ashland Inc.

Typical conventional cooling water treatment programs require corrosion control, scale inhibition, and microbiological control. Common water-treatment chemicals include potentially hazardous and toxic materials. Ashland developed a turnkey application that significantly reduces the negative environmental, health, and safety impacts 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 (including PSA, a low-P phosphonate), and other organic and inorganic components. ENVIROPLUS® products reduce the environmental impact of treated water discharge because they are inherently biodegradable and contain very low phosphorous, but no heavy metals. 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 plus micro-bubble aeration. 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 its newest component, Ultra-Serv®, in 2006. Ashland holds a number of recent patents for this technology.

Solventless, Low-Toxicity, Thermosetting Oligomers that Require Only Low Energy to Cure

Ashland Inc.

An important technical achievement in the last 40 years has been the development of coatings, inks, and adhesives that cure essentially instantly with UV light or electron beam radiation. Equipment and processes cured these materials very efficiently without solvents or energy-intensive ovens. Although this produced a dramatic net reduction of pollution, the technology was not risk-free. The acrylic monomers and photoinitiators in traditional formulations for UV-curable coatings can be very toxic (e.g., corrosive or skin sensitizers) and odiferous; as a result, they require stringent safety controls.

Ashland's resin technology uses facile chemical conversion to reduce the toxicity of traditional formulating monomers and resins, resulting in novel compounds that cure without additional photoinitiators. Ashland's DREWRAD™ radiation-curable acrylate oligomer resins are manufactured as 100-percent-reactive liquid resins to be formulated into radiation-curable coatings, inks, and adhesives. These products allow the application of coatings to substrates without releasing solvents into the environment. Radiation curing eliminates large, energy-intensive processing steps such as baking in gas-fired ovens. Emissions from the use of this resin product are expected to be nearly zero.

To produce DREWRAD™, Ashland selected the same essential formulation building blocks according to performance requirements. These chemicals are then reacted with β-diketones or β-ketoesters (or amides, anilides, etc.) in a base-catalyzed Michael addition to produce oligomers of higher molecular weight and viscosity. The product is typically of higher acrylic bond functionality and, more important, the oligomeric product possesses a photolabile ketone moiety that can initiate free-radical polymerization upon exposure to UV light. These novel compounds have virtually unlimited architectural design flexibility, enabling changes to be made that maximize the green character of each product. Ashland Water Technologies, a division of Ashland Inc., has commercialized this novel green technology. Ashland received its most recent patent for DREWRAD™ in 2007.

ATK Lake City Ammunition Division

P_4rimer™: A Non-Toxic, Heavy-Metal-Free Primer Fueled by Red Phosphorus for Small Arms Cartridges

Small arms primer designs have not undergone major changes since 1949, when the U.S. Army Ordnance Department (USAOD) introduced formulations based on lead styphnate as noncorrosive primers. These primers release considerably more lead during a typical training session in an indoor firing range than recommended under current exposure guidelines set by the U.S. military. Red phosphorous (RP) has been patented as a substitute for use in percussion caps, but RP primers are unstable and tend to produce corrosive byproducts. After limited use, they were eventually abandoned.

The chemical stability of RP remained an issue until manufacturers began using polymers to microencapsulate water-sensitive oxidizing agents. Encapsulating the hygroscopic lighter alkali and alkali earth metal nitrates in polymers greatly reduces the rate at which they take up water. Encapsulated in polymers, the abandoned phosphorous primer formulas have proven to be effective primer mixtures without the stability and hygroscopicity issues. P_4rimer™ is a unique combination suitable for use as a percussion priming composition. It contains phosphorus, potassium nitrate, pentaerythritol tetranitrate (PETN, a high explosive), aluminum, and a polymer-based binder. P_4rimer™ is encapsulated during manufacture with an epoxy coating that reduces the active catalytic sites for conversion into phosphoric acid. It is less hazardous, less explosive, more thermally stable, and less costly than formulations based on lead styphnate. Its combustion products are bioavailable and recyclable. It maintains the necessary chemical energy to ignite propellant efficiently.

At the Lake City Army Ammunition Plant alone, a formulation containing 26 metric tons of RP and 64 metric tons of potassium nitrate can now replace 71 metric tons of lead nitrate, 49 metric tons of barium nitrate, and 22 metric tons of antimony sulfide. According to a 2002 survey by the U.S. Department of Commerce, there are seven other large commercial U.S. cartridge sites manufacturing formulations based on lead styphnate.

Baker Hughes Incorporated

AuRACOR™ C-101 Encapsulated Time-Release Oilfield Corrosion Inhibitor

Corrosion-induced leaks in hydrocarbon-producing equipment threaten safety, health, and the environment. Corrosion-inhibiting chemicals are among the highly effective means of preventing corrosion in oil and gas wells, tanks, and pipelines and of eliminating the risk of a petroleum release or spill due to corrosion. The two traditional methods of delivering corrosion inhibitors are batch treatment and continuous injection: the former often requires excess chemicals to ensure adequate protection between treatments, whereas the latter requires storing chemicals at each injection point and is more prone to chemical spills. Although the industry has used corrosion inhibitors in oilfields for decades, only recently has anyone focused on the environmental effects of inhibitors.

Baker Petrolite, a U.S. technology center of Baker Hughes, recently developed AuRACOR C-101 Encapsulated Corrosion Inhibitor, one of their most ambitious efforts in their long-standing pursuit of safer oilfield products. Their encapsulation technology is a step-change concept that is more environmentally friendly than either traditional batch or continuous treatments. By encapsulating judiciously selected chemicals, Baker Petrolite achieved a safe, nonhazardous corrosion inhibitor that can substantially reduce the amount of chemicals needed to treat corrosion effectively. AuRACOR C-101 is based upon formulated fatty acid amide and imidazoline. Baker Petrolite engineered the encapsulated inhibitor to float at the brine–hydrocarbon interface in the well; here, it releases its corrosion inhibitor for months at a time. Because AuRACOR C-101 is a solid, nonhazardous product, it does not require reporting in case of a spill. Further, its time-release properties mean fewer well-site interventions, which translate into less risk of mechanical damage or personal injury during chemical application. By eliminating the need for chemical storage at each wellhead, AuRACOR C-101 greatly reduces the potential environmental impact of corrosion protection programs.

During 2006, Baker Petrolite received a patent for this technology and commercialized AuRACOR C-101 as the first "floating" encapsulated corrosion inhibitor.

GreenWorks™ Natural Cleaners from the Makers of Clorox: Home Cleaning Products

The Clorox Company

GreenWorks™ Natural Cleaners set a new standard for natural cleaning. These products perform as well as conventional cleaners and are composed of over 99 percent natural, plant-based ingredients from renewable sources and minerals.

GreenWorks™ products include plant-based ingredients derived from such sources as coconut and lemon oil. The formulas optimally blend natural ingredients and naturally derived surfactants to achieve excellent cleaning performance. One key to the GreenWorks™ technology was Clorox's development of a novel, nanoemulsion that dissolves ingredients such as essential oils in the formulation as well as dirt or soil, while maintaining phase stability in a clear product. The products are formulated to be biodegradable and non-allergenic, are not tested on animals, and come packaged in recyclable containers. The manufacturing facilities used to produce GreenWorks™ have zero emissions discharge. Further, all GreenWorks™ products perform as well as or better than leading conventional cleaners in laboratory and blind in-home consumer tests. This level of cleaning is important to convince consumers to switch from their traditional cleaning products. The EPA Design for the Environment initiative recognized four of five GreenWorks™ products, representing a significant level of achievement.

Fossil fuels contribute significantly to greenhouse gas emissions. By switching from petrochemicals to natural source ingredients in the GreenWorks™ line, Clorox calculates that approximately 250,000 gallons of petroleum will be saved in the United States every year. Compared to using petrochemicals that can contribute to the production of carbon dioxide (CO_2, a greenhouse gas), plant-based renewable sources capture CO_2 during their growth.

Clorox will launch GreenWorks™ Natural Cleaners in January 2008. The GreenWorks™ line of products sells at only a modest premium to conventional cleaning alternatives, despite the inclusion of the costlier plant-based renewable ingredients, the environmentally friendly manufacturing process, and the innovative science, which together offer the consumer the most natural, powerful cleaning on the market.

Cytec Industries Inc.

Cylinderized Phosphine as a Safer, More Environmentally Friendly Alternative to Traditional Fumigants for Stored Products

Agricultural fumigants are used to control pests that infest stored products, such as dried fruits and nuts; grains such as wheat, rice, and corn; and nonfood commodities such as tobacco.

For over 50 years, stored products have typically been fumigated with methyl bromide or metallic phosphides. Because methyl bromide is being phased out in accordance with the Montreal Protocol on ozone-depleting substances, an alternative fumigation method is needed.

Metallic phosphides (typically aluminum or magnesium phosphide) release phosphine gas when exposed to the ambient moisture in the air. Phosphine gas by itself is a very effective fumigant with no known chronic toxicity. The efficient release of phosphine gas from the metallic phosphides, however, requires certain temperature and humidity levels that may not be reached in practice; unreacted phosphide residues are often left after fumigation. These residues must be deactivated and disposed of in a time-consuming and often dangerous process; typically, they are hazardous waste.

Cytec Industries has developed and commercialized a new technology for fumigating stored products. Cytec supplies phosphine gas in recyclable cylinders. With cylinderized phosphine, workers can easily adjust phosphine concentrations from outside the fumigation space, applying only the amount necessary for complete fumigation. As a result, fumigation requires less phosphine. Further, cylinderized products leave no unreacted residue or byproducts.

Cytec's cylinderized phosphine products are inherently safer than traditional fumigants: they require less worker exposure and do not significantly impact the environment. Cytec's two products, ECO_2FUME and $VAPORPH_3OS$, are currently used by some of the largest food processing, milling, and storage facilities.

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 EPA and Cytec's Solvent Selection Guide, which includes hazard information on 120 common solvents. Cytec incorporated 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.

Revolutionizing Energy-Curing Resins for Food Packaging Applications

Cytec Industries Inc.

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. Cytec anticipates even greater savings in the future.

Novel Process for Producing Polyols Based on Natural Oils

The Dow Chemical Company

In recent years, the gradual shift of industry away from petroleum-based feedstocks toward less price-sensitive, renewable resources has focused on the polyurethane industry. These opportunities spawned a new generation of biorefineries that are bringing new products and processes to market. The Dow Chemical Company started exploring the use of seed oils as raw materials in the late 1990s and subsequently envisioned a seed oil refinery as a new source of monomers and polymers.

Several technologies emerged to enable the use of renewable feedstocks in polyurethanes. One of these, Union Carbide's hydroformylation and reduction technology, is critical for enabling the practical use of seed oils to produce polyols for polyurethane applications. The strategy adopted by Dow involves the methanolysis of triglycerides to discreet fatty acid components followed by the selective functionalization of the fatty acid methyl esters in a controlled fashion to prepare designed polyols. Fatty acid methyl esters with a tightly controlled functionality enable the preparation of polyols with a range of molecular weights, polydispersities, and functionalities that are similar to conventional polyols. The process creates very little waste; its only byproduct is glycerol. The Dow process allows the preparation of key intermediates and final products from a variety of seed oils ranging from commodity soybean oil to high-oleic seed oils such as Natreon™ sunflower oil.

RENUVA™ technology is Dow's commercial implementation of natural oils to produce polyols for the polyurethane industry. This novel technology enables the production of high quality, oil- and odor-free polyols. These polyols have the broadest range of applicability and the possibility of the highest natural content in the final polymer structure achievable in the industry. Compared with the chlorohydrin process for preparing conventional polyols, the Dow process reduces fossil fuel use by approximately 74 percent. Dow began commercial implementation during 2007.

The Dow Chemical Company; BASF AG

Innovative Industrial Process for Synthesizing Propylene Oxide via Hydrogen Peroxide

Propylene oxide (PO) is among the top 50 largest-volume chemical intermediates produced in the world. It is a key raw material for a wide range of industrial and commercial products, including polyurethanes, propylene glycols, and glycol ethers. Historically, the synthesis of propylene oxide has required either producing significant volumes of coproducts or recycling organic intermediates.

Dow and BASF jointly developed a new, innovative route to propylene oxide based on the reaction of hydrogen peroxide and propylene, referred to as HPPO. Hydrogen peroxide is a clean, versatile, environmentally benign oxidant that substitutes for chlorinated oxidants, which present environmental challenges in many manufacturing operations. In the HPPO process, propylene is epoxidized by hydrogen peroxide in a tubular reactor at moderate temperature and low pressure. A proprietary catalyst facilitates the reaction, achieving both high conversion and product selectivity. The reaction occurs in liquid phase using methanol as a solvent. Hydrogen peroxide is completely converted and the propylene conversion is nearly quantitative. The crude propylene oxide is purified by distillation and the methanol solvent is recycled. The reaction of hydrogen peroxide and propylene is high in yield and produces no significant coproducts except for water.

HPPO also provides environmental benefits. Dow and BASF expect this technology to reduce wastewater production by as much as 75–80 percent and energy use by 35 percent over current technologies. During 2007, Dow constructed a pilot plant in Freeport, Texas to support development of this technology. The first commercial process based on this technology is scheduled to begin operation in early 2008 at a BASF production facility in Antwerp, Belgium.

Water and Energy Conservation in Denim Finishing

Dow Corning Corporation

Traditionally, the processing and finishing of denim to achieve the popular, well-worn, soft look and feel requires large amounts of water and energy. To provide a faded look, processors traditionally use silicones, particularly amino-silicones, as softeners in wet finishing. Often the enzymes and other chemicals used in denim garment and fabric processing do not have good compatibility with silicones. Consequently, most processors use silicones and enzymes only in different processing steps when they desire a faded look. The conventional denim garment process requires from 7 to 10 steps and uses large quantities of water in each step. Typically, a basic denim wash that includes desizing and fading with enzymes can consume as much as 70 to 110 liters per kilogram of denim garments.

Dow Corning® GP 8000 Eco Softener is a granulated, modified polysiloxane textile enhancer. Its nonionic formulation contains four to five ingredients. It has the potential to reduce the amount of water consumption needed for traditional methods of denim processing by as much as 30–50 percent, to as little as 20 liters of water per garment containing 500 grams of denim. Used in different stages of denim garment or fabric wet-finish processing to achieve a natural, soft hand, this water-dilutable, ready-to-use granular silicone material has a unique formulation and delivery that provides good compatibility with fabric finishing enzymes and washing stones. This novel combination of properties enables previously incompatible steps to be combined, thus eliminating separate washing requirements and conserving significant amounts of water and energy. Combining processing steps using Dow Corning® GP 8000 Eco Softener also results in improved productivity, reduced utility costs and processing time, and improved environmental sustainability without sacrificing performance or fabric characteristics. Dow applied for a patent for this technology and expects the patent to be published in June 2008.

DuPont™ Cerenol™ – A New Family of Renewably Sourced, High-Performance Polyether Glycols

E. I. du Pont de Nemours and Company

Cerenol™ is a proprietary new family of high-performance poly(trimethylene ether) glycol polymers manufactured in a sustainable process using the renewably sourced ingredient, 1,3-propanediol (Bio-PDO™). Bio-PDO™ is made from corn-derived glucose by fermentation and is an inherently safer raw material; it replaces 1,3-propanediol derived from petroleum. The Cerenol™ family of products includes homo- and copolyether glycols and their ester derivatives with 50–100 percent renewable content and molecular weights ranging from 500 to 3,000. Cerenol™ polymers can replace synthetic polyalkylene glycols that rely on high-cost crude oil and natural gas feedstocks.

Cerenol™ polymers are ether-linked long-chain molecules with an odd number of carbon atoms in the repeating unit. These carbon-ether linkages give Cerenol™ polymers unique attributes, such as better flexibility at low temperatures and tougher soft segments when incorporated into elastomers. Unlike traditional synthetic polyether glycols (which are made from ring-opening polymerization of cyclic ethers), these new environmentally friendly polymers are produced through a novel route by polycondensation of Bio-PDO™ in the presence of a soluble acid catalyst. The process uses less material and energy and reduces greenhouse gas emissions compared to such traditional processes as polytetramethylene ether glycol.

This unique combination of properties makes Cerenol™ exceptionally attractive for a variety of end-use applications that include performance coatings, inks, lubricants, functional fluids, and personal care products. In addition, Cerenol™ polymers are ideal building blocks for several value-added thermoplastic elastomers such as polyurethane, spandex, copolyether ester, and copolyether ester amide. Cerenol™ combines uncompromising product performance with renewable sources, resulting in a reduced environmental footprint and less dependence on petroleum.

During 2007, DuPont launched Cerenol™ and began batch manufacturing in Pascagoula, Mississippi. It plans to scale up the facility from a 500-gallon reactor to a 6,000-gallon reactor in early 2009, increasing its annual production capacity to 5–10 million pounds.

Eastman Chemical Company

IntegRex Technology

In conventional manufacturing processes, poly(ethylene terephthalate) (PET) is produced in the melt phase at high temperature, formed into pellets and cooled, reheated for solid-state polymerization, and cooled again. Eliminating the slow, costly, solid-state phase had not been feasible because problems arose during polymerization entirely in the melt phase.

Eastman's innovative reactor design and integrated process chemistry have solved the problems of making polymers entirely in the melt phase, enabling the production of melt-phase polymers that are superior to those made in conventional processes. In the IntegRex process, the polymer is heated to a lower maximum temperature, cooled only once, and, thanks to intensified reactor technology, made with less equipment. Other advances include the innovative use of pipe reactors in polyester processes and novel catalyst systems. The viscosity of the in-process polymer is about three times higher than that encountered in conventional PET processes, in which much of the viscosity of the final product is achieved in the solid-state operation. The higher melt-viscosity makes it more difficult to move polymer through the process and also significantly impedes the mass transfer necessary to remove the ethylene glycol and water released during polymerization.

Eastman's IntegRex Technology produces recyclable PET resin in a way that reduces energy consumption by 54 percent, reduces associated greenhouse gas emissions by more than 47 percent, occupies a smaller environmental footprint, and eliminates the need for wastewater treatment. Eastman uses the IntegRex process to manufacture its ParaStar resins. These resins are a drop-in replacement for standard PET in bottle-manufacturing equipment; they can be recycled along with traditional PET resins.

In late 2006, Eastman opened a new 350,000-metric-ton PET plant at its Columbia, SC site. The facility is now home to the world's first PET plant that uses IntegRex Technology: Eastman's proprietary breakthrough process for producing PET resin that completely eliminates the solid-state process.

Eli Lilly and Company

A Practical and Green Chemistry Strategy for the Manufacture of Neurokinin 1 Antagonist, LY686017

Eli Lilly and Company developed an innovative, environmentally benign route for the commercial production of an investigational new drug candidate. This candidate, LY686017, is an antagonist of the Neurokinin 1 (NK1) subtype of tachykinin receptor. It has undergone Phase II clinical trials for the treatment of anxiety and irritable bowel syndrome (IBS). LY686017 is Lilly's name for {2-[1-(3,5-bis-trifluoromethyl-benzyl)-5-pyridin-4-yl-1*H*-[1,2,3]-triazol-4-yl]-pyridin-3-yl}-(2-chlorophenyl)-methanone. The improved route of manufacture delivers LY686017 in exceptionally high purity (greater then 99.9 percent), despite its complex structure.

Eli Lilly and Company uses a metric called "e-factor" internally that is similar, but not identical to, Sheldon's E-factor. The e-factor measures the total mass of all raw materials (including water) that are used to produce each kilogram of active pharmaceutical ingredient (API). Overall, the new route for LY686017 has a net e-factor of 146 kilograms per kilogram API, which is an 84 percent reduction relative to the original route designed for Phase I clinical trials. Key technology developed includes a chemoselective S_NAr reaction that has potential broad impact within the pharmaceutical industry. For example, industry-leading antidepressants Prozac™ and Cymbalta™ use S_NAr chemistry in key manufacturing steps. In addition, COX-2 inhibitors such as pyrazolopyridines can potentially be prepared by this novel green methodology. Using the novel S_NAr chemistry to manufacture these large-volume drugs could eliminate over 100 million pounds of processing waste per year per drug.

Eli Lilly demonstrated the selected commercial route for LY686017 on a pilot plant scale during 2006 in Indianapolis, IN. Two prior synthetic routes have been executed at pilot plant scale at Eli Lilly's 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 a testimonial to the importance of incorporating green chemistry into the design and definition of synthetic processes.

Ecomate® – Environmentally Benign Blowing Agent for Polyurethane Foams

Foam Supplies, Inc.

For many years, chlorofluorocarbons (CFCs) were the preferred foam blowing agents in the manufacture of polyurethane insulating foams. CFCs gave foam good insulating and structure properties for use in refrigerators, building construction, and spray foam. CFCs were removed from polyurethane foam in the 1990s, however, due to their potential to destroy the ozone layer. Alternative hydrochlorofluorocarbons (HCFCs) were lower in ozone depletion potential (ODP), but still had the potential to deplete the ozone layer. It was also discovered that some of the foam blowing agents, including CFCs, HCFCs, and hydrofluorocarbons (HFCs), had very high global warming potentials (GWPs).

Foam Supplies developed ecomate® (trade name for methyl formate) to replace CFCs, HCFCs, and HFCs as blowing agents for polyurethane foams. Ecomate® is a zero-ODP, zero-GWP blowing agent. Ecomate® is also volatile organic compound (VOC)-exempt, which means it does not contribute to the formation of smog. The HCFCs and HFCs that ecomate® replaces have GWPs of 700–1700. (The GWP of carbon dioxide is defined as 1.00.) Because each pound of ecomate® replaces about two pounds of the alternative blowing agents, one million pounds of ecomate® would be the equivalent of replacing 700 million to 1.7 billion pounds of carbon dioxide emissions.

The cost of ecomate® blowing agent is substantially less than that of HFCs. There are no significant expenses associated with implementing the ecomate® technology, which requires little or no modification to existing foaming processes. The insulating and structural characteristics of ecomate® foam systems are equivalent to those of conventional polyurethane foams. Ecomate® has been demonstrated in pour-in-place, boardstock, and spray insulation systems, as well as boat flotation foam. It is a technology with outstanding properties as well as a low environmental impact. Manufacturers who use ecomate® foaming systems can help the environment without increasing costs.

GlaxoSmithKline

GlaxoSmithKline's Eco-Design Toolkit™

GlaxoSmithKline (GSK) developed the Eco-Design Toolkit™ to provide bench-level chemists and engineers with easy access to green chemistry information so they could design-out hazardous chemicals, identify alternative chemistries and technologies, and implement best practices. The Eco-Design Toolkit™ allows GSK to bring products to market more cost-effectively because it enables the company to produce medicines with fewer environmental, health, and safety (EHS) impacts throughout their lifecycle.

GSK developed its Eco-Design Toolkit™ following state-of-the-art scientific advancements and standards. It currently has five modules: a Green Chemistry and Technology Guide to applying green chemistry and engineering principles; Materials Guides on a wide range of solvents and bases with information and EHS rankings that include the lifecycle impacts of solvent manufacture; Fast Lifecycle Assessment for Synthetic Chemistry (FLASC™) for streamlining evaluations of environmental lifecycle and measuring green metrics including mass efficiency; a Green Packaging Guide to evaluating and selecting packaging that includes an environmental assessment tool; and a Chemicals Legislation Guide that identifies legislation phasing out hazardous substances (chemicals of concern). Each module is designed to ensure that GSK considers all EHS impacts from the manufacture of raw materials through the ultimate fate of products and wastes. The toolkit is accessible through the GSK intranet.

Methodologies of most of the tools are published in peer-reviewed scientific journals. Tools such as the Solvent Guide, FLASC™, or the Green Technology Guide are first in their class and are recognized by academic and industrial groups for their innovation as leading the green design of pharmaceuticals. GSK continues to update the toolkit to integrate new scientific advances and regulatory information.

GSK routinely uses the toolkit to develop new products. During 2006, the mass percent of chemicals of concern across all products decreased nine-fold and the estimated average lifecycle impacts were reduced four-fold as compounds moved to the last stage of development.

Hach Company

Arsenic-Free SPADNS Chemistry for Fluoride Analysis in Water

Many nations around the world fluoridate drinking water to reduce tooth decay. According to the Centers for Disease Control (CDC), roughly two-thirds of Americans are supplied with fluoridated water. Fluoride added to drinking water must be kept within a narrow range of concentrations, typically between 0.5 and 1.5 ppm F^- to be both effective and safe.

SPADNS is the common abbreviation for sodium 2-parasulfophenylazo-1,8-dihydroxy-3,6-naphthalene disulfonate. The SPADNS method for measuring fluoride is a simple spectrophotometric test used worldwide. Unfortunately, the SPADNS method utilizes high levels of arsenic, a persistent, tightly regulated toxin and carcinogen. Sodium arsenite in the SPADNS method acts as a reducing agent to prevent interference from chlorine and other oxidants that are typically present in drinking water. Although this approach is effective, the arsenic left over from each test is present in sufficient concentrations to be regulated as a hazardous waste in the United States.

Hach Company has developed an arsenic-free SPADNS reagent and commercialized it as SPADNS 2. In place of sodium arsenite, the new method uses a proprietary, nontoxic reducing agent. The waste from using SPADNS 2 can be disposed of safely without the special handling required for arsenic. The arsenic-free SPADNS 2 Hach Method 10225 outperforms both EPA-compliant methods (EPA Method 340.1 and Standard Method 4500-F D) in reagent water and matrix spike recovery and precision.

Apart from this change, the core chemistry of the new test is identical to traditional SPADNS. The new SPADNS 2 reagent can be used with any instrument, test procedure, and calibration curve currently used to measure fluoride with the original Hach SPADNS method. Although the SPADNS 2 reagent continues to be acidic and should be handled with care, its use generates no arsenic hazardous waste and operators have no risk of exposure. Hach commercialized this technology during 2007.

G^2 Catalyst for New and Improved SURFONIC® Non-Ionic Surfactants

Huntsman Corporation

Two billion pounds of surfactants are used in the United States annually. Nonionic surfactants, which comprise 40 percent of this total, are among the fastest-growing types of surfactants due to their compatibility in blends and efficacy in liquid formulations. The desire for nonionic surfactants that have both lower cost and higher efficiency (i.e., lower foaming) necessitates the use of renewable, low-cost feedstocks.

Ethoxylates of vegetable oils, their esters, and their alcohols are attractive nonionic surfactants that meet industry's needs. Detergent-range alcohols (C_{12}–C_{18}) derived from vegetable oil are used widely as hydrophobes to manufacture nonionic surfactants, but they require multiple manufacturing steps. Ethoxylated surfactants derived from vegetable oils or their esters require fewer manufacturing steps, but making them with standard catalysts produces slow, low-yield reactions that are impractical for commercial development.

Huntsman's team developed G^2, a novel, alkaline earth based catalyst that enables the direct insertion of ethylene oxide into fatty acid methyl esters (biodiesel) and vegetable oils in yields over 95 percent for the production of sustainably derived nonionic surfactants. Huntsman has demonstrated that its catalyst can ethoxylate a wide variety of sustainable, natural feedstocks from sources including coconut, palm kernel, soybean, linseed, canola, rapeseed, and palm stearin. The G^2 catalyst uses environmentally friendly calcium. After the batch reaction is complete, the catalyst is neutralized. It remains in the product, so there is no disposal of spent catalyst.

Biodiesel is a methyl ester of vegetable oil fatty acids. Its production has increased dramatically in the last few years to support America's national strategic intent to diversify its fuels. This catalyst technology is positioned to capitalize on the megatrend toward biodiesel by using biodiesel to make high-value, high-performance, biodegradable, and safe surfactants. During 2006, Huntsman began manufacturing fatty methyl ester ethoxylates at its plant in the United States; the product name is SURFONIC® ME530-PS surfactant.

Application of Green Chemistry Principles in the Scale-Up of the Darunavir Process

Johnson & Johnson

Johnson & Johnson used green chemistry principles to scale up the synthesis of darunavir, the active pharmaceutical ingredient in Prezista™, a new protease inhibitor. Prezista™ is indicated in the treatment of adults with HIV-1 strains that no longer respond to treatment with other anti-HIV medicines.

The principal objectives of the scale-up were to reduce the cost to manufacture darunavir and to reduce the negative safety and environmental impacts of the manufacturing process. By reducing the manufacturing cost, Johnson & Johnson could reduce the price of Prezista™ to allow more patients to benefit from it.

The company met three objectives. First, it reduced solvent use by replacing a single reaction in a relatively large volume of solvent with three consecutive reactions in a relatively small volume of solvent. Second, it eliminated the formation of hydrogen gas originally given off when excess hydride was quenched with hydrochloric acid by separating the acidification and quenching steps; it replaced hydrochloric acid with methane sulfonic acid and now adds acetone to react with excess hydride and form isopropanol. Third, it replaced a solvent system containing methylene chloride and triethylamine with a more benign solvent system containing acetonitrile and pyridine. It also eliminated a number of solid-liquid separation steps. Its accomplishments reduced the manufacturing cost by 81 percent and increased the overall yield by 40 percent.

The U.S. Food and Drug Administration granted accelerated approval to Prezista™ on June 23, 2006. With its improved, scaled-up process, Johnson & Johnson reduced raw materials and hazardous waste by 46 tons, reduced hydrogen gas by 4,800 cubic meters, and eliminated 96 tons of methylene chloride in 2006.

The Lubrizol Corporation

Novel Green Chemistries Extend the Useful Life of Automobile Catalytic Converters and Reduce Exhaust Gaseous Emissions

For the last 50 years, phosphorus in the form of zinc dialkyldithiophosphate (ZDDP) has been the most cost-effective antiwear, antioxidant, and anticorrosion component of engine oil. When ZDDP fulfills its function in the engine, however, the phosphorus can enter the exhaust stream, either by consumption or volatilization (released as a vapor). This phosphorus interacts with and decreases the effectiveness of catalytic converters used by automotive manufacturers to reduce exhaust gas emissions. This phenomenon, called catalyst deactivation, inhibits the ability of auto manufacturers to meet the EPA's requirements for a 120,000-mile or 10-year warranty on the catalyst system.

In 1994, the engine oil industry in the United States set an upper limit for phosphorus in engine oil at 0.08 weight percent. The same limit for phosphorus continues today. Although a phosphorus limit was set to protect catalysts, the phosphorus still present in the oil can volatize from the engine, then react with and deactivate the catalyst. Some ZDDPs are more prone than others to volatilize and, therefore, to deactivate catalysts. Concerns about losses in catalyst efficiency forced formulators either to design engine oils with lower concentrations of traditional ZDDP or to develop cost-effective, low-volatility ZDDP technology.

Lubrizol developed a new, low-volatility ZDDP technology and tested it for two years and 100,000 miles in New York City taxicabs. Taxicabs using oil with Lubrizol's ZDDP technology had an average of 46 percent lower volatile phosphorus, 10 percent lower oxides of nitrogen (NO_X), and 15 percent lower carbon monoxide (CO) than taxicabs using oil containing traditional ZDDP technology. In 2004, the Lubrizol Corporation introduced its patent-pending, low-volatility ZDDP technology to provide engine oil formulators with an alternative to designing higher-cost engine oils with lower levels of ZDDP.

An Efficient Green Synthesis of Isentress®: A Breakthrough HIV Integrase Inhibitor

Merck & Co.

Isentress® (raltegravir) works by inhibiting the insertion of HIV DNA into human DNA by the integrase enzyme, which limits the ability of the virus to replicate and infect new cells. It is the first medicine to be approved in the new class of antiretroviral drugs called integrase inhibitors.

For launch in the marketplace, Merck had developed a viable synthesis to produce Isentress®. Because the product is a critical new tool to fight the global HIV/AIDS epidemic, Merck pursued a synthetic pathway that was more efficient, environmentally enhanced, and more economical. Through scientific innovation, atom-economic synthetic design, reduction of byproducts, and the use of greener chemicals, Merck developed an improved process. The replacement process has a 35 percent increase in overall yield, a 49 percent reduction in production cost, and a reduction in waste byproducts equal to 253 metric tons per metric ton of Isentress® manufactured. The overall E-factor went from 388 for the original process to 121 in Merck's improved process, a 70 percent reduction. Given the recommended dose of 800 mg per day per patient of Isentress®, this waste reduction translates to 164 pounds of waste reduced per patient each year compared to the initial, original manufacturing route. A critically important improvement in the process is the replacement of the reagent methyl iodide (a carcinogen, neurotoxin, and respiratory toxicant) with trimethylsulfoxonium iodide, an innovative, less toxic substitute.

In 2007, Merck's innovative HIV Integrase Inhibitor, Isentress®, was approved for use in both the United Sates and the European Union.

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

Milliken & Company

Poor indoor air quality is one of the top five environmental health risks 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® high-friction coating 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® to include biobased raw materials in 2005.

Monsanto Company

Revolutionizing Insect Control: Bollgard® Insect-Protected Cotton Technology and Bollgard II® with Roundup Ready® Flex

Cotton is the most important textile fiber in the world, accounting for more than 40 percent of total fiber production as well as other important cotton products including cottonseed oil and animal feed. Protecting this important crop from targeted insects in a way that protects humans and the environment has been a persistent challenge. So, too, has developing technologies that simultaneously ease strains on the natural, human, and economic resources that help global agriculture meet the needs of our growing population.

In 1996, Monsanto successfully developed and commercialized the first insect-protected cotton, Bollgard®. Monsanto produced the technology using *Agrobacterium tumefactions* to mediate transfer of the insecticidal Cry1Ac protein coding sequence into the cotton genome. The Cry1Ac protein is nearly identical to a protein produced by *Bacillus thuringiensis*, or Bt. When this protein is introduced into the cotton plant through biotechnology, insects that feed on the plant stop eating and die. Specifically, Bollgard® cotton kills bollworm and budworm.

In 2006, Monsanto commercialized Bollgard II® cotton, a second-generation insect-protected cotton that contains an additional insecticidal protein, Cry2Ab2. The additional protein provides dual modes of action, creating powerful control of an expanded spectrum of most leaf- and boll-feeding worm species including budworms, bollworms, armyworms, and lopers, as well as saltmarsh caterpillars and cotton leaf predators, greatly reducing the need to spray for worms. Monsanto's Bollgard® and Bollgard II® traits have completely revolutionized insect control in cotton, providing growers with the ability to stop major cotton pests with fewer chemical sprays, maximize yield potential, and ultimately better steward natural resources. The National Center for Food and Agriculture Policy (NCFAP) calculated that Bt cotton planted in the United States alone has reduced insecticide use by 2.7 million pounds per year. During 2006, two million acres of Bollgard II® cotton were planted around the globe.

NCH Corporation

System for Bioremediation of Effluents

Traditional remediation of municipal, industrial, and agricultural wastewaters uses combinations of sulfuric acid, caustic, petroleum-based solvents, and synthetic emulsifiers, which are toxic or generally not biodegradable. Naturally occurring microorganisms are an alternative to chemical remediation. They are generally supplied as dormant or resting spores with low activity levels, however, making it too costly to use enough bacteria for effective treatment in many systems.

Extensive research and development by NCH Corporation has resulted in a novel, patented process for on-site fermentation that efficiently generates a renewable feedstock of naturally occurring strains of *Pseudomonas* and *Bacillus* bacteria at 30 trillion vegetative bacterial cells every 24 hours to treat wastewaters. Every 24 hours, the BioAmp® system delivers 292 gallons of liquid product, equivalent to 25–50 pounds of commercially available dry bacterial powdered product, directly into problematic drain lines. The bacteria degrade the organic matter in the drains, ultimately releasing carbon dioxide (CO_2) and water. This saves energy by producing active bacteria on-site and reducing the energy required for manufacturing and shipping. It costs less than 10 percent of comparable quantities of dry powdered bacteria. The BioAmp® system reduces the need for commonly used acid, caustic, and solvent drain maintainers. NCH's BioAmp® system also reproducibly reduces biochemical oxygen demand (BOD) compared to baseline in a number of case studies. This type of data generation is new to the industry and demonstrates the efficacy of the BioAmp® wastewater treatment system.

During 2007, Iowa State University tested the biobased content of BioAmp® pellets to provide data for the U.S. Department of Agriculture's BioPreferred Program in the category of Biological Drain Maintenance. NCH's BioAmp® system has been on the market since 2003; it is now in use in the food processing and petroleum refining industries with over 1,500 systems in all parts of the world.

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

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

NOTE: This project is the result of a partnership between Dr. Robert L. Augustine of Seton Hall University and The NutraSweet Corporation. The project was judged in both the greener synthetic pathways and academic categories. The abstract appears in the academic section on page 9.

Convergent Green Synthesis of Linezolid (Zyvox™), an Oxazolidinone Antibacterial Agent

Pfizer, Inc.

Pfizer has developed a novel, convergent, green, second-generation synthesis of linezolid, which is the active ingredient in Zyvox™. Approved by the U.S. Food and Drug Administration in 2000, Zyvox™ is the only member of the oxazolidinone class of antibacterials. This is the first new class of antibacterials approved in over 30 years. Zyvox™ is approved for the treatment of antibiotic resistant gram-positive bacterial infections, including vancomycin-resistant *Enterococcus faecium* (VREF), methicillin-resistant *Staphylococcus aureus* (MRSA), and multidrug-resistant *Streptococcus pneumonia* (MDRSP). These antibiotic-resistant bacterial infections have become an ever-increasing threat to public health.

Pfizer initially developed a linear synthesis for Zyvox™; the company is currently using this launch process to manufacture the drug. Rapid growth in global demand for this valuable life-saving drug, however, led Pfizer to develop a greener, more efficient, convergent synthetic process to meet future needs, as well as reduce the cost and environmental impact of production. The second-generation process will replace the launch process after approval by appropriate regulatory agencies. It has numerous green chemistry benefits: overall yield is increased by 8 percent; total waste is reduced by 56 percent; nonrecycled waste is reduced by 77 percent; methylene chloride waste is reduced by 78 percent; and a pressurized ammonia step is eliminated. At current production volumes, total waste will be reduced by 1.9 million kilograms per year, and 1.7 million kilograms per year of nonrecyclable waste will be eliminated.

The greater efficiency of the new synthesis will greatly reduce the use of natural resources. The greatly reduced waste will significantly reduce the transport of hazardous waste and consequent potential for accidental exposure of humans and the environment. Reducing the cost of linezolid production will make this life-saving drug more readily available to a larger proportion of humanity.

Rhein Chemie Corporation

Additives for Optimizing Renewable Resources in the Production of Polyurethane Systems and Plastics

As the world maintains its heavy reliance on oil, supply and demand are forcing manufacturers and consumers to find alternatives to petroleum-based products. Replacing petroleum-based polyols with biobased polyols in the polyurethane market is one potential way to reduce the need for oil.

Significant technical difficulties arose in early biobased polyol systems. The available acid groups in soy polyols caused hydrolytic degradation and variable reactivity, leading to polyurethanes with inferior properties. The additive technology from Rhein Chemie overcame many of these difficulties. Now, these green alternative systems are commercially viable products that reduce petroleum dependence, engage renewable feedstocks, and improve the longevity of polyurethane elastomers, adhesives, and foams. Currently, there are no known competing technologies with the same benefits as biobased polyol systems.

Rhein Chemie's soy-based polyol additives have proven effective for producing low-density insulated spray foams. 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 I Foams. The combination of these Rhein Chemie technologies enables their insulation system to be effective in reducing depletion of the ozone layer.

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® P 200 and Addocat® 102) to form a "green" polymer. The Stabaxol® additive, a carbodiimide, scavenges the acid groups on the biopolyols and improves both the reactivity and the hydrolytic stability of the foam system. The Stabaxol® additive also minimizes the deactivation of the catalysts by reacting out the acids that lead to variable reactivity. By 2004, only two years after Rhein Chemie developed this technology, its additives were being used in low-density insulated spray foams for industrial, commercial, and residential insulation.

Roche Carolina Inc.

Scalable Non-Aqueous Process to Prepare Water-Soluble Aminodiol

The p38(4) MAP (mitogen-activated protein) kinase inhibitor is a drug of the pyridinylimadazole class for the treatment of rheumatoid arthritis and, potentially, asthma and psoriasis. It blocks the destruction of joint tissue and the production of the tumor necrosis factor α (TNFα) and interleukin-1β (IL-1β) in monocytes and in animal models of arthritis.

Roche Carolina employs a convergent synthesis to produce this active pharmaceutical ingredient (API). One of the fragments involved in the synthetic route is 3-aminopentane-1,5-diol. Unfortunately, this aminodiol intermediate is highly water-soluble, making it difficult to isolate from an aqueous reaction mixture. Extraction from the aqueous system requires a very large volume of the organic solvent, dichloromethane. Purification of the resulting viscous liquid is either by distillation or via crystalline salt, but requires multiple operational steps. This process was sufficient to produce the API for Phase I and Phase II clinical trials, but was not appropriate for manufacturing larger quantities for commercial use. A non-aqueous isolation and purification of the aminodiol fragment on a larger development scale and, subsequently, on a commercial scale, presented important technical challenges to be overcome to implement a more environmentally appropriate manufacturing process.

Roche Carolina has developed a process addressing these environmental concerns. In this new process, 3-aminopentane-1,5-diol is synthesized in two isolated steps and four chemical reactions starting from readily available and inexpensive dimethyl acetone-1,3-dicarboxylate. The company has optimized the process through significant streamlining, resulting in the use of a single solvent, which is easily recovered and recycled. The key operations involve: sodium borohydride reduction of dimethyl 3-*N*-*tert*-butoxycarbonyl-aminoglutarate, a one-pot deprotection, and purification of the 3-aminopentane-1,5-diol using an acidic resin under non-aqueous conditions. The overall yield of the new synthesis is 89 percent and the API purity is 99.5 percent. Raw material costs and operating costs are both greatly reduced.

Adventures in Green Chemistry

Sepracor, Inc.

Trans-norsertraline is an active pharmaceutical ingredient (API) with promising activity in the central nervous system. Sepracor's Process Research & Development Group devised a green route to *trans*-norsertraline using a catalytic asymmetric hydrogenation that replaces a process based on a stoichiometric chiral auxiliary. To implement this synthesis, Sepracor had to identify an effective catalyst for a challenging asymmetric hydrogenation. The company also had to develop novel chemistry for two steps surrounding the catalytic transformation.

Because large-scale access to enamides is underdeveloped, Sepracor scientists developed a novel, nonmetal-based methodology to yield a high-quality substrate for the key reaction. A chiral catalyst at low loading delivered the desired diastereomer in superb purity and yield. The amide product was hydrolyzed to yield the drug product.

To improve on its first-generation scale-up and further streamline the process, Sepracor reevaluated each step, creating a second-generation process. Sepracor refined the enamide methodology using toluene as the solvent throughout and eliminating both methanol and the energy-demanding distillation its use required. In partnership with Dow/Chirotech, Sepracor identified a rhodium catalyst that enhanced the selectivity of the reaction to 98:2. And finally, because amide cleavage on sensitive substrates is also underdeveloped, Sepracor designed a facile cleavage of the key intermediate under mild conditions to deliver material in good yield and quality. Compared to the first-generation synthesis, the second-generation synthesis reduces waste by 30 percent, has a 41 percent shorter cycle time, has a 15 percent higher yield, and uses less energy.

Because Sepracor implemented the more efficient process early during the development cycle, the company will receive the environmental and economic benefits for the entire product lifecycle. Sepracor developed this chemistry during 2006 and 2007; the company subsequently used it to produce 75 kilograms of high-quality material at plant scale.

ech2o™ – Electrically Charged Water

Tennant Company

Traditional floor cleaning methods use an automatic scrubber filled with a large volume of cleaning solution consisting of water and a chemical detergent. Tennant Company's *ech2o*™ technology eliminates the need for adding a chemical detergent to the automatic floor scrubber. The *ech2o*™ technology electrically activates tap water, causing it to perform like an all-purpose detergent. By removing the need for chemicals in the automatic scrubber, this technology eliminates the negative environmental and health impacts associated with producing, packaging, transporting, using, and disposing of traditional chemical detergents. Compared to traditional cleaning methods, the *ech2o*™ technology reduces water use by 70 percent and eliminates the need for chemicals.

The electrically charged *ech₂o*™ solution is created in a special unit that is installed in Tennant's automatic floor cleaning machines. The *ech₂o*™ solution attacks the dirt and suspends it off the floor's surface, enabling the scrubber's pads or brushes to easily remove the soil. Approximately 45 seconds after the *ech₂o*™ cleaning solution is created, it returns to plain water. What is left in the automatic scrubber's recovery tank is plain water and the soil removed from the floor. In this process, 100 percent of the water used reverts to neutral tap water and can be handled and disposed of safely.

Tennant is the first in its industry to harness the cleaning power of water for cleaning hard floor surfaces and to use electrically charged water on a mobile platform. Tennant plans to make its patent-pending processing units available on several models of its cleaning machine platforms. Tennant launched its product during 2007; it has a number of patents pending.

Thermo Fisher Scientific

Green pH Electrodes

Glass tubing containing 20–30 percent lead is traditionally used to manufacture pH electrodes as it has the ideal workability and coefficient of expansion to easily fuse to the glass pH membrane tips. The solder used to join the electrodes' cables and connectors contains lead as well. Mercury–mercurous chloride reference systems are also currently used in some pH electrodes. Both lead and mercury create problems with electrode disposal; they are known to be detrimental to the environment and, thus, products containing these heavy metals must be disposed of as hazardous waste.

Thermo Fisher Scientific is now using a lead-free glass and lead-free solder to create completely lead-free pH electrodes. The replacement glass uses a nickel–iron alloy metal seal instead of lead to achieve the necessary properties. The cost of this lead-free glass decreased recently so that it became a feasible replacement for lead-containing glass without increasing the cost of the electrode. Eliminating lead from all pH electrodes in the world market would save more than 2,000 kilograms of lead annually.

Some pH electrodes contain a mercury–mercurous chloride reference junction that is known to be very stable, even in difficult sample matrices. Testing has shown that a silver–silver chloride reference held in a stable polymer-based electrolyte gives the same performance, thus eliminating the need for mercury in the electrode. Eliminating mercury from electrodes prevents them from requiring disposal as hazardous waste and also prevents the risk of exposing the user to mercury if the electrode breaks.

These new pH electrodes will have performance and cost comparable to current lead- and mercury-containing electrodes, but will be disposable as regular trash. Thermo Fisher Scientific manufactured and tested its first prototype pH electrodes using completely lead-free glass in 2007.

U.S. Department of Energy, Argonne National Laboratory

Resin Wafer Technology

With technical and financial support from several partners, Argonne National Laboratory (ANL) developed resin wafer technology to improve the energy and atom efficiency of separations. Resin wafer technology enables electrodeionization (EDI) to be extended well beyond its conventional applications in ultrapure water production to several high-volume applications that also have high environmental impacts. The new applications include production of biobased chemicals, management of industrial water, production and purification of chemicals, and, potentially, photocatalytic production of hydrogen from water or carbon dioxide (CO_2) sequestration from flue gases.

EDI is an electrically driven process that separates low-concentration charged species from process streams at higher efficiency than electrodialysis, its lower-tech counterpart. Resin wafer technology replaces the loose ion exchange resins that are employed in conventional EDI. The resin wafer offers several performance advantages: (1) controlled porosity, which makes stream flow more efficient; (2) enhanced ion conductivity, which reduces power consumption; and (3) reduced leakage, which increases product recovery and cuts waste stream loss. Compared with conventional EDI, resin wafer technology also provides new functionalities. 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 even in situ catalysis.

Resin wafer technology also offers significant green chemistry benefits. It reduces the cost of producing biobased chemicals, providing economic drivers for emerging biorefineries to displace petrorefineries. It decreases the use of fresh water and the release of waste water in power plants. It reduces energy and chemical use during the production of organic acids, esters, and other chemicals. Finally, it has the potential to enable enhanced hydrogen production from water and CO_2 capture from flue gases in coal power plants.

ANL has several patents for this technology. During 2007, ANL scaled up the technology to a pilot-scale field demonstration.

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Award winners are indicated with *.

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