



The Presidential Green Chemistry Challenge Awards Program:

Summary of 2009 Award Entries and Recipients



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Contents

Introduction	1
Awards	3
<i>Academic Award</i>	3
<i>Small Business Award</i>	4
<i>Greener Synthetic Pathways Award</i>	5
<i>Greener Reaction Conditions Award</i>	6
<i>Designing Greener Chemicals Award</i>	7
Entries from Academia	9
Entries from Small Businesses	19
Entries from Industry and Government	33
Index	59

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 2009 marks the 14th year of the program. This compilation summarizes the entries submitted for the 2009 awards. Five of the more than 90 entries were nationally recognized on June 22, 2009, 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 Presidential 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 2009 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 2009 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

Atom Transfer Radical Polymerization: Low-impact Polymerization Using a Copper Catalyst and Environmentally Friendly Reducing Agents

**Professor Krzysztof Matyjaszewski,
Carnegie Mellon
University**

Innovation and Benefits

Hazardous chemicals are often required in the manufacture of important polymers such as lubricants, adhesives, and coatings. Professor Matyjaszewski developed an alternative process called “Atom Transfer Radical Polymerization (ATRP)” for manufacturing polymers. The process uses chemicals that are environmentally friendly, such as ascorbic acid (vitamin C) as a reducing agent, and requires less catalyst. ATRP has been licensed to manufacturers throughout the world, reducing risks from hazardous chemicals.

Worldwide production of synthetic polymers is approximately 400 billion pounds per year; approximately half of this involves free radical polymerization. With the recent development of controlled radical polymerization (CRP), it is now possible to make well-defined polymers with precisely controlled molecular structures. Atom transfer radical polymerization (ATRP) is one such technology; it is a transition-metal-mediated, controlled polymerization process that was discovered at Carnegie Mellon University (CMU) in 1995. Since then, Professor Matyjaszewski and his group have published over 500 scientific papers on CRP; these papers have been cited over 30,000 times, making Professor Matyjaszewski the second-most cited researcher in all fields of chemistry in 2008. This explosive interest in ATRP is due to its simplicity and ability to tailor-make functional macromolecules for specialty applications. ATRP has become the most versatile and robust of the CRP methods.

Professor Matyjaszewski has been working continually to increase the environmental friendliness of his process. During the last four years, he and his team at CMU have developed new catalytic systems that dramatically decrease the concentration of transition metal, while preserving good control over polymerization and polymer architecture. The latest improvements are 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 conditions. The recent discovery of ARGET ATRP reduces the amount of copper catalyst from over 1,000 ppm to around 1 ppm in the presence of environmentally friendly reducing agents such as amines, sugars, or ascorbic acid. 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 (mini-emulsion, inverse mini-emulsion, microemulsion, emulsion, and suspension), and solventless bulk polymerizations. Professor Matyjaszewski's work is opening new “green” routes for producing many advanced polymeric materials.

ATRP has become an industrially important means to produce polymers. Since 2003, ATRP has been licensed to 8 of the over 40 corporations funding the research at CMU (PPG, Dionex, Ciba, Kaneka, Mitsubishi, WEP, ATRP Solutions, and Encapson). Licensees around the world have begun commercial production of high-performance, less-hazardous, safer materials including sealants, coatings, adhesives, lubricants, additives, pigment dispersants, and materials for electronic, biomedical, health, and beauty applications.

Small Business Award

BioForming® Process: Catalytic Conversion of Plant Sugars into Liquid Hydrocarbon Fuels

Innovation and Benefits

Virent's BioForming® process is a water-based, catalytic method to make gasoline, diesel, or jet fuel from the sugar, starch, or cellulose of plants that requires little external energy other than the plant biomass. The process is flexible and can be modified to generate different fuels based on current market conditions. It can compete economically with current prices for conventionally produced petroleum-based fuels. Using plants as a renewable resource helps reduce dependence on fossil fuels.

Virent has discovered and is developing an innovative green synthetic pathway to convert plant sugars into conventional hydrocarbon fuels and chemicals. Virent's catalytic BioForming® process combines proprietary aqueous-phase reforming (APR) technology with established petroleum refining techniques to generate the same range of hydrocarbon molecules now refined from petroleum. First, water-soluble carbohydrates are catalytically hydrotreated. Next, in the APR process, resultant sugar alcohols react with water over a proprietary heterogeneous metal catalyst to form hydrogen and chemical intermediates. Finally, processing with one of multiple catalytic routes turns these chemicals into gasoline, diesel, or jet fuel components. The technology also produces alkane fuel gases and other chemicals. Virent's BioForming® platform can generate multiple end-products from a single feedstock and enable product optimization based on current market conditions.

Compared to other biomass conversion systems, Virent's technology broadens the range of viable feedstocks, provides more net energy, and produces fuels compatible with today's infrastructure. The process uses either food or non-food biomass; it is scalable to match feedstock supply. Unlike fermentation, Virent's robust process can use mixed sugar streams, polysaccharides, and C₅- and C₆- sugars derived from cellulosic biomass. By using more plant mass per acre, the process provides better land use and higher value for farmers. The technology needs little energy input, and can be completely renewable. Virent's energy-dense biofuels separate naturally from water; as a result, the process eliminates the energy-intensive distillation to separate and collect biofuels required by other technologies. The hydrocarbon biofuels from Virent's process are interchangeable with petroleum products, matching them in composition, functionality, and performance; they work in today's engines, fuel pumps, and pipelines. Preliminary analysis suggests that Virent's BioForming® process can compete economically with petroleum-based fuels and chemicals at crude oil prices of \$60 a barrel.

The BioForming® process can speed the use of non-food plant sugars to replace petroleum as an energy source, thus both decreasing dependence on fossil hydrocarbons and minimizing the impact on global water and food supplies. Fuels derived from the process can have a 20–30 percent per Btu cost advantage over ethanol. The BioForming® platform is near commercialization. During 2008, Virent produced over 40 liters of biogasoline for engine testing and began fabrication of its first 10,000-gallon-per-year pilot plant to produce biogasoline.

Greener Synthetic Pathways Award

**Eastman Chemical
Company**

A Solvent-Free Biocatalytic Process for Cosmetic and Personal Care Ingredients

Innovation and Benefits

Esters are an important class of ingredients in cosmetics and personal care products. Usually, they are manufactured by harsh chemical methods that use strong acids and potentially hazardous solvents; these methods also require a great deal of energy. Eastman's new method uses immobilized enzymes to make esters, saving energy and avoiding both strong acids and organic solvents. This method is so gentle that Eastman can use delicate, natural raw materials to make esters never before available.

The cosmetics and personal care market is a vast enterprise of formulated specialty chemicals. Esters are an important class of cosmetic ingredients, comprising emollients, emulsifiers, and specialty performance ingredients. In 2006, the estimated North American consumption of esters as emollients and emulsifiers was 50,000 metric tons. Usually, such esters are manufactured using strong acid catalysts at high temperatures; unfortunately, this produces undesirable byproducts that must be removed by energy-intensive purifications. Other methods of producing cosmetic esters require organic solvents that are potentially hazardous to workers and the environment. The growing trend for natural ingredients and environmentally responsible processes in the cosmetics market requires new manufacturing methods.

In 2005, scientists at Eastman began investigating enzymes as catalysts to produce cosmetic esters. Eastman has now synthesized a variety of esters via enzymatic esterifications at mild temperatures. The esterifications are driven to high conversion by removing the coproduct, usually water from esterification of an acid or a lower alcohol from transesterification of an ester. The mild processing conditions do not lead to formation of undesirable byproducts that may contribute color or odor. The immobilized enzyme, such as lipase, is easily removed by filtration. The specificity of the enzymatic conversions and the relatively low reaction temperatures minimize the formation of byproducts, increase yield, and save energy.

Eastman's process can use delicate raw materials such as unsaturated fatty acids that would oxidize during conventional esterifications. Thus, Eastman can make ingredients never before available. It has manufactured hundreds of such new esters by combining different alcohols and acids. Biocatalysis can even yield new products that offer superior performance. For example, two esters can be formed from 4-hydroxybenzyl alcohol and acetic acid. One—esterification at the benzyl moiety—is only accessible via the enzymatic route. This particular ester inhibits tyrosinase, a key enzyme in melanin synthesis, and, therefore, is effective in reducing undesirable skin pigmentation and providing a more uniform skin tone.

Eastman's biocatalytic process can save over ten liters of organic solvent per kilogram of product. The ester product is often pure enough to obviate post-reaction processing. An early lifecycle assessment identifies Eastman's process as vastly improved over conventional processes, especially in energy use. Overall, this process improves quality, yield, cost, and environmental footprint compared to conventional chemical syntheses.

Leading cosmetic companies are currently evaluating many of Eastman's new esters, including emollient esters made from rice bran oil, glyceride emulsifiers, and new ingredients that combat the visible signs of aging.

Greener Reaction Conditions Award

Innovative Analyzer Tags Proteins for Fast, Accurate Results without Hazardous Chemicals or High Temperatures

Innovation and Benefits

Each year, laboratories test millions of samples of food for the presence of protein. Such tests generally use a large amount of hazardous substances and energy. CEM has developed a fast, automated process that uses less toxic reagents and less energy. The new system can eliminate 5.5 million pounds of hazardous waste generated by traditional testing in the United States each year. What's more, it differentiates between protein and other chemicals used to adulterate food, such as melamine.

The recent use of melamine to masquerade as protein and adulterate both baby formula in China and pet food in the United States makes accurate testing for protein imperative. The standard Kjeldahl and combustion tests for protein measure total nitrogen, however, and cannot distinguish melamine from protein. Kjeldahl testing uses sulfuric acid, sodium hydroxide, hydrochloric acid, and boric acid along with a catalyst of copper sulfate, selenium, or mercury. U.S. companies generate 5.5 million pounds of hazardous waste annually from Kjeldahl testing. Trained chemists are required to run these tests due to the hazardous materials and high temperatures required.

The Sprint™ Rapid Protein Analyzer automates a technique that tags protein directly and provides fast, accurate results. CEM's proprietary iTAG™ solution actually tags protein by attaching only to histidine, arginine, and lysine, the three basic amino acids commonly found in proteins. The proprietary iTAG™ solution contains an acidic group that readily attaches to the basic amino acids; iTAG™ also has an extensive aromatic group that readily absorbs light and appears orange. The iTAG™ bound to the protein is removed from solution by a filter and the remaining iTAG™ is then measured by colorimetry. The Sprint™ System ignores any other nitrogen that may be present, including the nitrogen in melamine. As a result, it enables food and pet food processors to be absolutely certain of the bulk protein content of their ingredients and final products for quality control, product safety, and nutritional labeling. Sprint™ may be used in the laboratory, on the processing line, or as a rapid check for incoming raw materials. The system does not require a trained chemist to obtain accurate results.

Sprint™ uses a green chemistry method: its iTAG™ solution is nontoxic, nonreactive, and water-soluble. It eliminates all of the hazardous waste created by Kjeldahl testing. In addition, Sprint™ does not require high temperatures, making it a much safer method than Kjeldahl or combustion techniques. It is easy to operate and can test most samples in 2–3 minutes, compared to 4 hours for a Kjeldahl analysis. It uses disposable filters and recyclable sample cups and lids; all other parts of the system that touch the sample are self-cleaning. Remarkably fast, accurate, cost-effective, and safe, Sprint™ is poised to become the method of choice for protein testing. The methods it automates are approved by AOAC (Association of Analytical Communities) and AACC International (previously: American Association of Cereal Chemists). It was commercialized in January 2008.

Designing Greener Chemicals Award

Chempol® MPS Resins and Sefose® Sucrose Esters Enable High-Performance Low-VOC Alkyd Paints and Coatings

**The Procter &
Gamble Company**

**Cook Composites
and Polymers
Company**

Innovation and Benefits

Conventional oil-based “alkyd” paints provide durable, high-gloss coatings but use hazardous solvents. Procter & Gamble and Cook Composites and Polymers are developing innovative Chempol® MPS paint formulations using biobased Sefose® oils to replace petroleum-based solvents. Sefose® oils, made from sugar and vegetable oil, enable new high-performance alkyd paints with less than half the solvent. Paints with less hazardous solvent will help improve worker safety, reduce fumes indoors as the paint dries, and improve air quality.

Solvent-borne alkyd coatings are in demand because they are cost-effective and high-performing in many applications including architectural finishes, industrial metal, and equipment for agriculture and construction. Millions of gallons of these paints and coatings are sold in the United States and around the world. Conventional alkyd resin paints and coatings require large amounts of volatile solvents to solubilize the organic components and attain appropriate viscosities. These solvents contribute to the formation of ground-level ozone and smog. Low-VOC alkyd coatings exist, but suffer from inferior performance. Some take too long to dry; others use substitute, VOC-exempt solvents that tend to be expensive and often have an undesired odor or other inferior performance. Low-VOC, waterborne acrylic latex paints are also available, but they have performance trade-offs such as low gloss and reduced corrosion resistance compared to solvent-borne alkyd coatings.

The Procter & Gamble Company (P&G) and Cook Composites and Polymers Company (CCP) have collaborated to develop a new alkyd resin technology that enables formulation of paints and coatings with less than half the VOCs of solvent-borne alkyd coatings. These alkyd formulations are enabled by Sefose® sucrose esters which are prepared from renewable feedstocks by esterifying sucrose with fatty acids in a patented, solventless process. The molecular architecture and functional density of Sefose® are controlled by selecting natural oil feedstocks with optimal fatty acid chain length distribution, unsaturation level, and degree of esterification. In applied paint films, Sefose® undergoes auto-oxidative cross-linking with other constituents and becomes an integral part of the coating films. Chempol® MPS alkyd resins are specially formulated to deliver performance advantages such as fast drying, high gloss, film toughness, and increased renewable content.

Replacement of conventional alkyd resins by Chempol® MPS could (1) reduce VOCs equivalent to the emissions from 7,000,000 cars per year; (2) reduce ground-level ozone by 215,000 tons per year; and (3) save 900,000 barrels per year of crude oil from the solvents and alkyd polymers it replaces. Chempol® MPS is cost-competitive with conventional alkyls on an equal-dry-film basis. In October 2008, CCP launched Chempol® MPS and began actively sampling the coatings industry. P&G is also evaluating and testing Sefose® oils as biobased alternatives to replace petroleum-based lubricants.

Entries from Academia

Liquid but Nonvolatile Sulfonic Acids and Amines: Greener Chemicals for Greening Processes

Chemistry impacts most aspects of the global economy. Acids and bases, many of the former as sulfonic acids and the latter as amines, impact chemistry. Pure or in solution, these acids and amines are commonly volatile, noxious, and malodorous, are frequently flammable, and often pose substantial risks to health and the environment. Professor Davis has effectively eliminated these problems by covalently anchoring acid and amine functionalities to non-volatile liquid salt matrices (ionic liquids; ILs). These ILs function as nonvolatile reagents and catalysts. Their application to important problems such as carbon dioxide (CO₂) capture and catalysis can lead to process efficiencies that are greener because they consume less energy.

Professor Davis and his group covalently tether reactive functional groups to ions that they then use to formulate ILs. Their term “task-specific ionic liquids” (TSILs) describes these materials. Their successes include developing nonvolatile liquid amine TSILs that reversibly scavenge CO₂. These TSILs can replace aqueous monoethanolamine and diethanolamine that scavenge CO₂ impurities from natural gas. First-generation TSILs have a CO₂-uptake capacity equal to that of the free amines and require only about one-third the energy to extrude the captured CO₂. Second-generation amine TSILs are even more effective, contain no fluorine or other exotic elements, have an atom-efficient synthesis, and are far less expensive. Three large U.S. companies are investigating amine TSILs for bulk CO₂ capture and membrane-based CO₂ separation. During 2008, Professor Davis licensed the rights for small-scale manufacturing and sales of second-generation amine TSILs to Frontier Scientific, Inc.

Professor Davis has also developed acid TSILs that are nonvolatile liquid Brønsted acids for catalyzing important industrial organic reactions. An industrial collaborator is investigating these TSILs. Professor Davis has licensed first-generation amine and acid TSILs to Merck KGaA. He is negotiating agreements with several large international firms for second-generation TSILs.

The University of California, Santa Barbara Green Chemistry Initiative

The University of California, Santa Barbara Green Chemistry Initiative (UCSB GCI) addresses the challenges of reducing hazardous waste in UCSB research labs and laboratory-based courses. Focusing on the campus is essential, as it is the training ground for future chemists. These efforts started with programs beneficial to the Chemistry department. The first program dealt with replacing mercury thermometers with less-hazardous, alcohol-based thermometers. The second was the introduction of the UCSB Surplus Chemical Program and website, which allow researchers to exchange chemicals with each other. These programs helped the Student Intern LabRATS build trust with the faculty in the Chemistry Department.

With 1,100 undergraduate students in 130 laboratories each week at UCSB, there are huge potential savings. Although lab manuals already used some microchemistry, the LabRATS did research to see how much more waste they could reduce. For example, their manuals had an experiment with lead nitrate that might be replaced by less-hazardous zinc nitrate. To test this, they ran the regular experiment with lead nitrate alongside the revised experiment with zinc nitrate. Although this was unsuccessful, the model they developed allowed them to investigate alternative, less-hazardous substitutions in any learning laboratory. Currently, they are extend-

**Professor James
Hillard Davis, Jr.,
Department of
Chemistry,
University of South
Alabama**

**Raminderjit (Sonam)
Gill and Jessica
Alvarez, Student
Intern LabRATS,
University of
California, Santa
Barbara**

Professor Arlin E. Gyberg, Augsburg College; SarTec Corporation

ing their efforts and model into organic chemistry with Professor Bruce H. Lipshutz and his ideas for aqueous alternatives to organic solvents.

Their multipronged approach to reducing hazardous waste has led faculty and students to interact on multiple levels to think about implementing green chemistry. Even after the failure of the zinc nitrate substitution, students and collaborators pushed forward with new ideas and approaches. This work has been supported by two grants from the Green Initiative Fund. The UCSB GCI has been leading efforts under the university's Campus Sustainability Plan, which requires the university to achieve net zero waste by 2020.

The Mcgyan Process: A Green Synthetic Route for Biodiesel Production

Fossil fuels have detrimental effects on the environment. Biobased fuels such as biodiesel are more environmentally friendly: their use recycles carbon through renewable biomass, and they burn cleaner than fossil fuels. Current manufacturing processes for biodiesel generate significant waste streams. They also require energy-intensive, high-purity, virgin oils (mostly soy oils), whose price 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 and his student Brian Krohn at Augsburg College, SarTec has developed a green synthetic route to produce biodiesel in a fixed-bed, flow-through catalytic 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 triglycerides and free fatty acids to biodiesel. The catalyst contains modified porous microspheres of zirconia, titania, or alumina.

SarTec's Mcgyan process offers many environmental advantages over the current biodiesel production method, including the following: (1) The Mcgyan process uses less energy overall. (2) The process can make biodiesel from waste and byproduct lipid sources such as brown grease and corn oil reclaimed from ethanol production as well as virtually any plant oil because free fatty acids and water in the feedstocks do not interfere. (3) The zirconia-based catalyst is contained in a fixed-bed reactor and is not continuously consumed (washed out) in the production process. (4) The new technology reduces the amount of hazardous waste produced by eliminating unwanted side reactions that produce soap wastes from free fatty acids. (5) The Mcgyan process does not require large quantities of base (or acid) to convert feedstocks into biodiesel. During 2008, SarTec neared completion of a three-million-gallon-per-year facility that will use this technology. The projected start date for the facility is February 2009.

Biosynthesis of Higher Alcohols from Renewable Carbon Sources

Higher alcohols, especially those with 3–8 carbon atoms, are useful as chemical feedstocks and transportation fuels. Higher alcohols offer advantages over ethanol as gasoline substitutes because they have higher energy density, lower hygroscopicity, and lower vapor pressure, which lead to better air quality. Branched-chain alcohols also have higher octane numbers than do their straight-chain counterparts. The current source of these higher alcohols is petroleum, which results in a net increase in atmospheric carbon dioxide (CO₂).

The biosynthesis of higher alcohols from renewable resources including non-food crops or CO₂ has the potential to reduce the carbon footprint of chemical manufacturing and transportation fuels. Although biosynthetic higher alcohols could be important to a sustainable economy, no native organisms make them.

Professor James C. Liao, Department of Chemical and Biomolecular Engineering, University of California, Los Angeles

Professor Liao and his colleagues have developed a platform technology for one-pot, microbial conversion of renewable carbon sources (sugars and cellulose) and waste (CO₂) to higher alcohols. They have used metabolic engineering, protein engineering, and genomics to develop strains of *E. coli* that produce higher alcohols including isobutanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 3-methyl-1-pentanol, and 2-phenylethanol from renewable carbon sources. Their strategy leverages the microbial host's highly active amino acid biosynthetic pathway and diverts its 2-keto acid intermediates into alcohol synthesis. They then extend the chain length of the 2-keto acids to synthesize non-natural higher alcohols. Their engineered microbes produce isobutanol from glucose in high, near-theoretical yields. Because almost all microbes possess pathways for amino acid biosynthesis, this technology is applicable to microorganisms that consume other carbon sources, such as cellulose (e.g., *Clostridium*) or CO₂ (e.g., cyanobacteria).

Professor Liao has licensed this technology to Gevo, Inc., which built a pilot plant to produce isobutanol from glucose. This technology can potentially save 67 million tons per year of CO₂ currently produced by the synthesis of 14 billion gallons of higher alcohols from petroleum.

Getting Organic Solvents Out of Organic Reactions

Organic solvents are routinely used as the medium for organic reactions. Unfortunately, many of them are derived from petroleum, and they produce an estimated 70–80 percent of the world's chemical waste.

Professor Lipshutz has found that a mono-PEGylated, α -tocopherylated sebacic acid derivative (PTS) is an atypical surfactant that allows several of the most common organic reactions catalyzed by transition metals (especially palladium and ruthenium) to take place in water as the only solvent, at room temperature, and in high isolated yields. These first-of-their-kind processes under mild, aqueous conditions include olefin metathesis reactions (chemistry for which the Nobel Prize was awarded in 2005), as well as palladium-catalyzed Suzuki, Heck, and Sonogashira cross-couplings. Importantly, product isolation is especially facile without frothing or foaming. By allowing catalysis in water, PTS eliminates the use of organic solvents in these reactions.

PTS is a nanomicelle-forming amphiphile that features vitamin E as the inner, lipophilic “solvent”, along with a 10-carbon linker, and a PEG-600 hydrophilic portion. PTS has no health or safety issues; in fact, it is currently being made in the United States at the metric ton level for intended use in food and beverages.

PTS forms micelles in aqueous solution that function as nanoreactors. The high concentrations of reactants and catalysts within PTS micelles lead to dramatically increased rates of reaction. This allows reactions at ambient temperatures and creates additional environmental savings. Other common, commercially available surfactants are less effective in the cross-coupling reactions studied to date.

Professor Lipshutz's broad-based technology addresses the major source of chemical waste: organic solvents. It offers opportunities for industrial processes to replace organic solvents with small percentages of PTS in water, even seawater, as the only solvent. PTS is covered by patents owned by the National Research Council in Canada and is under exclusive license to Zymes, LLC.

**Professor Bruce H. Lipshutz,
Department of
Chemistry and
Biochemistry,
University of
California, Santa
Barbara; Zymes, LLC**

Template-Controlled Reactivity in the Organic Solid State

Subtle changes in molecular structure can profoundly influence the solid-state packing and, thus, the reactivity of molecules. The problem of crystal packing prevents members of closely related molecules from exhibiting homologous, solid-state structures and reactivity patterns.

Professor MacGillivray has developed a general method to control chemical reactivity in the organic solid state. He uses small organic molecules as templates to assemble reactants in the solid state into positions suitable for chemical reactions. The templates assemble olefins via hydrogen bonds within stoichiometric solids known as co-crystals. The olefins then undergo intermolecular [2+2] photodimerizations. The key to the method is the ability of the templates to assemble the olefins in discrete assemblies for solid-state reactions. The solid-state arrangements of the olefins are controlled by the template rather than by long-range crystal packing. This work has the potential to open new avenues of organic synthesis because the medium allows molecules to react in geometries and orientations that can be inaccessible in solution.

Professor MacGillivray has used his method for the solid-state synthesis of molecules known as ladderanes with regiospecificity, no byproducts, and 100-percent yield. Ladderane structures are building blocks for many natural products; previously, they had presented a major synthetic challenge for many chemists.

In 2008, Professor MacGillivray demonstrated that the co-crystals used for his solid-state reactions form via solvent-free methods based on mortar-and-pestle dry grinding. Previously, co-crystal formation had required solvent. His methods can also be used in the green synthesis of ligands in inorganic chemistry. Specifically, his molecules can be used as building blocks of self-assembled metal-organic architectures and porous materials with structures akin to zeolites. His work succeeds where many researchers have failed. It now opens the organic solid state as a general solvent-free medium in synthetic organic chemistry, with further applications in inorganic chemistry and materials science.

High-Yield Conversion of Plant Biomass into a New Generation of Biofuels

These are days of extraordinary necessity in biofuel research. In the United States, large-scale automotive fuel production from biomass is limited to the fermentation of cornstarch hydrolysates to ethanol. Although cellulosic ethanol and biodiesel are gaining as reasonable alternatives to corn ethanol, they are, at present, insignificant as alternative fuels. The principal problem for cellulosic ethanol remains the difficult, expensive derivation of fermentable sugars from biomass. Biodiesel production, on the other hand, is seriously limited by the availability of plant oils. Other technologies including biopyrolysis oil and cellulosic gasoline are being tested, but may not be economically viable.

Recognizing opportunities in this area, Professor Mascal undertook a detailed study of the deconstruction of cellulose. He found that acid solution quickly hydrolyzed cellulose to glucose, but that subsequent reactions led to complex reaction mixtures including various furans and other compounds. When he carried out the process in a biphasic reactor under carefully worked-out conditions, however, he was able to sequester the initial furanic products away from the aqueous acid and isolate them in remarkably good yields. Cellulose was suspended in an aqueous HCl–LiCl solution and extracted into an organic solvent at a moderate temperature (65 °C). The solvent was evaporated (and recycled), leaving an oil consisting of 5-(chloromethyl)furfural (71 percent) and three minor furfural-derived products (14 percent) for a total 85-percent yield. No other process is known to give comparable yields of simple

organic products from cellulose. The method works equally well on raw biomass, producing not only substituted C₆-furfurals in high yield from the cellulose, but also furfural itself from the C₅-sugar (hemicellulose), constituting the total carbohydrate utilization of biomass. The resulting furfurals are nonvolatile, nontoxic, biodegradable liquids with an energy density similar to that of gasoline. Professor Mascall is planning to scale up the process to a 50-liter reactor.

Biodegradable, Chemically Modified Starch Polymers for Protective Foam Packaging and Insulation Applications

Almost all electronic, commercial, and industrial products come packaged with a protective foam plastic, which is generally petroleum-based polyethylene, polystyrene, or polyurethane foam. This plastic foam 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. As one example, the U.S. Government program for procurement of biobased products has targeted biobased, biodegradable foams with minimum 50-percent-biobased content for Federal procurement.

Starch is a readily available anhydroglucose polymer. It exhibits hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The strong hydrogen bonding association and crystallization lead to poor thermal processing, however, because the T_m is higher than the thermal decomposition temperature; degradation sets in before thermal melting. The hydrophilicity and thermal sensitivity render the starch molecule unsuitable for thermoplastic applications.

Professor Narayan has synthesized biodegradable, chemically modified thermoplastic starch polymers by reacting starch with maleic anhydride and glycerol using a twin screw extruder as the reactor. The chemically modified starch reacts with biodegradable polyesters like polybutylene adipate-co-terephthalate in the extruder to give starch-polyester graft copolymers. The modified starch polymer and graft copolymers can be processed like any other thermoplastic polymers to produce foam and insulation packaging products that can replace existing petroleum-based products. In addition, the starch-polyester graft copolymers can be formed into films and injection-molded articles.

KTM has successfully commercialized the biodegradable, starch foams under the trade name of GreenCell™. KTM is manufacturing GreenCell™ in its 23-million-board-foot-per-year facility in Lansing, MI and recently topped \$1,000,000 in sales revenues. Corn Products International has licensed Professor Narayan's technology for use in films and molded articles; it is partnering with BASF to manufacture ECOBRAS™ products.

Highly Efficient, Practical Monohydrolysis of Symmetric Diesters

The development of environmentally friendly, cost-effective organic reactions is of central importance in both academia and industry. Water is among the most environmentally friendly solvents because it generates no hazard during chemical conversion processes. Water-mediated organic reactions thus represent typical green chemistry. Among various synthetic conversions, desymmetrization of symmetric compounds is one of the most cost-effective reactions because the starting symmetric compounds are typically available commercially at low cost or are produced easily on a large scale from inexpensive precursors. Water-mediated desymmetrization of symmetric organic compounds has the potential to be a greener reaction process of tremendous synthetic value.

**Professor Ramani Narayan,
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**Professor Satomi Niwayama,
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Ohio State
University**

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, it is challenging to distinguish these ester groups chemically. Classical saponification usually produces complex mixtures of dicarboxylic acids, half-esters, and the starting diesters, which are difficult to separate. As a result, saponification yields a large amount of undesirable, dirty waste. The most common method for effective monohydrolysis uses enzymes, which provide no basis for predicting the yield or enantioselectivity. Ring-opening reactions of cyclic acid anhydrides require hazardous organic solvents.

Professor Niwayama has pioneered water-mediated desymmetrization and has been developing monohydrolysis of symmetric diesters with remarkable success. She discovered a highly efficient, practical ester monohydrolysis of symmetric diesters. In this reaction, aqueous sodium hydroxide or potassium hydroxide is added to a symmetric diester suspended in water that may or may not contain a small amount of tetrahydrofuran or acetonitrile at 0 °C. This reaction produces pure half-esters in high to near-quantitative yields without producing dirty waste or requiring hazardous organic solvents. During 2008, Professor Niwayama applied for a patent and licensed her technology to Kishida Chemical Company.

Ethylene in Catalytic Asymmetric Synthesis: A General Route to Profen Drugs from Styrene Derivatives and a General Solution to the Exocyclic Stereochemistry Problem

In this era of heightened environmental awareness and the ever-increasing demand for more efficient chemical processes, one major challenge facing organic synthesis is the selective incorporation of abundantly available carbon, hydrogen, oxygen, and nitrogen sources into other common substrates. Working on this challenge, Professor RajanBabu and his group have discovered a new co-dimerization of ethylene and various functionalized vinylarenes, 1,3-dienes, and strained alkenes (asymmetric hydrovinylation). They found highly catalytic (substrate–catalyst ratio up to 7,412:1) protocols for nearly quantitative and highly selective reactions. These reactions proceed under mild conditions (–52 °C to 25 °C, 1 atmosphere of ethylene) to produce highly valuable 3-arylbutenes. These reactions consume both starting materials; they leave no side products. Prototypical examples of this chemistry include highly enantioselective syntheses of the nonsteroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen, naproxen, flurbiprofen, and fenoprofen from the corresponding styrenes and ethylene.

Cyclic and acyclic 1,3-dienes also undergo efficient heterodimerization with ethylene. Yields up to 99 percent can be realized for several 1-vinylcycloalkenes and 1-substituted-1,3-butadienes. Phospholanes and finely tuned phosphoramidites are excellent ligands for an asymmetric variation of this reaction, the latter giving 99-percent yield and over 95-percent-enantiomeric excess for selected substrates. An exocyclic chiral center can be used to install other stereocenters in the ring (e.g., the carbon to which the side-chain is attached). These discoveries open an expeditious route to several biologically relevant classes of compounds, including many steroid derivatives.

Professor RajanBabu also synthesized several new ligands and discovered new control elements that may have broader applications in the discovery of other highly selective catalytic processes. Examples include (1) the effects of electronic and steric tuning of ligands, and (2) the role of hemilabile ligands and their synergy with highly dissociated counterions in enhancing selectivity.

Terephthalic Acid Synthesis at High Concentrations in High-Temperature Liquid Water

Terephthalic acid (TPA) is a monomer used to produce polyethylene terephthalate, a plastic material used for disposable water bottles and beverage containers. The main commercial route to TPA is the partial oxidation of *p*-xylene in acetic acid at approximately 200 °C and 15–30 atmospheres with a manganese–bromine–cobalt catalyst. The environmental profile of this route is poor. Acetic acid is flammable; it also reacts with the bromide catalyst to produce high levels of methyl bromide emissions. (According to EPA's Toxics Release Inventory, a single terephthalate acid plant can release approximately 25,000 pounds of methyl bromide annually.) Separating the acetic acid solvent from water for recycling requires an expensive, energy-intensive distillation. Further, acetic acid oxidizes during the reaction so that approximately one billion pounds of make-up acetic acid are required each year. Manufacturing this make-up acetic acid requires substantial raw materials and energy. It also creates pollutant emissions.

Professor Savage and his group have discovered reaction conditions and a reactor strategy to synthesize terephthalic acid by the catalyzed partial oxidation of *p*-xylene at high concentrations in high-temperature liquid water. This reaction has high yields and nearly 100-percent selectivity. Replacing acetic acid with water has many benefits. Water is not flammable. Using water eliminates methyl bromide emissions and the oxidative solvent losses that required make-up acetic acid. Because water is both byproduct and solvent, the large distillation column is unnecessary, saving associated costs and energy.

Professor Savage has also developed and analyzed conceptual designs for his chemical process to show quantitatively that it is competitive on the bases of economics, energy consumption, and environmental impacts. He has also developed processing strategies so that the high concentrations needed for a commercial process could be used with his greener reaction conditions. The University of Michigan has filed a provisional patent application for this technology.

EarthTec®: Green Water Treatment

EarthTec® is an EPA-registered algacide and bactericide (EPA Number 64962-1) that is certified by the National Sanitation Foundation (NSF) Standard 60 as a drinking water additive. It uses no chlorine and contains less copper than competing products. The proprietary copper formulation made by EarthTec® is 99.9-percent-suspended cupric ions (Cu(II)); its proprietary base product, ET-3000, keeps the copper biologically active and suspended. The copper remains fully dissolved indefinitely, thereby insuring long-term organic control as well as less environmental release. EarthTec® is not an organic compound.

Earth Science Laboratories has done extensive empirical research to develop and design the proprietary chemical technology that makes EarthTec® environmentally superior to chlorine. These studies conclude that EarthTec® lowers trihalomethane production, reduces disinfection byproducts and their precursors (natural organic matter), and reduces geosmin, eliminating the taste and odor in drinking water. EarthTec® also lowers haloacetic acid levels and reduces total organic carbon, both particulate and dissolved. Unlike chlorine, EarthTec® creates no carcinogenic disinfection byproducts. EarthTec® reduces the use of copper and other chemicals, eliminating hazardous chemical substances from the environment relative to the competing, chlorine-based technology. One can use 88.5-percent less EarthTec® than other copper sulfate products.

Compared to other copper sulfate products and chlorine, EarthTec® is less toxic than those current products, is safer for the atmosphere, is nonflammable, and reduces toxicity to hu-

Professor Phillip E. Savage, Chemical Engineering Department, University of Michigan

Professor Linda Schweitzer, Oakland University; Professor Robert Reed, University of Missouri; Earth Science Laboratories, Inc.

**Professor Xiuzhi
Susan Sun,
Department of
Grain Science and
Industry and
Director, Center for
Biobased Polymers
by Design, Kansas
State University**

**Professor Paul
A. Wender,
Department of
Chemistry,
Stanford
University**

mans, animals, and plants, producing human health and environmental benefits. EarthTec® is also more cost-effective than other copper sulfate products and chlorine.

The motto of Earth Science Laboratories is “clean water for the planet” and their mission, in part, is to produce environmentally responsible water treatment products in an ecologically accountable manner. Earth Science Laboratories manufactures EarthTec® and sells it worldwide. Professors Schweitzer and Reed performed empirical research comparing the product to chlorine.

Green Process for Unfolding Soy Protein Polymers for Green Adhesives

About 20 billion pounds of adhesives are used annually in the United States for applications including wood products, foundries, packaging, and labeling. These adhesives are mainly petroleum-based. Industry is seeking biobased adhesives and coatings, but enabling technologies are lacking. On the other hand, byproducts of the current annual production of soybean biodiesel and corn ethanol include about 90 billion pounds of low-cost, protein-based meals aside from food and feed uses.

Most proteins contain both hydrophobic and hydrophilic regions. Hydrophobic interactions are a dominating factor in protein folding, unfolding, aggregation, gelling, self-assembly, adhesion, and cohesion properties. Hydrophobic regions are often buried inside of the complicated protein body, however.

Professor Sun's technology unfolds protein molecules with 0.5–5 percent of nonhazardous agents such as urea, detergents, organic/inorganic salts, and pH adjustment agents (i.e., NaOH, HCl). After the proteins unfold, some of their covalent and hydrogen bonds break and form individual polypeptides. Because hydrophobic groups are now exposed on the polypeptide surface, the resulting polypeptides become surface-active and interact with other hydrophobic polymers and chemicals. Potential applications include adhesives, surfactants, coatings, medical materials such as tissue engineering, drug delivery, and pharmaceuticals, thickeners and binders for food or feed, and cosmetic products. This technology makes high-value products from biofuel residues and, thus, can have great impact on bioenergy and the environment. It will replace at least 6 billion pounds of hazardous materials including formaldehyde, vinyl acetate, isocyanine, and acrylic acid based adhesives. The performance of Professor Sun's adhesives is superior or similar to urea-formaldehyde, phenol-formaldehyde, and many other synthetic latex-based adhesives.

Dr. Sun's adhesive technologies are in the pipeline for commercialization. Biodegradable, edible feed containers for livestock were commercialized in 2007. One company has licensed the technology for pet food binders and others are evaluating samples for a variety of commercial uses.

Green Chemistry through Function-Oriented Synthesis, Step Economy, and Ideal Synthesis

For decades, Professor Wender has pioneered the development of chemical methods for preparing biologically important molecules and has advanced the concepts of ideal synthesis and step economy. Recently, he has developed Functional Organic Synthesis (FOS), a multifaceted, inclusive approach. FOS simplifies biologically active natural products to create new target structures that are amenable to preparative organic synthesis with greater efficiency and less waste while maintaining or improving their original activity. Professor Wender has revolutionized the preconceptions of other chemists by inventing new synthetic reactions that

rapidly and efficiently raise the complexity of simpler starting materials to product-like intermediates in just a few steps. Professor Wender has impressed the chemistry community with his arene-olefin photocycloaddition, cyclopropane and other rearrangements, and numerous so-called “impossible” annelation reactions (e.g., [5+2], [2+2+2+2], [5+2+1], [4+4]).

FOS has not only guided the design of improved drug-like targets and their more efficient syntheses, but has also led to new reactions that achieve those goals better and with less waste. Recent examples of FOS from his laboratory include (1) simple arenes that modulate protein kinase C and mimic the more complex phorbols; (2) simplified enediyne compounds for cancer treatment; (3) simplified bryostatin analogs that contain only key pharmacophores, but have improved potency; (4) laulimalide analogs with simplified structures that remove the inherent functional instability of natural laulimalide, thus rendering them more desirable as drug candidates; (5) the design, synthesis, and optimization of polyarginine drug transporters to improve potency and circumvent multidrug resistance pathways in cancer cells; and (6) an efficient “reverse” process to transform a more plentiful natural product, phorbol, into prostratin, an important HIV drug adjuvant that activates the latent virus rendering it more available to conventional drug therapy. Professor Wender’s FOS concept has many facets, any of which can lead to greener chemistry in drug discovery.

Biobased Polymers and Composites

Professor Richard Wool’s research has shown that recent advances in green chemistry, genetic engineering, composite science, and natural fiber development offer significant opportunities for new, improved materials from renewable resources that are recyclable, biocompatible, and biodegradable, thereby enhancing global sustainability. Combining his biobased resins with natural fibers (plant and poultry), starch, and lignin produces new low-cost composites, pressure-sensitive adhesives, elastomers, and foams that are economical in many high-volume applications. These high-performance composites are being designed for use in energy-efficient solar-integrated roofs, wind foil blades, hurricane-resistant housing, sub-aqua hydro turbines, and hydrogen storage, in addition to agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, electronic materials, and sports equipment. The development of biobased materials is consistent with the principles of green chemistry and engineering, which pertain to the design, commercialization, and use of processes and products that are technically and economically feasible, but also minimize the generation of pollution and the risk to human health and the environment.

Professor Wool’s recent work includes developing biobased printed circuit boards made with chicken feathers and chemically modified plant oils. He did this work for Microsoft in collaboration with Rogers Corporation, Cara Plastics, and Hunter PCB. Another example is the biobased composite resins he developed in collaboration with Cara Plastics and DynaChem Inc.; worldwide distribution of these resins began in 2008. A third example is his development of biobased non-polyurethane foams that are free of highly toxic diisocyanates. These foams will be commercialized during 2009 for applications in equipment insulation. Finally, windmill blades for windfarms will be made with his resins; each blade will contain 9 tons of biobased resins. The Boone Pickens windfarm of 2,000 turbines in Texas will require 123 million pounds of biobased resins every twenty years.

Professor Richard P. Wool, Affordable Composites from Renewable Resources (ACRES) Center for Composite Materials, University of Delaware

Entries from Small Businesses

A. S. Trust & Holdings Inc.

A Climate-Friendly Hydrocarbon Refrigerant for Safer, More-Efficient Cooling

Historically, chlorofluorocarbons (CFCs) have been used as refrigerants in air conditioners and refrigerators. CFCs have the advantages of safe incombustibility, high stability, and low toxicity, but unfortunately they destroy the ozone layer. In the past decade, various hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have replaced CFCs. HCFCs and HFCs are, indeed, safer for the ozone layer, but they have been shown to be strong greenhouse gases.

A. S. Trust & Holdings has developed HCR-188C, a substitute hydrocarbon formulation that has been independently evaluated to have zero ozone-depletion potential and a global warming potential of less than 5 over the standard 100-year time horizon. HCR-188C is made from all naturally occurring substances approved for common use. It includes ethane, propane, isobutene, normal butane, isopentane, and normal pentane, plus hexane and heptane for specific applications. The key element to its performance is the exact proportions of these components.

HCR-188C can be used independently of CFCs and HFCs/HCFCs. Its cooling efficiency exceeds that of CFC R-12 and HFC R-134a. One-quarter the mass of HCR-188C in a refrigerator or automotive air conditioning system provides the same cooling as a full charge of the CFC R-12 while using only 68 percent of the electricity. A major safety improvement of HCR-188C over current hydrocarbons lies in its reduced charge rate compared to common propane-butane combinations. Another problem with current HFCs is decomposition upon leakage, which causes the HFC to become less efficient and require more frequent replacement. The higher molecular weight of HCR-188C makes it less apt to leak through joints or o-rings; as a result, it retains its cooling properties, extending the lifetime of the unit. In 2008, EPA's Significant New Alternatives Program approved HCR-188C for sale in the United States as a replacement for CFC-12 coolant fluid in household refrigeration and air conditioning units.

Bend Research Inc.

Spray-Dried Dispersions Based on Hydroxypropyl Methylcellulose Acetate Succinate for Delivery of Low-Solubility Drugs

Increasingly, drug candidates emerging from drug-discovery programs have low solubility. These candidates frequently have low oral bioavailability and require high doses to achieve a therapeutic effect.

Bend Research has developed a novel drug-delivery technology using hydroxypropyl methylcellulose acetate succinate (HPMCAS). HPMCAS is an amphiphilic polymer whose hydrophobic regions interact with insoluble drug molecules whereas its hydrophilic regions allow these structures to remain as stable colloids in aqueous solution. HPMCAS forms amorphous dispersions with a broad range of low-solubility drugs for use in solid oral dosage forms. Spray-dried dispersions (SDDs) of low-solubility drugs and HPMCAS dissolve rapidly and disperse in the body to enhance the bioavailability of the drugs by 10-fold or more. Tests of SDD technology with hundreds of low-solubility compounds exhibiting a wide range of challenging physical properties have demonstrated that the technology can enable the development of many promising drug candidates that would otherwise be halted due to low solubility.

SDD technology has several environmental benefits. The increased bioavailability of drugs administered as SDDs can reduce the amount of drugs required and, thus, the amount manufactured by up to 27 percent. Reduced drug manufacture can also reduce manufacturing wastes including waste solvents by up to 27,000 tons annually. The increased bioavailability greatly reduces the amount of drugs that pass unabsorbed into the environment after consumption by patients. The process for manufacturing HPMCAS is atom-economical and uses renewable materials.

SDD technology is well-understood and has been applied to over 400 drug candidates, 23 of which have advanced to human clinical testing including one to Phase 3 testing. A \$90 million commercial manufacturing facility was constructed in 2007; subsequently, one HPMCAS SDD has been manufactured in batches of up to 2,000 kilograms for Phase 3 clinical trials and drug registration. Many companies are currently testing SDDs with numerous drug candidates.

Greening Atorvastatin Manufacture: Replacing a Wasteful, Cryogenic Borohydride Reduction with a Green-by-Design, More Economical Biocatalytic Reduction for a Higher Quality Product

Atorvastatin calcium is the active ingredient in Pfizer's cholesterol-lowering drug Lipitor®. The key advanced chiral intermediate in the manufacture of atorvastatin is *t*-butyl (4*R*,6*R*)-6-cyanomethyl-2,2-dimethyl-1,3-dioxane-4-acetate (i.e., ATS-8, also known as TBIN). It is the control point for stereopurity and the first isolated intermediate comprising both of atorvastatin's chiral alcohol centers. Pfizer's traditional ATS-8 process used a NaBH₄ 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 was first converted with hazardous triethylborane in situ to a diastereo-directing boron chelate, which was then reacted with NaBH₄ at or below -85 °C to promote diastereoinduction. After this reaction, the boronic wastes were removed by repeated methanol quenches and vacuum distillations. The diastereoinduction was inadequate, however, and several percent of the wrong (3*S*) diastereomer was formed. Subsequently, the ATS-7 diol, an oil, was protected as its acetonide, ATS-8, whose diastereopurity required upgrading by crystallization, with concomitant product loss.

Codexis developed a greener, more economical process for reducing ATS-6 to diastereopure ATS-7. This process uses a ketoreductase biocatalyst specifically evolved to reduce ATS-6 with perfect diastereoselectivity under greener, aqueous, ambient reaction 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. The ATS-7 from this reaction is already more diastereopure than was the atorvastatin in Pfizer's Lipitor® pills as of 2006. Codexis's biocatalytic process is now supplying tens of metric tons per year, and growing, of high-quality ATS-8 to manufacturers of atorvastatin for geographic generic markets. During 2008, Pfizer announced the conversion of its ATS-8 manufacture to a biocatalytic reduction using a ketoreductase in-licensed from a third party.

Rapid Enablement of Green, Economic Processes for Chiral Alcohols by the Codex™ Panel of Recombinant, Robust, Divergent Evolvants of One Ancestral Ketoreductase

Biocatalytic reduction of ketones has long been recognized as an attractive, green alternative to using hazardous reagents, energy, or mass-intensive processes for making chiral alcohols. This promise went largely unfulfilled, however, due to the practical inefficacy of the available ketoreductase (KRED) biocatalysts, which were hampered by narrow substrate-specificity, low activity, poor in-process stability, inadequate stereoselectivity, and productivity-limiting product inhibition.

By directed evolution from a common wild-type ancestor, Codexis has successfully evolved a number of stable, high-activity KRED biocatalysts to make important chiral alcohols for commercial applications. This success gave rise to the concept of the Codex™ KRED panel, developed to increase the speed and lower the cost of identifying suitable biocatalysts. Codexis's widely applicable platform of pre-evolved, diverse KREDs from one ancestor successfully addresses the long-unmet needs for greener, commercially practical processes for chiral alcohols. The Codex™ KRED Panel includes diverse variants of one KRED that are “pre-evolved” for in-process stability and efficient manufacture. The variant enzymes contain combinatorial mutations that confer, as a population, activity on a wide structural variety of ketones and selectivity to either alcohol stereoisomer. The variants, all of known sequence, are arrayed on microtiter plates for rapid screening to find the desired activity on a new ketone substrate. If a new custom variant is needed, the Codex™ panel provides “Protein Sequence Activity Relationship” (ProSAR) data to jump-start further directed evolution.

Codexis launched its Codex™ KRED panel in 2007 and now provides it by subscription to three pharmaceutical companies. Merck is using KREDs from the Codex™ panel to produce materials for clinical trials and has stated that KRED reductions are now their preferred method for making chiral alcohols. Building on its success, Codexis has since developed panels for other generally useful biocatalytic organic chemical conversions including panels of transaminase, nitrilase, acylase, and halohydrin dehalogenase biocatalysts.

Nitro-tuff Tubes: Eliminating Genotoxic Carcinogenic Waste in Cylinder Tubes

Hydraulic and pneumatic cylinders are used in industries and applications from oil and gas production to food processing. The fluid power market relies heavily on chrome-plated rods and tubes to produce these cylinders. Chrome-plated interior diameter (CPID) tubes and chrome-plated outside diameter (CPOD) tubes are inert. The plating process, however, generates a mist that contains hexavalent chromium (Cr(VI)), a known toxin linked directly to lung cancer. Hexavalent chromium can also be released during further fabrication such as welding or by disposal.

Commercial Fluid Power is developing and marketing Nitro-tuff tubes as a safe, environmentally friendly replacement for chrome-plated tubes. Nitro-tuff tubes are ferritic nitro-carburized steel. During their manufacture, the surface of the steel is converted to a nonmetallic epsilon iron nitride (ϵ -Fe₃N) in an atmosphere of ammonia and carrier gas. Following nitriding, an oxidizing atmosphere is introduced to produce a thin, corrosion-resistant, black surface film of Fe₃NO₃₋₄. The iron nitride layer is the basis for the steel's extraordinary wear

**Commercial Fluid
Power LLC**

and corrosion resistance. Advances in mechanical properties, size, and finish control now allow Nitro-tuff tubes to substitute for CPID or CPOD tubes without loss of quality or strength. These efforts are reducing the use of hexavalent chromium and its release into the environment.

Most large chrome-plating facilities currently meet government standards for air quality, disposal, and containment of toxic waste products. Ever-tightening controls continue to increase the cost of chrome plating, however, and have helped drive technology toward greener alternatives such as Nitro-tuff tubes. Nitrided tubing can meet current market pricing structures for CPID and CPOD tubing.

Commercial Fluid Power continues to strive to bring an eco-friendly solution to the fluid power market. Recent research, development, and testing have opened new markets for Nitro-tuff tubes. The journey for a safer, more environmentally friendly replacement product at Commercial Fluid Power is ongoing.

Cortec Corporation

Corrosion-Control Chemicals Based on Sustainable Resources

Several years ago, a Federal government-commissioned survey estimated the cost of corrosion in the United States at \$275 billion annually. 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 Corporation (derived from corrosion technology) develops and provides products for corrosion control. Thirteen 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 develops, manufactures, and sells corrosion control products and systems using solvents such as *d*-limonene, natural oils such as soybean, canola, and castor, films of polylactic acid, and gluconic acid derivatives from sugar beets.

Cortec now sells eleven corrosion-control products based on natural oils, 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 (i.e., rebar) in concrete from corrosion due to salt. The 2005 selection of a Cortec product to protect the rebar in the world's largest Mosque in the United Arab Emirates led to several large orders of the gluconate inhibitor for other buildings under construction, including the Burj Dubai Tower. In the United States, a Cortec product containing gluconates was used in the restoration of the exterior walls of the Pentagon. Cortec has received nine U.S. patents for its new systems. Cortec's program, "Going Green", continues with several products in the development mode.

Dober Chemical Corporation

Smart Release™ Technology: Intelligent, Green, Water Treatment

Smart Release™ Technology is a controlled-release process for treating water in cooling towers to prevent corrosion, scale, and fouling. It is based on osmotic pressure. A proprietary membrane or polymer coating separates the active chemicals from exterior elements. When water is applied to the membrane or polymer coating, it forms a high concentration of liquid or slurry chemicals inside the container or polymer-coated tablet that creates osmotic pressure and forces the water-treatment chemicals out. The membrane or polymer coating controls the

release of the chemicals into the water and produces a linear dissolution of the solid chemicals. The technology allows dry products to be applied consistently to treat water.

Smart Release™ has been scientifically demonstrated to maintain treatment levels more consistently with less maintenance and intervention by maintenance staff than do commonly used liquid feed systems for small- and medium-sized tower systems. Customers report that the system improves tower efficiency by up to 10 percent. A 10-percent improvement in a 500-ton cooling system results in estimated savings of over 250,000 pounds per year of carbon dioxide (CO₂). Smart Release™ reduces the carbon footprint by 74 percent due to reduced packaging and shipping because the solid product contains 95-percent active ingredients compared with 10-percent active ingredients for liquid products. It reduces energy consumption because it uses a feeder made of recycled material that has no moving parts. Smart Release™ provides safer handling for workers because it is less toxic than competing liquid products, primarily because Smart Release™ is a pH-neutral solid. It also reduces accident potential because solids are less prone to spills than are liquids.

Smart Release™ also has applications in other water-treatment applications, including potable water, biocides, biocides, and reverse-osmosis membranes. Dober conducted plant trials for these innovations in 2008 and expects to introduce them commercially during 2009.

Recycling Carbon Dioxide into Carbon-Neutral Liquid Fuels

The planet urgently needs a transportation fuel that is much more carbon-neutral than the 5–25-percent carbon-neutrality of most biofuels. Doty Energy shows that off-peak, low-carbon grid energy (mostly wind energy) and waste carbon dioxide (CO₂) can be converted into clean, stable, liquid fuels: their WindFuels™. They plan to use waste CO₂ from coal-burning power plants.

Doty Energy's detailed simulations predict that plant efficiency, from input electrical energy to chemical energy in the fuels, will approach 60 percent, which is about twice what was generally expected a few years ago. Moreover, the proposed process could respond in milliseconds to major changes in grid supply and demand. Thus, it has the potential to stabilize the grid completely, even if over half of its energy comes from wind. Carbon-neutral products that can compete in the current global market are essential to prevent a climate disaster within decades.

In Doty Energy's process, water and renewable electrical power are fed into an alkaline electrolyzer, which produces hydrogen (H₂) when excess low-carbon energy is locally available. Then waste CO₂ and the renewable hydrogen are piped into an improved Reverse Water Gas Shift (RWGS) process, which permits practical reduction of CO₂ to carbon monoxide (CO) at efficiencies approaching theoretical limits (ultimately, over 94 percent). The renewable CO and H₂ are then fed into a Fischer-Tropsch Synthesis (FTS) process. The FTS reactor converts some of the CO and H₂ into liquid fuels containing light hydrocarbons and alcohols. The unreacted feedstocks and undesired products are recycled efficiently. The desired liquid fuels and chemicals may be stored and distributed by conventional means such as pipelines and tanker trucks. The International Patent Searching Authority issued a completely favorable written opinion under the Patent Cooperation Treaty (PCT) for this technology and the PCT was published in September 2008.

Doty Energy

**Earth Science
Laboratories, Inc.;
Professor Linda
Schweitzer,
Oakland
University;
Professor Robert
Reed, University
of Missouri**

**FlyAshDirect Ltd.;
Cognis Corporation**

**French Creek
Software, Inc.**

EarthTec®: Green Water Treatment

NOTE: This project is the result of a partnership between Professor Linda Schweitzer of Oakland University, Professor Robert Reed of the University of Missouri, and Earth Science Laboratories, Inc. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 15.

Carbon Blocker™ Fly Ash Conditioning Treatment

Coal combustion in the United States produces over 70 million tons of fly ash each year. Fly ash is made up of the finely divided, non-combustible materials from coal combustion including silica, aluminum, iron, and a variable amount of unburned carbon in a highly adsorptive form. The silica materials in fly ash can combine with the calcium hydroxide in hydrated cement to form calcium silicate hydrate, the mineral glue in cement. Unfortunately, the carbon in fly ash tends to adsorb the special chemicals added to form the matrix of tiny air pockets in cement that provide the cement's freeze/thaw durability. As a result, many specifications limit the carbon content of fly ash, usually to somewhere between 3 and 6 percent, and much of the fly ash produced in the United States is discarded in landfills.

If the carbon interference can be eliminated, fly ash can be used as a mineral admixture in concrete products to replace up to 30 percent of the cement in concrete. FlyAshDirect, a Cincinnati-based company, has invented a process called Carbon Blocker™. This is a patent-pending chemical treatment for fly ash that coats the carbon and prevents it from adsorbing air-entraining chemicals. Carbon Blocker™ contains no metals or inorganic salts; its active ingredient is an ester derived from renewable raw materials. It is readily biodegradable, does not add to volatile organic compounds (VOCs), and is generally recognized as safe (GRAS) for food applications. It is used in its pure state without any solvent or other additives. There are currently five commercial Carbon Blocker™ systems installed at three power plants: one each in Ohio, Indiana, and Pennsylvania. The use of Carbon Blocker™ could allow thousands of tons of fly ash to be used in concrete rather than landfilled.

Chemical Treatment Modeling and Optimization Software: The French Creek Software Calculation Engine

Most of the water taken out of the environment is used for cooling of industrial and power-generating operations. Some of the water is returned to the environment through evaporation, but most is returned after being heated and treated with persistent chemicals. Any reduction in the amount of water used or the quantity of treatment chemicals discharged has a major impact on the quality and long-term availability of water.

The user-friendly French Creek Software Calculation Engine provides scale prediction, corrosion modeling, and dosage optimization for cooling water treatment. Before French Creek Software introduced its line of software in 1990, few tools were available to predict scale and corrosion problems or to optimize treatment. The available tools such as simple indices and rules-of-thumb contained inaccuracies that resulted in operation at lower-than-desired concentration ratios, in increased water use within plants, and in higher-than-necessary discharges of treatment chemicals to the environment.

Using a sophisticated ion-association model, the French Creek Software Calculation Engine pinpoints the operating conditions at which scale and corrosion become problems and prescribes the most effective dosage of chemicals to inhibit or prevent them. These dosages are often far less than those suggested by typical rules-of-thumb.

In 2006, one of the largest water treatment service companies used the Calculation Engine to save over 21 billion gallons of water by implementing an award-winning automated cooling system controller and companion software. Through applications by other major companies and approximately one-third of the smaller regional companies, French Creek's commercial and private-label programs are estimated to have saved additional billions of gallons of water. In typical applications, French Creek technology has optimized dosages of water treatment chemicals and reduced treatment rates by up to 50 percent.

Sustainable Chemicals from Renewable Resources: A Breakthrough for Biomanufacturing

Genomatica develops and commercializes novel, biomanufactured, sustainable industrial chemicals for all major industry sectors. The company enables the production of sustainable chemicals through a proprietary technology platform that fundamentally transforms the way in which natural processes can be used to convert low-cost, renewable feedstocks into high-value products. It defines sustainable chemicals as those that are designed and manufactured using efficient, effective, safe, and more environmentally benign raw materials and processes. This new approach tightly integrates computational modeling and design with experimental execution in the laboratory.

Genomatica's latest breakthrough uses a genetically engineered microorganism (*E. coli*) and 100-percent-renewable feedstocks (sugar and water) in an anaerobic fermentation to directly produce 1,4-butanediol (BDO), a large-volume chemical used in many polymer applications. This breakthrough is important because no organism has previously been found or engineered to produce BDO from sugars. Genomatica used proprietary metabolic models and simulation algorithms to test all possible ways that BDO could be produced inside a cell, then selected the optimal paths from sugar using criteria such as yield and the number of enzymatic steps. The company then implemented these pathways and strain designs in the laboratory to produce a microorganism and fermentation process for BDO synthesis. Subsequent process development led to optimum separation and purification designs for a fully integrated, cost-advantaged, energy-efficient, clean, safe, renewable bio-BDO production process.

This new bio-BDO process creates less waste and emissions, uses less energy, and requires lower per-unit capital investment than do petroleum-based BDO processes. The new process is estimated to produce at least 25-percent less carbon dioxide (CO₂) and require at least 30-percent less energy relative to current petroleum-based BDO processes. Genomatica expects its bio-BDO process to be cost-competitive at sustained oil prices as low as \$40 per barrel. The company is currently designing a one-ton-per-day demonstration plant.

Novel, Solvent-Free, Fluoropolymer Coating Process

Fluoropolymers and other specialty polymer coatings are used widely. Conventionally, these coatings are applied using liquid-based methods. Polymer formulations are dissolved in a solvent or emulsified as a powder in a liquid medium, applied to the part, and then cured and dried with heat. The problems with this approach include the adverse human health and environmental effects related to the key processing agent and surfactant, perfluorooctanoic acid (PFOA); solvent waste; and energy-intensive curing processes.

Genomatica

GVD Corporation

GVD Corporation has developed solvent-free, chemically pure polytetrafluoroethylene (PTFE, Teflon®) polymer coatings formed by initiated chemical vapor deposition (iCVD). In GVD's green coating process, a precursor gas such as hexafluoropropylene oxide decomposes as it passes over heated metal filaments to produce reactive molecules that migrate to the surface of the part and polymerize to form the desired coating. GVD selects precursors and operating conditions that use minimal energy and low temperatures.

This green technology is valuable for creating ultra-thin (10 nm to 10 micron) layers of insoluble, infusible polymers (like PTFE), which are hard to process by conventional means. GVD's PTFE coatings are deposited from the vapor phase and are spectroscopically indistinguishable from conventional PTFE coatings. Critically, GVD's clean PTFE process does not use any of the solvents or surfactants (e.g., PFOA) incorporated into spray-on PTFE formulations. GVD's vapor-deposited, conformal PTFE coatings are well-suited to high-surface-area substrates and those with micro- and nanoscale features, such as foams, microelectromechanical systems, and carbon nanotubes. GVD's coatings can be deposited at room temperature such that they can easily coat even facial tissue and other temperature-sensitive substrates. Other iCVD polymer compositions include cross-linkable silicones, functional coatings, cross-linked hydrogel coatings, antimicrobial coatings, and even electrically conductive polymer coatings.

GVD PTFE-coated parts and coating services are being sold commercially. During 2008, GVD negotiated a multiyear PTFE manufacturing agreement with a major semiconductor equipment manufacturer.

Green Chemistry for Energy Conservation and Indoor Environmental Quality

Ultraviolet photocatalytic oxidation (UVPCO) mimics naturally occurring atmospheric processes to improve indoor environmental quality (IEQ) by reducing levels of volatile, particulate, and biological contaminants. In UVPCO modules, UVC light activates nanoparticles of a titanium dioxide catalyst coated on a pleated flexible mesh support to initiate photocatalytic reactions. These reactions oxidize volatile organic compounds (VOCs), primarily to water and carbon dioxide (CO₂); they also agglomerate fine particles and inactivate bioaerosols. UVPCO modules are integrated with air filters and instrumental controls into customized engineered systems that are more energy- and cost-efficient than conventional processes, such as carbon adsorption or particulate filtration. The scientific validity of UVPCO technology has been proven in environmental test chambers and at field test sites.

UVPCO technology is expected to replace carbon adsorption, which requires media derived from carbonization of petroleum feedstocks at high temperatures. UVPCO can destroy contaminants both in air circulated within buildings and in air exhausted to the atmosphere. Because UVPCO systems reuse indoor air for more cycles, they reduce the introduction of contaminants from outside air to indoor air. This broadly applicable technology offers benefits to human health and the environment by treating building environments to reduce air contaminants, thereby reducing ventilation demands and conserving energy.

Ingenuity IEQ, a small business in Midland, MI, incorporates UVPCO modules manufactured by Genesis Air into customized engineered systems that they design, install, and maintain in a variety of new and existing buildings. Genesis Air, Inc., a small business in Lubbock, TX, develops unique UVPCO modules that are generally applicable to healthcare, homeland security, LEED™ green building systems, and ASHRAE High-Performance buildings in institutional, commercial, and governmental facilities within the United States. Ingenuity IEQ is positioning UVPCO, marketed as GAP™ technology, into new and existing systems to ensure proper residence time and effectiveness for optimized air purification.

Biodegradable, Chemically Modified Starch Polymers for Protective Foam Packaging and Insulation Applications

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 13.

**KTM Industries;
Professor Ramani
Narayan,
Department of
Chemical
Engineering and
Materials Science,
Michigan State
University**

LS9, Inc.

Microbial Production of UltraClean™ Diesel

Developing large-scale, sustainable petroleum replacements has become both a national and global priority. Among renewable, scalable, domestically derived fuels, those that are cost-competitive with petroleum and compatible with the existing distribution and consumer infrastructure have the greatest potential for rapid, widespread consumer adoption.

LS9 has developed an efficient route for producing diesel fuel from renewable biomass by fermentation. Using synthetic biology, LS9 has engineered established industrial microorganisms (*E. coli*) to convert fermentable C₅- and C₆-sugars to fatty acid methyl esters (FAMES) in a single unit operation. Their engineered microorganisms (Micro-Refinery™ Catalysts) continuously release FAMES to the culture medium. The FAMES are recovered from the fermentation broth by simple centrifugation and washed. Without further chemical processing, they can exceed requirements for on-road vehicle use. LS9 has demonstrated production of FAMES from a diversity of feedstocks including glucose, xylose, sucrose, glycerol, and hydrolysates from stover, woodchips, and bagasse. The process enables precise genetic control of the molecular composition and performance characteristics of the resulting fuel.

LS9 is now producing an advanced biofuel, UltraClean™ Diesel, which is superior to plant-derived biodiesel in performance, land yield, and cost. UltraClean™ Diesel lacks the environmental pollutants (nitrogen and sulfur) and heavy metals (lead, manganese, and arsenic) found in petroleum diesel. Based on Argonne National Laboratory's GREET model for lifecycle analysis, UltraClean™ Diesel will result in a 75-percent decrease in greenhouse gas emissions. LS9 has demonstrated efficient production of the fuel from diverse plant-based feedstocks at the 1,000-liter-pilot-plant scale; they have produced over a barrel of UltraClean™ Diesel. During 2009, LS9 will move to commercial demonstration scale, with large-scale commercial production planned for 2012. The unique simplicity, high yield, and specificity of the process enable a high-performing product that is cost-competitive. Together these aspects will facilitate broad environmental benefits through rapid product adoption.

Method Products

Method Smarty Dish for Fish: An Environmentally Responsible and Effective Cleaning Solution: No Phosphates, Acrylates, or Ethylenediaminetetraacetic Acid

In the United States, the market for automatic dishwashing products is approximately \$525 million. These products release roughly two million pounds of environmentally persistent polyacrylates into U.S. waterways annually, placing a burden on wastewater treatment. The polyphosphates in these products are of even greater concern; they release phosphates, which are potent fertilizers that lead to algal eutrophication and fish kills.

Method has developed a product without phosphate or acrylate. An early challenge was to optimize green chelants, dispersants, and complexation agents to deliver functionality equal to or better than that of blends of polyacrylate, polyphosphate, and ethylenediaminetetraacetic acid (EDTA). Not all green materials can directly replace these stalwart ingredients. Critical performance functions include: (1) Water hardness and metal ion control over the wide pH and temperature ranges encountered during automatic dishwashing. This affects spotting, filming, and soil breakdown. (2) Stabilization of biodegradable components.

Method developed a synergistic green chelant dispersant system. It found that polyaspartate could replace acrylate-copolymer dispersant backbones because polyaspartate delivers both anticorrosive properties and crystal inhibition. Iminodisuccinate (IDS) provides the chelant backbone; IDS works with the critical cleaning agent, Fe(III), which has a stability constant high enough to be useful, but not high enough to persist in the environment. Method's formulation includes gluconate and other organic acids to buttress water control above the favorable pH range for IDS. Method selected the raw materials in Smarty Dish to be ultra-low in phosphate, totaling less than 10 ppm in the final product. Method invented a novel, cellulose-coated tablet, which required a custom manufacturing process. Method gave thorough attention to health, safety, sustainability, environmental considerations, and performance, each undergoing rigorous, third-party reviews. The result is Smarty Dish, an exceptionally well-considered green chemical development with top-level industry performance. Method launched its Smarty Dish Tablets nationally in 2008.

Cleaning and Disinfecting with Ozone: Making Green Chemistry with WhiteWater™ Ozone

In recent years, bacterial contamination in food processing plants has caused a significant increase in food recalls and demands for improved sanitation. Traditional sanitation procedures include direct treatment of food with disinfectants during production plus multistep cleaning and disinfecting of food-handling equipment during downtime. Most disinfectants used in food processing facilities have been based on oxidizers containing chlorine.

In 2001, the FDA approved the use of ozone as a disinfectant in food plants. Ozone is a potent oxidizer; compared to chlorine-based disinfectants, ozone has higher atom efficiency and is used at lower concentrations. Replacing only conventional disinfectants with ozone was not a commercial success, however, because cleaning and sanitation still required significant plant downtime and the ozone equipment was expensive.

Ozone International has researched, developed, and commercialized new technology that enables the effective, safe use of ozone in food plants, not only for disinfecting but also for cleaning during and after production. The technology, WhiteWater™ ozone, generates ozone on-site as needed and applies it in dilute aqueous solutions. WhiteWater™ ozone replaces both conventional cleaning chemicals, such as surfactants and degreasers, and conventional disinfectants, such as chlorine-based products. WhiteWater™ ozone also continuously cleans and disinfects food handling equipment during production, enhancing food safety while reducing downtime for sanitation. WhiteWater™ ozone saves energy because it does not require heated water as do traditional sanitation procedures. WhiteWater™ ozone also offers substantial cost savings.

Used as directed, WhiteWater™ ozone does not expose workers or the environment to hazardous levels of ozone gas. Discharge from a food plant using WhiteWater™ ozone contains water, oxygen (O₂), and oxidized bacteria and organics that are more readily biodegradable and less likely to contain chlorinated organic compounds such as chloroform. Ozone International's most recent patent was issued in 2007. WhiteWater™ ozone is in use by approximately fifty food-processing facilities nationwide.

The Mcgyan Process: A Green Synthetic Route for Biodiesel Production

NOTE: This project is the result of a partnership between Professor Arlin 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 10.

**SarTec Corporation;
Professor Arlin E.
Gyberg, Augsburg
College**

Renewable Oil Production from Algae as a Replacement for Petroleum-Based Products

Solazyme, Inc.

Algae possess biochemical pathways that synthesize oil more efficiently than any other known natural or engineered process. They can produce over 70 percent of their dry cell weight as oil. Indeed, the fossilized remains of prehistoric algae account for much of the world's petroleum deposits.

Using algae obtained through strain selection, screening, classical mutagenesis, and metabolic engineering, Solazyme has, for the first time, created a practical bridge from carbohydrates, sugars, and cellulosic biomass to low-carbon lipids and hydrocarbons, compounds critically important to mankind's need for fuels and chemicals. Solazyme has developed a heterotrophic algal fermentation process that allows algae to manufacture chemicals, biofuels, and edible oils, all in a scalable manner. Solazyme's approach includes selecting algae that quickly accumulate high levels of desired biobased materials (e.g., lipids). From a productivity standpoint, Solazyme's heterotrophic process is 1,000-times more productive than any comparable, scalable, photosynthetic process. In addition, all of Solazyme's algal oils are compatible with the existing petroleum-refining infrastructure.

Solazyme's algae can be grown on a wide variety of carbon sources including industrial byproducts such as molasses and biodiesel waste glycerin as well as traditional fermentation feedstocks. Solazyme's algae also grow well on sugars from cellulosic feedstocks derived from corn stover, sugarcane bagasse, or switchgrass. As a consequence, Solazyme's renewable fuels will bring a range of environmental benefits, including a reduced reliance on fossil carbon and reduced greenhouse gas emissions. Using sugarcane as a feedstock, for example, reduces greenhouse gas emissions by 88 percent compared to ultra-low sulfur diesel (ULSD). Using energy crops such as switchgrass or miscanthus reduces these emissions by over 95 percent.

During 2008, Solazyme produced algal lipid feedstocks successfully at industrial scale in commercial facilities, allowing Solazyme to produce fuels that meet multiple standards for transportation fuels. Solazyme has repeatedly carried out fermentation and recovery at the 75,000-liter scale.

Replacement for Solvent-Based, Chromate-Containing Primer

**TDA Research, Inc.;
Cytec Industries Inc.**

Corrosion of bonded metal parts is a major concern for the aerospace industry. Historically, aerospace manufacturers have used solvent-based primers containing hexavalent chromium (Cr(VI)) to protect metals from corrosion. Hexavalent chromium has, however, been classified as a known human carcinogen and is subject to increasing regulations globally. In addition, the solvents in these primers contain volatile organic compounds (VOCs) that are precursors to ozone formation.

To comply with new environmental and safety regulations, major aerospace manufacturers including Boeing and Airbus are looking to qualify water-based, chromium-free primers for

structural bonding applications. Aerospace manufacturers and primer suppliers have been evaluating several chromium-free corrosion inhibitors, but chromium-free primers with corrosion performance to match that of chromium-based primers are not commercially available.

TDA Research has developed a platform technology for releasable chromium-free inorganic–organic corrosion inhibitors. Cytec Engineered Materials, a subsidiary of Cytec Industries, is collaborating with TDA Research to develop a water-based, chromium-free, bonding primer to give corrosion performance comparable to that of chromium-based primers. The new water-based primer chemistry has synergistic effects with these chromium-free corrosion inhibitors to give excellent corrosion performance over extended periods of time. In addition to eliminating chromium, the technology also eliminates VOCs, reduces the need for refrigeration during storage, and reduces potential waste due to extended shelf life. Customers who substitute the new technology for existing solvent-based primers are expected to reduce their annual operating costs by 25 percent. A patent application was submitted in December 2008.

Green Synthesis of Nanometal Catalysts and Plant Surfactant-Based, In Situ Chemical Oxidation for Sustainable Treatment and Remediation

According to EPA's 2004 publication, "Cleaning up the Nation's Waste Sites", an estimated 294,000 sites will need to be cleaned up at an estimated cost of approximately \$209 billion. Many of these sites contain Non-Aqueous-Phase Liquids (NAPLs). EPA also estimates that there are as many as 15,000 contaminated sites of former manufactured gas plants and coal-burning factories nationwide. Beyond digging up these sites and hauling large quantities of contaminated soils to landfills, there are extremely limited options currently available to treat NAPLs.

VeruTEK Technologies has developed a novel green reaction process called Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO™) to reduce the amount of NAPLs in soils. Its patent-pending S-ISCO™ technology uses VeruSOL™ (e.g., coconut oil, castor oil, citrus extracts: biodegradable, U.S. FDA Generally Recognized as Safe (GRAS) surfactants) to solubilize immiscible phase organic contaminants into groundwater where oxidation reactions readily destroy them.

Under a Cooperative Research and Development Agreement (CRADA) with EPA, VeruTEK has also produced nanometals made from simple plant extracts such as tea or other high-antioxidant plant polyphenols and dissolved metals at ambient temperature and pressure. VeruTEK has used these nanometals to catalyze advanced oxidation reactions; they have no hazardous materials in their synthesis and produce no hazardous wastes. In 2008, VeruTEK and EPA submitted a patent application for the green synthesis of these nanometals. VeruTEK has also developed green chemical reactions using plant-based co-solvents and surfactants to simultaneously solubilize and oxidize toxic, organic-phase contaminants in situ. These two processes will (1) reduce the use of toxic chemicals associated with the individual chemical reactions; (2) eliminate hazardous chemicals and wastes in the synthesis of many useful nanometals; (3) profoundly reduce the quantities of hazardous, regulated waste generated by excavating contaminated sites; and (4) eliminate the wasteful use of clean sand and gravel to backfill contaminated sites after excavation.

Sustainable, Natural Green Chemistry for Cooling Water Treatment

**Water Conservation
Technology
International, Inc.**

Pure water evaporates from cooling towers to the atmosphere, but minerals in the water stay behind and typically require 20–40-percent tower discharge to avoid scale or corrosion problems. Chemicals added to inhibit scale and corrosion can save water, but low-solubility, corrosive minerals still lead to water waste. Along with wastewater, towers also discharge treatment chemicals including inorganic or organic phosphates, heavy metals, organic polymers, biocides, and halogens.

Natural green chemistry (NGC) provides a paradigm shift in cooling water treatment, with economical methods to reduce toxic and persistent chemicals, reduce water and energy use, and support sustainable water ecosystems. Patented NGC methods use the natural minerals present in water as sustainable feedstocks, providing superior corrosion and scale protection that replaces chemical treatments. An NGC pretreatment step for scale control uses proprietary high-efficiency softening equipment to remove calcium and magnesium ions, which lead to scale formation. The NGC process also polymerizes natural silica monomer to high-molecular-weight multimeric and colloidal silica particles that are stable and do not form scale. NGC concentrates minerals in tower water, facilitating natural biostatic chemistry that reduces biocide use by 95 percent or more. NGC permits tower operation with 95-percent-reduced water waste and less than 2 percent of makeup water. NGC obviates costly systems to purify water for reuse by permitting over 99-percent evaporation of water used to remove waste heat energy in existing tower systems. NGC reduces the tower discharge volume for liquid or dry disposal and averts capital cost, chemicals, materials, and energy consumption.

NGC technology can eliminate the discharge of over 400 million pounds of organic and toxic chemicals in the United States annually. NGC can potentially reduce fresh water use by an estimated 500 billion gallons annually, with over \$1.5 billion savings in costs from reduced water, chemicals, and energy.

Cellulose-Based Fuels and Intermediate Chemicals

ZeaChem Inc.

ZeaChem's pioneering biorefinery technology uses a hybrid of biochemical and thermochemical processes to make liquid transportation fuels and industrial chemicals. Other approaches have thermodynamic restrictions that limit ethanol production to practical yields of 60–90 gallons per dry ton of biomass. The ZeaChem technology has a practical yield limit of 135 gallons per dry ton. This higher yield dramatically improves process economics, allowing farmers to get more ethanol from their biomass crops.

Unlike other processes, the ZeaChem process uses all fractions of the plant: cellulose, hemicellulose, and lignin. Their process allows both fermentable and nonfermentable fractions of the biomass feedstock to contribute chemical energy to the product. First, they fractionate biomass into a sugar-rich stream and a lignin-rich stream. Homoacetogenic bacteria convert the sugars to acetic acid, which is esterified to ethyl acetate and recovered from the fermentation broth. The ethyl acetate is then hydrogenated to ethanol using hydrogen derived from the lignin fraction. The lignin fraction also undergoes thermochemical processing to generate steam and power, making the plant self-sufficient in energy.

Two environmental advantages of ZeaChem's technology are reduced fossil-derived carbon dioxide (CO₂) emissions and smaller land-use footprints. The ZeaChem route generates roughly 1.45 pounds of fossil-derived CO₂ per gallon of ethanol compared to 3.63 pounds and 12.54 pounds of fossil-derived CO₂ per gallon of ethanol from sugarcane and corn dry milling, respectively. Projections on the combination of ZeaChem's high-yield factory technology with high-yield energy farms and improvements in automobile efficiency suggest that as

**Zymes, LLC;
Professor Bruce H.
Lipshutz,
Department of
Chemistry and
Biochemistry,
University of
California, Santa
Barbara**

much as 30 percent of America's light-duty fuels could be produced from the amount of agricultural land currently used to produce corn ethanol. Such projections fundamentally change the policy debate on the environmental aspects of ethanol as a liquid transportation fuel. During 2008, ZeaChem began construction of a 10-ton-per-day cellulosic ethanol facility.

Getting Organic Solvents Out of Organic Reactions

NOTE: This project is the result of a partnership between Professor Bruce Lipshutz of the University of California, Santa Barbara and Zymes, LLC. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 11.

Entries from Industry and Government

Reformulation of 3M™ Neutral Cleaner and 3M™ General Purpose Cleaner for the 3M™ Twist 'n Fill™ Chemical Management System Reduces Air Pollution and Employee Health Hazards

3M

3M™ has a long-standing commitment to product lifecycle management and pollution prevention. In 2007, as part of that commitment, the company reformulated its 3M™ Neutral Cleaner and 3M™ General Purpose Cleaner for the 3M™ Twist 'n Fill™ Chemical Management System. The reformulated cleaners significantly reduce volatile organic compounds (VOCs) in the product and maintain high-quality product performance. These new formulations are certified by Green Seal® as were the previous formulations; they are part of a portfolio of 3M™ products that can help its customers reduce their environmental footprint and provide social and economic benefits.

The previous concentrated formulations for these hard-surface cleaners included 5–10-percent solvents to provide effective cleaning. These solvents were generally low-molecular-weight alcohols or alkyl glycol ethers. They had the potential for higher skin irritation and health hazards; due to their lower flashpoints of about 100 °F, they had transportation, storage, and other regulatory issues when shipped in the concentrated formulations.

The new formulations result from a unique combination of several active ingredients including an alkyl pyrrolidone and an alkyl glucoside that provide superior cleaning and non-streaking properties. All of the organic ingredients in the new formulations are readily biodegradable, and the primary surfactant in the formulation is made from renewable resources. Compared with previous formulations and with traditional chemical management systems, the new formulations offer several environmental and health advantages including (1) a higher flashpoint of over 175 °F, which lessens dermal irritation without using a solvent mixture; (2) an estimated reduction of 600,000 pounds in VOC emissions from product use in 2008; and (3) a reduction in waste from the Twist 'n Fill™ system packaging. Based on its 2007 sales and production data, 3M™ estimates that these reformulations will save the company nearly \$600,000 per year. The savings come from raw material costs and manufacturing process improvements.

RegenSi™: Low-Carbon-Footprint Wafer Reclaim Solution Extends the Lifecycle of Silicon Test Wafers

Advanced
Technology
Materials, Inc.

Because producing a prime 300-mm silicon wafer costs approximately \$300, semiconductor manufacturers typically use test wafers, which cost over \$100 apiece, to optimize and monitor their manufacturing processes. A large fabricator might spend \$2 million a month on test wafers. The industry uses more than 27 million test wafers annually, and, as a result, chip makers are now focusing on reusing test wafers as many times as possible.

A traditional wafer reclamation process involves chemically stripping unwanted films from the wafer surface, mechanically polishing the surface to remove damage or impurities (i.e., surface planarization), and cleaning to ensure that the reclaimed wafers meet customers' stringent requirements. Currently, a wafer may only be reclaimed a limited number of times because the combination of stripping and polishing physically reduces the thickness of the wafer by tens of microns. Eventually, the test wafers become too thin and are discarded.

RegenSi™ is a novel, all-wet, single-step process that strips away most films from test wafers while limiting damage to the underlying silicon. This eliminates or reduces the need for wafer surface planarization following the film stripping step. Surface planarization is energy-intensive, uses a large volume of consumables, and is expensive. In addition, the much longer bath-life of the RegenSi™ chemicals reduces both chemical waste and worker exposure. The process has a carbon footprint 18-fold lower than that of the traditional three-step process and consumes 85-percent less energy.

Processing its test wafers internally with RegenSi™, a Taiwanese manufacturer achieved four times more life from each test wafer. Reported yields rose to 85 percent and silicon loss was reduced by 75 percent. This combination of higher yields, greater productivity, and increased reuse leads to significant overall cost savings, energy savings, and waste reduction. Currently, eleven semiconductor manufacturers are using RegenSi™, and twelve more are testing it.

Replacement of Phosphates in Automatic Dishwashing Detergents with GLDA, a Readily Biodegradable Chelating Agent Manufactured from a Renewable Feedstock

Chelates are chemical agents that interact or complex with metal ions, often increasing the solubility of the metal ion. They are used in many types of cleaners and industrial processes. Conventional chelates are based on aminocarboxylic acids (e.g., ethylenediaminetetraacetic acid, EDTA) and phosphates (e.g., sodium tripolyphosphate). Unfortunately, because EDTA is not readily biodegradable and because phosphates can cause pollution via eutrophication, these conventional materials are often viewed as environmentally unfriendly.

AkzoNobel has developed a readily biodegradable chelating agent that is manufactured principally from a renewable feedstock. This new chelate, called tetrasodium L-glutamic acid, *N,N*-diacetic acid (GLDA), will replace phosphates in automatic dishwashing detergents throughout the United States to comply with regulations from the State of Washington that will limit phosphorous in such cleaners starting in 2010. GLDA is an effective chelate that also has low animal toxicity and ecotoxicity. AkzoNobel has devoted significant research and development, environmental health and safety testing, evaluations, and engineering/manufacturing design to developing and commercializing this new material.

GLDA is manufactured from the flavor enhancer monosodium glutamate (MSG) in an essentially waste-free synthesis. MSG is made by fermenting readily available corn sugars and is considered a renewable material. The synthesis of GLDA includes classic cyanomethylation of the primary amino nitrogen on the MSG followed by in situ alkaline saponification. In contrast with EDTA whose carbon is currently all fossil-based, over half of the carbon in GLDA is biobased. Because GLDA is highly soluble, it will be offered at a significantly higher concentration (approximately 30-percent-higher molar aqueous concentration) than EDTA, reducing transport and packaging costs as well as packaging waste. Most significantly, GLDA is readily biodegradable and will reduce pollution by replacing phosphates in dishwashing detergents in the United States. In early 2009, AkzoNobel will begin commercial manufacture of GLDA at its plant in Lima, Ohio.

Inert Filler TB-1

The U.S. Army has a requirement for projectiles and mortars to be loaded with inert (non-explosive) filler for training exercises and demonstration purposes. The primary inert filler used for many years at the Iowa Army Ammunition Plant (IAAAP) was Inert Filler E (Type II Filler; Spec: MIL-I-60350). This inert filler required ergonomically inferior methods to drill

a 5" fuze well for a typical inert build (M549). The previous methods required either (1) drilling a 5" deep by 2" wide fuze well with drill bits that quickly became gummed up with filler so that the drilling required to install a fuze could take several hours per round, or (2) inserting a 5"-long shaft funnel into the poured inert filler before the filler set up to limit the drilling required. Removing the funnel required striking it with a rubber mallet to break it loose; frequently the suction created made the funnel difficult to pull out and more drilling was still required to finish the fuze well.

IAAAP achieved its goal by replacing Inert Filler E with inert filler TB-1, which meets all filler requirements. Inert filler TB-1 is easy to machine and drill: it takes only 20 seconds to drill a 5" long by 2" wide fuze well. Inert Filler TB-1 contains no hazardous materials and costs 40-percent less than the former Inert Filler E. Funnel scrap from pouring the Inert Filler TB-1 into projectiles should be 100-percent recyclable without separation, which allows the scrap to be saved for later use and minimizes waste generation. Excess Inert Filler TB-1 easily flakes off from projectiles and equipment, so cleanup is very easy. Cleaning previous inert fillers required solvent and paper wipes; the solvent-contaminated paper wipes were hazardous waste. The U.S. Army has approved the loading of 2,000 inert 760 ammunition rounds with Inert Filler TB-1.

Pulp Mill Defoamers Based on Vegetable Oil

Defoamers are widely used in the pulp and paper industry, particularly in pulp washing. The best defoamers for brown stock washing are based on silicone oils, although some defoamers are based on paraffin oils. These defoamers have serious disadvantages, however. Silicone oils are not biodegradable and can carry over onto the paper sheets, giving them undesirable surface properties. Paraffin oil can cause dioxin formation during the pulping process.

Ashland Hercules Water Technologies has developed a new family of defoamers based on vegetable oils. These biodefoamers eliminate paraffin oil, minimize the use of silicone oil, and increase the use of natural, renewable ingredients. The technology is based on (1) a specific blend of soybean oil and castor oil that has an optimal, low surface tension; (2) lecithin, a natural product that stabilizes the system; and (3) modified silicone products that optimize the defoaming characteristics, enhance the surface properties, and promote compatibility between phases. The formulations contain vegetable oil, appropriate silicone product(s) such as modified silicone polymers, a stabilizing agent, hydrophobic silica particles, two or more surfactants and dispersants, biocides, and thickeners (natural gums and biodegradable polymers). The formulation is an effective defoamer and produces a stable emulsion. The new defoamers can be used as a concentrate without dilution or as an emulsion.

The new defoamers have been shown to be as effective as the pure silicone defoamers and analogous petroleum-based defoamers, but are more cost-effective. Ashland Hercules launched its first Advantage® biodefoamer in 2005 and its second-generation product in 2007. These biodefoamers are being used on pulp mill washers and also on mill effluents. Although these defoamers are designed for pulp and paper applications, they also are appropriate for other non-food industrial uses. The products satisfy FDA requirements for food contact (21 CFR 176.210).

Water-Based Refractory Coatings with Wet/Dry Color Change Indication

The use of refractory coatings in metal casting processes has been a common practice in the foundry industry for decades. These coatings are applied to dies, cores, and molds to provide a protective barrier facing the hot liquid metal. When applied to sand cores and molds, the

**Ashland Hercules
Water Technologies**

Ashland Inc.

coatings prevent casting defects like metal penetration and erosion, improve veining resistance and casting surface finish, or simply mitigate imperfections resulting from molding media and processes.

Traditionally, solvent-based refractory coatings have been widely preferred over water-based coatings. More recently, workplace health and safety concerns, environmental concerns, and economic considerations due to increasing costs of petrochemical-based materials such as solvents are spawning the development and use of water-based coating technologies. Although optimum drying of these water-based coatings is critical, the metal-casting market has not had a simple analytical method to determine whether the coating has completely dried. Incomplete drying can cause casting defects that could be expensive to fix or may require scrapping of the cast piece. Conversely, excessive drying wastes energy and may reduce productivity.

Ashland Performance Materials has developed a water-based refractory coating that undergoes a distinctive color change as it dries. The water-based refractory coating with wet/dry color change is an innovative approach that combines intended purpose, environmental considerations, and a high level of functionality within an otherwise ordinary product. Ashland successfully introduced this technology to the industry in 2005; it is now widely accepted among metal casters. Some customers have saved more than 10 percent overall, including a 50-percent reduction in gas used by the heaters to dry coated material. Ashland continues to develop technologies and innovative solutions that deliver performance to their customers and are environmentally responsible.

Environmentally Friendly Biobased Plasticizers for Polyvinyl Chloride

Plasticizers are used in combination with polyvinyl chloride (PVC) resins to make flexible and semi-rigid articles. Globally, over 13 billion pounds of plasticizer are produced annually with 90 percent for use in PVC. Ninety percent of all plasticizers are phthalates, which are derived from petroleum feedstocks. Some classes of phthalates have come under severe scrutiny as suspect endocrine disruptors and are facing regional and federal regulation. For example, California Assembly Bill AB1108 bans the use of six phthalates. Nationally, the Consumer Product Safety Improvement Act (CPSIA) takes effect on February 10, 2009, banning some uses of phthalate ester plasticizers. Besides their regulatory issues, phthalates have other deficiencies such as poor thermal stability and high levels of volatility and exudation.

Battelle has developed a green plasticizer technology based on vegetable oils that addresses these deficiencies and the market's need for alternatives to phthalates. Battelle used molecular modeling to tailor the structure of soybean oil to be compatible with PVC resin at high levels with reduced migration and volatility compared with dioctyl phthalate, a common commodity plasticizer. Battelle then synthesized and tested six soy-based PVC plasticizer candidates such as epoxidized propylene glycol disoyate. These environmentally friendly bioplasticizers have excellent compatibility with PVC resin and function as primary plasticizers and thermal stabilizers. They are not expected to pose any health issues.

Replacing 25 percent of the global plasticizer consumption with a biobased product derived from vegetable oil offers energy savings in the range of 5 billion Btu per year. Each pound of phthalate replaced by a soy-based plasticizer replaces one pound of carbon dioxide (CO₂). Several soy-based primary plasticizers have been scaled up to pilot plant scale and are entering early-stage commercialization. Ohio-based PolyOne Corporation, a Battelle licensee, has developed an aggressive commercial plan to market the new plasticizer starting in 2009.

AURA® Infusion Technology: A Green Method to Incorporate Color and Performance Additives

Thermoplastics are all around us from housings of electronic devices to household appliances, car interiors, sports equipment, and, increasingly, architectural components. The current technology to incorporate color or other performance additives relies on continuous processes that distribute the additives throughout the plastic parts. This can generate significant solid waste or low-value material during transition into and out of each customized product or when the product does not meet the color specification.

AURA® Infusion Technology customizes a thermoplastic part with a colorant or other performance additive down the supply chain close to the end consumer. The technology uses a batch process that has no transition periods. For example, coloring a part with AURA® Infusion Technology versus using pre-colored resin pellets to make the part can reduce the amount of resin waste by 15–25 percent and significantly reduce inventory because part producers can color parts on demand. AURA® Infusion Technology minimizes the amount of colorant or performance additive needed in the thermoplastic part by concentrating the additive near the surface. The colorant or performance additive is infused by means of a hot bath for smaller parts or a hot solution spraying system for larger parts. The solution typically contains a leveling agent, a plasticizing agent, and water in addition to the desired additive. The AURA® Infusion Technology process generates less than 1-percent waste because it is designed to recover and recycle the unused performance additive for efficient customization and to recycle the water and the small amount of solvent used.

By eliminating the additive in the bulk material, AURA® Infusion Technology makes more virgin resin available for recycling. Part producers can now take back customized products at end-of-life, remove the surface color, and recycle or recolor them. Currently four companies are licensing this technology in the United States.

IMPACT Technology: A Greener Polyether Polyol Process

Polyether polyols have a multibillion-pound worldwide market. Traditional manufacturing is a semibatch process including potassium hydroxide catalysis and a number of steps including removal of the catalyst. Early double metal cyanide (DMC) catalysts were more reactive, but were inhibited by low-molecular-weight materials like glycerin; they also required catalyst removal and the same amount of equipment. As a result, they were restricted to niche, high-value products.

Bayer MaterialScience's IMPACT process for polyether polyols includes modifying the DMC catalyst to increase its reactivity by ten-fold and taking advantage of an unusual kinetic property: the modified DMC selectively adds alkylene oxides to the lower-molecular-weight molecules in a mixture of molecular weights. Combining these two inventions gives a continuous process that requires less equipment. The modified DMC catalysts tolerate and convert low levels of low-molecular-weight initiators, overcoming the inhibition observed in traditional processes. Even though glycerin is continuously charged to the reactor, catalyst selectivity results in the overall reaction mixture having a steady state with a narrow polydispersity product and an average molecular weight of 3,000. The continuous process makes little or no waste. It also saves energy by eliminating the heat-up cycle of the semibatch process, in addition to the energy it saves by eliminating waste treatment. The IMPACT technology lowers carbon dioxide (CO₂) equivalents by around 75 percent and increases productivity

Champion Technologies, Inc.

over the conventional technology. In Bayer MaterialScience's plant in Channelview, TX, this technology is eliminating about 75 million pounds of wastewater and 54 million pounds of CO₂ each year.

The Channelview plant produced its one-billionth pound of polyether polyol during January 2006; Bayer has licensed its technology to others including Dow, Shell, and BASF. Bayer has used its technology to double polyether polyol production at its Channelview plant within four years to 440 million pounds and has lowered variable production costs by 40 percent.

Lysine Phosphonate Scale Inhibitor: Improved Biodegradation While Maintaining Performance over Traditional Phosphonates

Scale inhibitors for use in off-shore oil production are in increasing demand as reservoirs age and secondary recovery techniques such as injection with saltwater are used more frequently. Off-shore oil wells are susceptible to scale as ions in the injected seawater mix with ions present in oil-bearing formations. The precipitation of calcium carbonate, barium sulfate, and other scales from water that is produced with oil can reduce production rates, increase maintenance costs, or even block pipelines completely. The annual worldwide market for oilfield scale inhibitors is \$200 million.

Organic phosphonates inhibit scale formation as low-dose additives (sometimes at levels below parts-per-million); they have high efficacy, low toxicity, and a low tendency to bioaccumulate. They typically exhibit low rates of biodegradation, however, and legislation in the United States and North Sea has driven research into biodegradable scale inhibitors to replace them. Polymeric scale inhibitors have been developed as an alternative to phosphonates because they have greater biodegradation rates and a low tendency to bioaccumulate. Unfortunately, polymers cost more and require higher treatment rates.

Champion Technologies chose to develop new phosphonate scale inhibitors designed to biodegrade more readily yet maintain their inherently high performance, low toxicity, and low bioaccumulation. Champion replaced the polyamine starting material for the phosphonates, typically diethylenetriamine (DETA), with lysine, which is a naturally occurring, renewable polyamine. They optimized the extent of phosphonomethylation to maximize both performance and biodegradation. Lysine phosphonate exhibits the desired scale inhibition but is inherently biodegradable, resulting in 20–60-percent biodegradation in 28 days by OECD 306 (the Organisation for Economic Co-operation and Development's seawater biodegradation test). By comparison, traditional phosphonates are nonbiodegradable, with less than 20-percent biodegradation in 28 days by OECD 306. During 2008, Champion submitted a provisional patent application for this technology.

Clarke Mosquito Control

Natular: Engineering Green Chemistry for Mosquito Control

Spinosad, a product of Dow AgroSciences and a 1999 winner of the Presidential Green Chemistry Challenge, is a low-risk pesticide in widespread use on crops. Spinosad adsorbs strongly to soils and organic matter, degrades photochemically at the site of application, and is inherently unstable in water. These characteristics make it excellent for use on land, but had precluded its use in aqueous environments. Clarke Mosquito Control has overcome this challenge by innovations in tablet formulations and slow-release matrix chemistry to develop Natular, a spinosad-based mosquito larvicide that provides excellent control in aquatic environments. Recently EPA-registered, Natular's six formulations are designed to suit all mosquito-control environments, from catch basins to salt marshes. Natular is effective at use rates

2–10 times lower than traditional larvicides, is 15 times less toxic than the organophosphate alternative, does not persist in the environment, is not toxic to wildlife, and eliminates the use of hazardous materials and processes in its manufacture.

Natular is the first new chemical larvicide for mosquito control in nearly three decades. With an innovative structural matrix of active ingredient and organic inert components, Natular effectively moves through the water column, providing both immediate availability of appropriate amounts of spinosad to target organisms and time-release spinosad for extended control in tough aquatic environments. Formulation innovations reduce the potential for application error and decrease the risk of damage to people and the environment from mosquito control operations. The manufacturing process of Natular eliminates hazardous processes, products, agents, and hazardous wastes, thereby decreasing health and environmental risk throughout the supply chain and workplace. Clarke anticipates a significant shift in the vector management industry to Natular, which will reduce the overall synthetic load in the environment while improving health and quality of life in treated areas. Clarke launched Natular in the U.S. market in December 2008.

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. 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. The reduced particle sizes provide optimized surface interactions and increase the one-phase stability region. This technology enables GreenWorks™ products to be isotropic clear upon infinite dilution, reducing the ingredients by ten-fold compared to normal all-purpose or glass cleaners. The products are biodegradable and non-allergenic, are not tested on animals, and come in recyclable containers. The manufacturing facilities used to produce GreenWorks™ have zero emissions discharge. All GreenWorks™ products perform as well as or better than leading conventional cleaners in laboratory and in blind, in-home consumer tests. This level of cleaning is important to convincing consumers to switch from traditional cleaning products. The EPA Design for the Environment (DfE) initiative has recognized the safe ingredients and cleaning performance of GreenWorks™ products, which proudly display the DfE logo.

Fossil fuels contribute significantly to greenhouse gas emissions. By switching from petrochemicals to natural ingredients in its GreenWorks™ line, Clorox achieved a savings of approximately 450,000 gallons of petroleum in the United States during 2008. In addition, plant-based renewable sources reduce emissions of carbon dioxide (CO₂), a greenhouse gas, during photosynthesis.

Clorox launched GreenWorks™ Natural Cleaners in January 2008. GreenWorks™ products sell at only a modest premium over conventional cleaners, despite their use of costlier plant-based renewable ingredients, an environmentally friendly manufacturing process, and innovative science, which together offer the consumer the most natural, powerful cleaning products on the market.

Carbon Blocker™ Fly Ash Conditioning Treatment

NOTE: This project is the result of a partnership between FlyAshDirect Ltd. and Cognis Corporation. The project was judged in both the small business and greener synthetic pathways categories. The abstract appears in the small business section on page 24.

Sodalite Scale Inhibitor

The Bayer process converts bauxite ore to alumina. The heat exchangers and interstage piping used in the process build up sodalite scale (i.e., aluminosilicate crystals), which reduces the heat transfer efficiency of the exchangers. Periodically, the equipment is cleaned with 5–10-percent sulfuric acid, which removes scale but also leads to worker exposure and a waste stream.

Cytec developed its MAX HT® Bayer Sodalite Scale Inhibitor family of products to eliminate sodalite scaling in the Bayer process. The active ingredient is a proprietary polymer containing a silane functional group that interacts with a growing sodalite crystal. The silane inhibits crystal growth either by incorporation into the crystal or by adsorption onto its surface. Dosages range from 20 to 40 ppm.

Eliminating the formation of sodalite scale on heater surfaces produces a number of benefits. First, the heat from steam produced in various unit operations is recovered more efficiently. Second, increased evaporation allows the plant to use more water in the countercurrent washing circuit for recovering caustic. Third, reduced production of new steam reduces emissions from burning carbon-based fuel. Last, the reduced use of sulfuric acid results in less worker exposure and less waste from cleaning the heaters.

There are about 50 Bayer plants worldwide with annual capacities of 0.5–6 million tons of alumina; most plants are in the 1.5–3-million-ton range. Since Cytec introduced MAX HT® in 2004, eight Bayer plants worldwide have adopted it and twenty more plants are in various stages of testing it. Plants using MAX HT® save \$2–20 million annually per plant and save 0.25–1.25 Btu per ton of alumina produced. Fewer cleaning cycles and less acid per cycle create significant reductions in waste: a typical 1.5-million-ton alumina plant can reduce its waste by 1,500–4,500 tons of 5-percent acid per year.

Primer to Replace Solvent-Based, Chromate-Containing Primer

NOTE: This project is the result of a partnership between TDA Research and Cytec Industries. The project was judged in both the small business and designing greener chemicals categories. The abstract appears in the small business section on page 29.

Glycerin to Epichlorohydrin Process: How Green is my Epichlorohydrin?

Epichlorohydrin is a large-volume, commodity chemical used mostly to manufacture liquid epoxy resins. Estimated worldwide capacity for epichlorohydrin was two billion pounds in 2006. The predominant manufacturing process today is a multistep route using petrochemical-derived propylene and electrochemically generated chlorine as the primary feedstocks. This route has significant environmental issues including the formation of chlorinated

byproducts and large amounts of wastewater. Further, the route incorporates only one of the four chlorine atoms it uses into the final product; the other three appear as aqueous chloride waste or hydrogen chloride.

The Dow Glycerin to Epichlorohydrin (GTE) process exploits the increasing availability of low-cost glycerin, which is a byproduct of biodiesel production from renewable seed oils. Likewise, it uses hydrogen chloride, a byproduct from several commodity-scale manufacturing processes such as the incumbent epichlorohydrin process, vinyl chloride, or isocyanate manufacture; hydrogen chloride is often neutralized and wasted. The GTE process uses a simple, two-step route with a carboxylic acid catalyst to synthesize epichlorohydrin. The key innovation is the use of hydrogen chloride at elevated pressure. The resulting elevated liquid-phase hydrogen chloride concentration drives the reaction to high conversions to the desired dichlorohydrins without removing the coproduct water from the reaction. Water in the reaction prevents the formation of chlorinated byproducts.

The GTE route has additional environmentally desirable attributes, including more efficient use of chlorine, formation of fewer chlorinated byproducts, and less production of aqueous chloride waste. The process will reduce wastewater by over 70 percent and reduce the formation of organic byproducts by over 75 percent. It is significantly more energy efficient: it uses 30-percent less steam and uses less energy to make chlorine and caustic. Commercialization of this economically and environmentally advantageous process is planned for 2011, when it will produce up to 150,000 metric tons per year of highly pure epichlorohydrin.

Innovative Industrial Process Using Hydrogen Peroxide to Synthesize Propylene Oxide

The Dow Chemical Company; BASF AG

Propylene oxide (PO) is among the 50 largest-volume chemical intermediates 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 either produced significant volumes of coproducts or required recycling of organic intermediates.

Dow and BASF jointly developed a new 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 fixed-bed reactor at moderate temperature and low pressure. A catalyst facilitates the reaction, achieving high conversion and product selectivity. This proprietary catalyst is a ZSM-5 type in which tetrahedrally coordinated titanium replaces several percent of the silicon; it has been formulated for use in a fixed-bed reactor system. The reaction occurs in liquid phase with 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 has a high yield and produces no significant coproducts except water.

The HPPO process also provides environmental benefits. Dow and BASF expect this technology to reduce wastewater production by as much as 70–80 percent and energy use by 35 percent over current technologies. During 2007, Dow constructed a pilot plant in Freeport, TX to develop this technology. The first commercial process based on this technology began production in 2008 at a BASF production facility in Antwerp, Belgium. During 2008, Dow broke ground on a world-scale plant in Map Tha Phut, Thailand, which will begin production in 2011.

Chlorantraniliprole: Designing Green Chemistry for Insect Control

Historically, the developers of pesticide active ingredients focused primarily on creating pesticides that were effective against target pests with little regard for the safety of humans or the environment. Now, however, new active ingredients must not only meet societal demands for safety but also have novel modes of action that preclude the target pest(s) from developing resistance. Consumers now expect affordable, high-quality food that is produced with minimum impact on the environment; higher regulatory hurdles for pesticide registration reflect these expectations.

To meet these demands, DuPont redesigned the early stages of its discovery process to optimize three factors: pest efficacy, low toxicity to mammals and other nontarget species, and environmental attributes. In searching for insecticides that best fulfilled all three factors, DuPont realized that the best overall product might not be the most biologically active one. DuPont evaluated over 2,000 candidate analogs to find one product with the right balance of these factors. The result, chlorantraniliprole, is one of the most active and least toxic chemical insecticides ever discovered. It can replace organophosphate insecticides. Chlorantraniliprole is effective at lower application rates and requires fewer applications per growing season than other pesticides. It is effective against many pests that have developed resistance to other pesticides.

Chlorantraniliprole controls insect pests by a new mode of action: activating their ryanodine receptors (RyRs) in an unregulated manner, depleting internal calcium stores, and thereby paralyzing the target insects. Chlorantraniliprole is remarkably selective for insect RyRs over mammalian RyRs; this selectivity is a key to its low toxicity and high margins of exposure. Chlorantraniliprole is known by the trade names Rynaxypyr® and Calteryx™ for crop and turf applications, respectively. In spring 2008, EPA registered Rynaxypyr® as a Reduced Risk pesticide; by the end of the year, Rynaxypyr® had completed its first season of commercial use.

Wash 'n Walk™ Floor Care System

Foodservice operations can be dangerous places for employees because grease and other food soils fall onto floors throughout the work day. Grease creates slippery floors, leading to slips and falls that impact employee safety and the bottom line for Ecolab's customers. Traditional floor cleaning and maintenance systems include surfactants to emulsify grease, highly alkaline chemicals to hydrolyze grease, hydrofluoric acid to etch floor tiles for greater traction, and EDTA (ethylenediaminetetraacetic acid; not readily biodegradable) for water conditioning.

Ecolab has designed a revolutionary floor care system that both results in cleaner floors and increases the coefficient of friction (the primary measure of slipperiness of floors). The formula is unique in exhibiting superior performance and providing environmental and human health benefits. Ecolab's floor care system incorporates three innovative platforms. First is a proprietary blend of surfactants, including a silicon surfactant uniquely capable of removing complex organic or greasy soils from a variety of substrates. Second is a suite of stabilized enzymes, including lipases, that are stable at alkaline pH values and in the presence of high concentrations of water. Third is an optional suite of stabilized bacterial spores that germinate and then decompose proteins, starches, and fatty acids. The Wash 'n Walk™ formula also includes Trilon M water conditioner that is composed of amino carboxylates and is readily biodegradable. Wash 'n Walk™ can be used with cold water. It uses a no-rinse procedure that leaves enzymes and spores on the floor to break down grease and other soils that accumulate over time.

The Wash 'n Walk™ formula received Green Seal Certification in 2006 under the GS 37 standard. To achieve this certification, the formula passed a rigorous review to demonstrate both superior environmental and human health benefits. Between 2004 and 2008, Wash 'n Walk™ saved Ecolab's customers 546 million gallons of water annually.

New Manufacturing Route for Arzoxifene Hydrochloride

Eli Lilly and Company

Arzoxifene hydrochloride (HCl) is an investigational new drug candidate currently in phase III clinical trials. Prior to manufacturing arzoxifene HCl commercially, Eli Lilly reviewed its original manufacturing process. The review identified several major environmental burdens including a large excess of trifluoroacetic acid as a solvent, an extremely high loading of palladium catalyst, and extensive use of methylene chloride as a solvent. Eli Lilly decided to abandon this route and accept the risk of designing and developing a greener route. Moreover, Eli Lilly had to discover, develop, and introduce the new route on an accelerated schedule to ensure that ongoing patient needs would be met.

An intensive effort by chemists, engineers, and environmental professionals resulted in the discovery of a new route that meets these requirements. The new process eliminates trifluoroacetic acid and methylene chloride. It reduces the amount of palladium-carbon catalyst and subsequent contaminated waste by over 100-fold. Several innovations across reaction methodology and reaction engineering also enable the new route. Fundamental discoveries include replacing benzyl with diethylcarbamyl (DEC) as the phenol protecting group and implementing novel sulfide oxidation conditions. The DEC protecting group meets the needs of the synthesis and is still removable. This change enables alternative oxidation conditions, which allow the novel route to succeed.

Process mass intensity (PMI) is the total mass of raw materials put into a process (including water) for every kilogram of drug produced. Overall, the new route has a net PMI of 145 kilograms per kilogram of arzoxifene HCl, which is 31-percent less than the original route. Eli Lilly demonstrated its new route at a commercial scale in Lafayette, IN during 2006. It finished validating the process in 2008 and has now manufactured commercial quantities. Eli Lilly's application of the 12 green chemistry principles led it to reinvestigate its synthetic route and significantly improve its manufacturing process.

Ecomate®: An Environmentally Benign Blowing Agent for Polyurethane Foams

Foam Supplies, Inc.

For many years, chlorofluorocarbons (CFCs) were the preferred foam blowing agents used to manufacture polyurethane foams. CFCs gave good insulating and structural properties to foam used 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) are lower in ozone depletion potential (ODP), but will be phased out in the United States by 2010. A related problem is that some foam blowing agents, including CFCs, HCFCs, and hydrofluorocarbons (HFCs), have very high global warming potentials (GWPs). The HCFCs and HFCs have GWPs of 725–1810, compared to 1.00 for carbon dioxide (CO₂).

Foam Supplies developed ecomate® (its 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. Because it does not contribute to the formation of smog, ecomate®

is also volatile organic compound (VOC)-exempt. Each pound of ecomate® replaces about two pounds of alternative blowing agents, so one million pounds of ecomate® would eliminate the equivalent of 1.4–3.4 billion pounds of carbon dioxide emissions (CO₂e). Replacing high-GWP compounds, such as HFC-134a and HFC-245fa, with ecomate® has led to saving close to 2.2 billion pounds per year of CO₂e.

Ecomate® costs substantially less than do HFCs. Further, ecomate® technology requires little or no modification to existing foaming processes. The insulating and structural characteristics of ecomate® foams 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 has outstanding properties and a low environmental impact. Products made with ecomate® are widely available in the United States; Foam Supplies has also licensed its technology in the UK, Brazil, China, Australia, and Poland.

Henkel Corporation

Aquence® Autodeposition Coating: The Smart Coating Solution

Conventional electrodeposition processes for applying coatings to automotive and industrial equipment parts require that the parts be electrically charged. These processes require 12–15 steps, including surface conditioning and pretreatment with metal phosphate coatings. They contain both volatile organic compounds (VOCs) and heavy metals.

Henkel has developed Aquence® coatings as sustainable options to conventional coatings. Aquence® coatings are low-VOC, water-based functional organic epoxy–acrylic–urethane. The formulation includes epoxy–acrylic copolymer, proprietary blocked isocyanate cross-linker, coalescent, surfactant, and pigment. The autodeposition process consists of a mildly acidic bath that contains a negatively charged polymer dispersion, ferric chloride, and deionized water. The mildly acidic, oxidizing bath liberates a small amount of iron from the immersed steel parts resulting in a locally high concentration of positively charged ferrous ions at the steel surface. These ions cause the negatively charged polymer dispersion particles to deposit a coating on the surface. The process has only 7 steps. The absence of electric current from the process shortens the cycle time and lowers the curing temperature of the coating, which saves energy. The low pH of the coating bath discourages bacterial growth, and the elimination of heavy metals reduces time and expense in chemical maintenance and waste treatment.

The water-based Aquence® autodeposition coating technology developed by Henkel recently set a new industry precedent by coating an entire vehicle body in assembly. Aquence® customers can realize a 40-percent footprint reduction, reduced capital expense and paint shop complexity, decreased energy consumption, elimination of heavy metal sludge, and improved inside-out corrosion performance. Henkel launched its Aquence® 925G epoxy–acrylic coating for industrial primers and automotive body primer in 2007 and its Aquence® 930 epoxy–acrylic coating for improved cyclic corrosion resistance in the frame and chassis market in 2008. Aquence® is in trials globally at over 150 locations.

Henkel Corporation

Bonderite® TecTalis: Next-Generation Coating

The conventional zinc phosphate pretreatment process promotes adhesion and corrosion resistance on painted surfaces. It has been the automotive standard for over 60 years, but it contains regulated heavy metals, requires expensive wastewater treatment, and uses large amounts of energy. Zinc phosphating also requires accelerator compounds such as nitrite, hydroxylamine, or nitro-compounds. The process produces approximately as much sludge as it does coating; only about one-half of the zinc ends up as coating; the remaining zinc is lost as sludge that contains Zn₃(PO₄)₂ and FePO₄. Zinc phosphate baths require continuous removal of sludge.

Henkel developed TecTalis, the automotive industry's first non-phosphate conversion coating, as an efficient, sustainable replacement for traditional zinc phosphate treatments. Henkel developed TecTalis from its earlier-generation, ambient-temperature Bonderite® NT-1 technology. In the TecTalis process, fluorozirconic acid reacts with the metal substrate to form a zirconium oxide layer approximately 20–50 nm thick; this layer is much thinner than a zinc phosphate layer, which measures 2,000–10,000 nm. The TecTalis process deposits approximately 99 percent of the zinc onto the coating, so there is essentially no sludge formation. The Bonderite® TecTalis process is simpler than a traditional zinc phosphate process in that TecTalis requires no conditioning or final seal stages. In addition, the new technology can fit into an existing zinc phosphate plant. Customers can design a smaller pretreatment footprint that uses less water and energy than a traditional system. TecTalis provides the corrosion performance necessary to meet automotive standards.

TecTalis is an environmentally sustainable technology that eliminates pretreatment sludge, reduces landfill requirements, and simplifies wastewater treatment. The conversion coating is free of phosphate, volatile organic compounds (VOCs), and carbon dioxide (CO₂) equivalent emissions. The process operates at ambient temperature, reducing utility and natural resource requirements. Henkel's TecTalis has been in use in the United States and internationally since 2007.

Refrigerant for Automotive Air Conditioning with Low Global Warming Potential

Driven by the European Union's (EU's) F-Gas Directive to phase out the automotive refrigerant HFC-134a, Honeywell and DuPont have jointly developed first hydrofluoro-olefin refrigerant, HFO-1234yf (CF₃CF=CH₂), for use in mobile air conditioning (MAC) systems. HFO-1234yf has a very low 100-year global warming potential (GWP) of 4 versus 1,430 for HFC-134a, a potent greenhouse gas, and easily meets the EU's F-Gas mandate for refrigerants with GWP below 150. HFO-1234yf also has zero ozone depletion potential (ODP) and an excellent Life Cycle Climate Performance (LCCP), due its low GWP and its high energy efficiency. LCCP calculations predict a potential annual global savings in carbon dioxide (CO₂) equivalent of 5.2–5.9 million metric tons per year in 2017 when the refrigerant is fully implemented.

DuPont and Honeywell have completed extensive testing for toxicity, materials compatibility, stability, and air conditioning performance. Based on its low toxicity, HFO-1234yf is safe in MAC systems. Its unique structure leads HFO-1234yf to be stable inside MAC systems, but to break down quickly upon release to the atmosphere. HFO-1234yf exhibits only mild flammability and low potential for ignition. With minimal modifications, MAC systems designed for HFC-134a can be converted to HFO-1234yf.

Honeywell and DuPont have applied for EPA SNAP approval and ASHRAE and REACH registrations. They have also provided detailed information to the SAE Cooperative Research Program for an evaluation of HFO-1234yf. The program sponsors included automobile manufacturers representing 70 percent of the global market. They concluded that HFO-1234yf was the preferred low-GWP refrigerant. EPA's Mobile Air Conditioning Climate Protection Partnership sponsored an industry stakeholder meeting in December 2008. Stakeholders reviewed options for low-GWP refrigerants and selected HFO-1234yf as the preferred option. If adopted globally in all new vehicles, HFO-1234yf would eliminate about 60 million pounds of HFC-134a representing a substantial climate change benefit of approximately 40 million metric tons of CO₂ equivalent.

**Honeywell
International, Inc.;
DuPont**

Manufacturing More Efficient Fuel Cells to Reduce Carbon Dioxide Emissions

Huntsman Advanced Materials and GrafTech have collaborated to develop two new grades of high-performance, resin-impregnated, expanded graphite composites for GRAFCCELL® bipolar plates targeted at high-temperature fuel cell applications. The Huntsman resins that enable the new composites were developed to offer improved properties yet remain compatible with GrafTech's continuous manufacturing process.

Composites incorporating benzoxazine resins allow continuous operation at 120 °C and will meet the aggressive targets for performance and cost set by the U.S. Department of Energy for automobiles in 2015. Composites incorporating bismaleimide resins allow operation at temperatures up to 180 °C in concentrated acid environments, enabling these composites to be used in phosphoric acid fuel cells and polymer electrolyte membrane (PEM) fuel cells incorporating polybenzimidazole (PBI) membranes. These new systems are superior to existing commercially available systems in mechanical testing, gas permeability, dimensional stability, and single cell fuel testing. Compared to the metal bipolar plate, the graphite composite bipolar plate with new Huntsman resins has the following advantages: (1) superior corrosion resistance, (2) lighter weight for greater efficiencies, (3) a long operating life because there is no poisoning of the PEM membrane, and (4) consistent electrical performance because no insulating surface forms. These benefits have a direct impact on the reduction of carbon dioxide (CO₂) emissions during the lifecycle of the fuel cell.

These resin systems also enable the use of cost-effective, high-volume manufacturing techniques that will lower plate costs per kilowatt and ultimately accelerate the widespread commercial adoption of hydrogen-based energy systems. Huntsman anticipates the commercialization of fuel cells with its benzoxazine resins for stationary power applications in 2009; it anticipates the commercialization of fuel cells with its bismaleimide resins for automobiles during late 2009 or early 2010.

Development of Sustainable Disinfectants

Fourteen types of disinfectant chemicals are found in over 90 percent of current disinfectant formulations. Several of these chemicals kill microbes too slowly to be practical, have a poor safety profile, or both. Among these disinfectants, hydrogen peroxide is environmentally preferable because it decomposes to water and oxygen. It has a broad spectrum of activity but is typically slow-acting and relatively unstable. For example, 3-percent hydrogen peroxide takes 20 minutes to inactivate *Staphylococcus aureus*. This long contact time is not practical in most applications.

JohnsonDiversey developed Oxivir™ TB based on Virox's accelerated hydrogen peroxide (AHP™) technology. Oxivir™ TB is a highly stabilized hydrogen peroxide solution that addresses most of the disadvantages of traditional products. It has a broad spectrum of activity as a bactericide, virucide, fungicide, and tuberculocide. It is very fast-acting. It is safer to use than other disinfectants. Oxivir™ TB is less corrosive than straight hydrogen peroxide, thus widening its compatibility with a variety of surfaces. Its ingredients are food additives, nontoxic, and/or biodegradable. These ingredients include hydrogen peroxide, citric acid, phosphoric acid, linear alkyl benzene sulfonic acid, alkyl diphenyl oxide disulfonate, benzyl alcohol, and linear alcohol ethoxylate. The improved stability of Oxivir™ TB allows it to have a shelf life of at least two years.

Accelerated Hydrogen Peroxide (AHP™) technology creates a synergy between hydrogen peroxide, anionic surfactants, and chelating agents. It takes only one minute for 0.5-percent hydrogen peroxide (AHP™) to inactivate *S. aureus* and many other bacteria and viruses.

Although its mode of action is not understood completely, it appears that specific surfactants in AHP™ solution facilitate the penetration of hydrogen peroxide into the cell and hence increase the antimicrobial activity.

In 2006, EPA cleared Oxivir™ TB for sale in the United States. EPA classifies it as a Category IV pesticide; this class requires no precautionary labeling.

Green Chemistry in Action: A Remarkably Efficient and Sustainable Synthesis of the HIV Integrase Inhibitor, Raltegravir™

ISENTRESS® (raltegravir™) is the first medication to be approved in a new class of antiretroviral therapies called integrase inhibitors. It represents a critical advance for the treatment of HIV/AIDS. Merck developed the initial route to raltegravir™ rapidly in response to a fast-paced clinical development program. This route produced enough of the drug for development and initial commercial launch. As Merck required quantities of this drug in the thousands-of-kilograms range, however, it became clear that the company needed a more efficient and sustainable route.

Merck's process redesign resulted in a remarkably efficient, environmentally sustainable, eight-step process for raltegravir™. The revised process combines a highly innovative, atom-economical Michael addition/cycloisomerization sequence used in the first-generation route with exceptional streamlining of the final steps. The improved process increases overall yield by 35 percent, reduces total waste by 70 percent, eliminates toxic reagents, and reduces the manufacturing cost. The process replaces methyl iodide, a well-known carcinogen, neurotoxin, and respiratory toxicant, with trimethylsulfoxonium iodide, an innovative, substantially less toxic substitute. The optimized process requires no special equipment.

Overall, Merck reduced the e-factor or process mass intensity (PMI) from 314 for the original process to 97 for the new process. This is a remarkable reduction of 12 PMI per step. The waste reduction is equal to 217 metric tons per metric ton of raltegravir™ manufactured. Given the required dose of 800 milligrams per person per day of ISENTRESS®, the waste reduction translates to 140 pounds per person per year compared to the original manufacturing route. Merck completely developed the revised process and introduced it into production at manufacturing scale in April 2008. Because Merck converted to its new optimized route shortly after it launched ISENTRESS®, the benefits of the greener process will accrue throughout the lifecycle of this important medicine.

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

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® antiskid, 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

Merck & Co.

Milliken & Company

installations, thus eliminating related VOCs. Milliken estimates that each year TractionBack® eliminates the use of 400 tons of sealants and adhesives as well as 16,000 five-gallon containers for the sealants and adhesives.

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 landfills 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 poly(vinyl chloride), PVC, which has environmental issues related to its production, installation, and eventual disposal. TractionBack® uses fewer resources in its manufacturing and installation, which reduces both its eco-footprint and its associated waste. TractionBack® has been on the market since 2003. Milliken revised its formulation for TractionBack® to include biobased raw materials in 2005.

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

Cotton accounts for over 40 percent of global fiber production, but is also the most pesticide-intensive commodity crop. Cotton production alone uses 25 percent of all insecticides. It has been a persistent challenge to both protect cotton from insects and weeds and reduce the negative health and environmental impacts of cotton-protecting pesticides.

Monsanto has developed genetically engineered cotton plants that meet this challenge. The resistance of Bollgard® and Bollgard II® cotton to insects is based upon natural insect control. *Bacillus thuringiensis* (a ubiquitous soil microbe) produces Cry (crystalline) proteins that are insect toxins. Monsanto pioneered plant molecular genetics to create cotton plants that express these Cry proteins to control many devastating caterpillar pests. The specificity of Cry proteins ensures that only target organisms are affected.

Bollgard II® with Roundup Ready® Flex cotton is also tolerant of Monsanto's herbicide, Roundup (glyphosate). Roundup kills plants by inhibiting 5-enolpyruvylshikimate-3-phosphate synthase, a key enzyme in the aromatic amino acid synthesis pathway common to all plants. By inserting a glyphosate-insensitive version of that enzyme into the cotton plant's genome, Monsanto rendered the cotton tolerant to Roundup. With Roundup Ready® Flex cotton, growers can use Roundup throughout the season to control weeds safely and effectively. This eliminates more-toxic herbicides and conserves energy by eliminating farmers' trips across fields.

Cotton growers can increase yields and reduce input costs with Bollgard II®. Monsanto's products also provide measurable environmental and health benefits by reducing global applications of pesticide active ingredients by 14 percent for herbicide-tolerant crops and 24 percent for insect-resistant crops.

In 2007, EPA approved a natural refuge for Bollgard II® cotton for most of the United States, further increasing yields and decreasing pesticide use. As of 2007, 43 percent of world cotton production or 15 million hectares contained genes for insect resistance, herbicide tolerance, or both. Virtually all of this is Monsanto's technology.

A Green, Energy-Efficient, Biocatalytic Process to Manufacture Pregabalin

Pregabalin (the active ingredient in the drug Lyrica®) is a compound for the successful treatment of several indications associated with neuropathic pain. The drug is approved in 154 countries. Pfizer launched Pregabalin in the United States in 2005, but replaced its original process with a biocatalytic one in 2007.

Pfizer's new process uses an innovative enzymatic reaction to eliminate a wasteful enantiomeric separation in the final step. The biocatalytic process eliminates organic solvents from all four reaction steps. The process operates at a high substrate concentration, which dramatically improves environmental performance, worker safety, and process efficiency. Pfizer's exceptional green chemistry innovation includes using a biocatalytic reaction, conducting reactions in water rather than organic solvents, selectively synthesizing chirality earlier in the process sequence, recycling the undesired enantiomer using a continuous process, telescoping reactions for higher efficiency, and implementing catalytic as opposed to stoichiometric reactions. Pregabalin is one of the very few small-molecule pharmaceutical agents where every chemical step in the manufacturing process is performed in water. Pfizer has published this chemistry in a peer-reviewed scientific journal and made the methodology available to the wider scientific community.

Pfizer has implemented its new process in a production facility at a 10-metric-ton batch size. Between 2007 and 2020, Pfizer estimates that this process will eliminate 185,000 metric tons of solvent, 4,800 metric tons of mandelic acid, 10,000 metric tons of the starting cyano-diester and 1,890 metric tons of Raney® nickel. The process also uses 83-percent less energy than the original process.

Pfizer's biocatalytic process is much more sustainable than the chemical process it replaced. The efficiency, safety, and environmental improvements for the Pregabalin synthesis demonstrate how green chemistry principles can produce significant benefits for society. Pfizer believes that it has brought an important pain-relieving medicine to the patient in the most environmentally responsible manner.

Openair™ Plasma Surface Treatment: Reducing Emissions of Volatile Organic Compounds and Improving Environmentally Sensitive Paint Processes

**Plasmatreat North
America Inc.; Ford
Motor Company**

World-class manufacturing processes require surface treatments that produce clean, highly activated surfaces for optimal adhesive bonding, coating, and printing. Openair™ is the first industrial surface-preparation process to use plasma for nanoscale cleaning and surface activation. The Openair™ process provides reliable, cost-effective, environmentally friendly surface treatment of metals, ceramics, glass, and polymers to enable the highest-quality bonding, coating, and printing. This enabling technology allows full automation with total process control.

Openair™ plasma treatment breaks up organic contaminants on the surface of the part to be painted; the resulting small molecules vaporize or are oxidized to carbon dioxide (CO₂) and water vapor. Openair™ plasma treatment removes dust and neutralizes static. It activates surfaces by incorporating oxygen-containing functional groups that can form strong chemical bonds to the applied paint. Plasma treatment allows true chemical bonding between the substrate and paints.

Compared to current processes, plasma treatment technology eliminates or reduces solvents, adhesion promoters, primers, volatile organic compound (VOC) emissions, wastewater

streams, non-degrading parts from landfills, and high energy use. Previously, the technology had only been successful in treating small plastic components.

Plasmatreat and Ford Motor Company expanded plasma treatment technology to large, complex parts such as automotive bumpers made of thermoplastic olefins. Transferring the technology to large parts was difficult, primarily because suitable, large-scale processing equipment did not exist. Ford's Dearborn, MI laboratory developed such equipment, opening a huge market for Openair™ plasma technology. Large paint facilities adopting this technology can eliminate annually over one million gallons of toxic wastewater and tens of thousands of gallons of highly toxic sodium hydroxide, hydrochloric acid, and flocculating agents. Because a single plasma treatment replaces multistage power-wash systems, dry-off ovens, solvent wiping, and adhesion-promoting primers, the process has a shorter cycle time and a smaller fixed capital investment. During 2008, two patent applications were filed for the technology.

PPG Industries, Inc.

Green Logic™: Chitosan-Enhanced Paint Detackifier

GREEN LOGIC™ is a liquid, chitosan-containing, paint denaturant technology that provides an alternative to traditional chemistries based on melamine–formaldehyde or acrylic acid. Paint denaturants, also referred to as “paint detackifiers”, are added to the water curtain circulating in downdraft, water-washed paint spray booths to render oversprayed paint non-sticky. In traditional, wet paint spraying operations used in automotive original equipment manufacturing (OEM), only 50–80 percent of the paint is transferred to the vehicle; the residual 20–50 percent remains in the air until it is trapped in the circulating water curtain. The chemicals added to the water curtain detackify, coagulate, and flocculate this oversprayed paint, allowing it to be removed from the water later. The available melamine–formaldehyde-based detackifiers contain small amounts of free formaldehyde, a known carcinogen. The alternative acrylic acid based paint denaturants rely on two nonrenewable petroleum-based feedstocks: ethylene and propylene.

PPG derives its GREEN LOGIC™ technology from the chitin of crab, lobster, and shrimp shells that are waste products of food production. Chitosan, the main component of GREEN LOGIC™ technology, is poly(glucosamine), a glucosamine polysaccharide structurally similar to cellulose. PPG's technology requires less overall tackification chemical and reduces the use of sodium hydroxide by 87 percent. Chitosan has been demonstrated to have antimicrobial properties and, therefore, it decreases the use of hazardous biocides. GREEN LOGIC™ exhibits superior foam control, which reduces environmental stack emissions. The GREEN LOGIC™ technology has performed as well as and in some cases better than traditional products used in this area while providing significant cost savings to customers and reducing their carbon footprints. Financial data from a number of customers show a 40-percent savings in wastewater treatment (approximately 5.5 million gallons per year per plant) and a 28-percent overall process savings. Seventeen automobile manufacturing plants in the United States are currently using this technology.

PPG Industries, Inc.

Zircobond™ Pretreatment

Pretreatments protect metal substrates against corrosion and improve adhesion of paints. Conventional zinc phosphate pretreatment forms a sludge byproduct containing suspected carcinogens and heavy metals such as zinc, nickel, and manganese that are hazardous and subject to environmental regulations. These heavy metals also create challenges in wastewater management. Increasing demand for the raw materials used for zinc phosphate pretreatment is also rapidly outpacing the capacity of suppliers worldwide.

PPG has developed Zircobond™ pretreatment as an alternative to conventional pretreatment technologies. The Zircobond™ process is based on dilute, aqueous fluorozirconic acid. It

contains no regulated heavy metals, phosphates, or volatile organic compounds (VOCs). With its zirconium-based chemistry, Zircobond™ pretreatment uses a more stable supply chain and alleviates some of the strain on supplies of zinc, manganese, nickel, and phosphoric acid, which are used by other industries such as farming and steel. It can be used in existing equipment and is safe for the conventional waste treatment systems in most manufacturing facilities following a simple pH adjustment.

Zircobond™ pretreatment provides manufacturers with a new, environmentally friendly option with greener chemicals and reaction conditions. It generates at least 80-percent less sludge than do conventional processes; this translates to significant savings on waste disposal costs, as well as fewer stage cleanings and boil-outs. In addition to savings on maintenance, PPG's new chemistry operates in an ambient temperature bath that requires minimal agitation and fewer water rinses than do current processes. The result is substantial operating savings from reductions in energy use, water consumption, and wastewater treatment. Brownfield automotive plants that have converted to Zircobond™ pretreatment demonstrate potential annual operating savings of almost \$600,000. The savings in greenfield facilities are more than double: there, the smaller process footprint can save millions on new capital costs. In 2008, the first commercial launch took place in Canada.

Chemical Conversion of Post-Consumer Recycled Polyethylene Terephthalate Waste into Sustainable Valox iQ™ and Xenoy iQ™ Engineering Thermoplastic Products

Polyethylene terephthalate (PET) resin for soft drink bottles is made from virgin, petroleum-based terephthalic acid (TPA) and ethylene glycol (EG). After use, most PET bottles are discarded as waste. U.S. consumers generate approximately five billion pounds of PET bottle waste each year. Another resin typically made from virgin, petroleum-based TPA is polybutylene terephthalate (PBT). PBT is an important engineering thermoplastic commonly used in durable applications such as automotive components and electrical devices. PBT is usually comingled with other polymers and is not practical for recycling. PET scrap, however, is a good source of TPA for use in making polyesters such as PBT.

SABIC Innovative Plastics has developed a novel approach to chemically “up-cycle” PET waste into durable PBT-based products. The PET waste is chemically decomposed to oligomers using excess ethylene glycol, a catalyst, and heat. The recovered TPA oligomers are transesterified with butanediol and repolymerized; ethylene glycol, excess butanediol, and other volatile components are recovered by distillation. The result is Valox iQ™ PBT neat resin. The Valox iQ™ PBT neat resins and the molding compositions containing them exhibit performance equivalent to materials made by conventional methods. This chemical up-cycling process converts single-use, nondurable PET objects like water bottles into molding compositions containing Valox iQ™ PBT neat resins for durable applications.

SABIC has commercialized these environmentally sustainable products under the trade names Valox iQ™ and Xenoy iQ™ resins. These resins have up to 65-percent carbon content from recycled waste. The environmental benefits of Valox iQ™ and Xenoy iQ™ resins include up to 55–75-percent reduction in both carbon dioxide emissions and process energy. These benefits are accomplished without sacrificing the quality of the final product. During 2008, the first full year of commercialization, the materials were used successfully in more than 20 applications, generating \$3.5 million in sales.

SABIC Innovative Plastics

High-Solids Hybrid Sucrose Ester Polymer Technology

In 2007, the U.S. paint market included approximately 500 million gallons of solvent-borne paints and coatings. In general, these were solvent-rich, oil-based products containing over 350 grams per liter of volatile organic compounds (VOCs). Upcoming regulations in the United States, however, are tightening the limits for VOCs in coatings, especially architectural and industrial coatings. As one example, EPA's VOC targets for 2010 are less than 100 grams per liter for non-flat architectural coatings. These and other regulations have necessitated a search for alternate, VOC-compliant products that feel and apply by brush, roller, and spray like high-VOC coatings.

Sherwin-Williams developed its innovative, high-solids, hybrid sucrose ester polymer technology to address this urgent need. Sherwin-Williams's novel, high-solids, oxidative cross-linking hybrid sucrose ester technology uses a modified sucrose ester technology from the Procter and Gamble Company (P&G). At the request of Sherwin-Williams, P&G converted its Sucrose Ester 7.75 (Sefose® 7.75, which has no reactive groups) into a reactive Sucrose Ester 6.0 (Sefose® 6.0) with two reactive hydroxyls available for further modification.

Sherwin-Williams then acrylated Sucrose Ester 6.0 with methacrylic anhydride in a solventless process to obtain a 100-percent-solids acrylated sucrose ester polymer. This ester polymer was formulated, scaled-up, and commercialized into pigmented, oil-based coatings with excellent performance and application features for architectural and industrial maintenance applications. A single coat of the higher-solids product gives the opacification desired by customers. Subsequently, Sherwin-Williams replaced methacrylic anhydride with glycidyl methacrylate for industrial applications; this second-generation technology was acrylated and urethanated without generating waste byproducts via ring-opening of the epoxide.

This technology is enabling Sherwin-Williams to market the only compliant, oil-based, pigmented coating in the United States with VOCs less than half of the current oil-based coatings. In 2006 and 2007, Sherwin-Williams filed a patent application and commercialized three products using this technology.

Waterborne Hybrid Cross-linking Dispersion Technology

The recent record-high cost and uncertain availability of petroleum- and oil-based raw materials makes complete dependence on synthetic raw materials questionable. Further, the tightening of volatile organic compound (VOC) regulations by the Ozone Transport Commission (OTC) and the South Coast Air Quality Management District (SCAQMD) is necessitating VOC-compliant waterborne technologies that perform like solventborne coatings in industrial and architectural applications. Current technologies are challenged to meet the performance of the solventborne coatings that are being restricted by regulation.

Polyethylene terephthalate (PET) is commonly used in beverage bottles; it is recyclable but typically ends up in landfills. Sherwin-Williams has developed chemistry to use PET as an inexpensive starting material. Sherwin-Williams depolymerized post-industrial, recycled, or virgin PET with soy fatty acids and a tin catalyst and then added trimethylol ethane to repolymerize it into a polyester. This soy-PET liquid polyester was grafted with hydrophobic and hydrophilic acrylic monomers in the presence of soybean oil (a reactive diluent) instead of solvent. The anionic prepolymer was dispersed in water using triethylamine under high-shear conditions and then the resulting dispersion was formulated into a pigmented coating.

Sherwin-Williams's new coating performs as well as a typical oil-based coating, but contains VOCs of less than 100 grams per liter. This technology takes advantage of the hardness of the

polyester and the flexibility of soy oil to replace solvent and combine the durability of acrylics with the dry times of alkyds. The resulting resin incorporates about 30-percent renewable materials and 15-percent post-industrial PET. Sherwin-Williams is targeting its technology as a protective finish over metal substrates and as an adhesion modifier and gloss enhancer in combination with latex emulsions for architectural coatings. Sherwin-Williams scaled up its synthesis and performed testing and validation of its high-gloss coatings during 2008 in anticipation of commercial launch in early 2009.

An Environmentally Friendly Alternative for Cleaning Surgical Instruments in Healthcare Facilities

Cleaning is the single most important step in processing surgical instruments for reuse. Instruments must be cleaned effectively each and every time they are used. Instrument cleaning, as defined by the Association for Advancement of Medical Instrumentation (AAMI), is “the removal, usually with detergent and water, of adherent visible soil, blood, protein substances, and other debris from the surfaces, crevices, serrations, joints, and lumens of instruments, devices, and equipment by a manual or mechanical process that prepares items for safe handling and/or further decontamination.” Any inorganic or organic soils that are not removed during cleaning can interfere with subsequent disinfection and sterilization. Repeated exposure to harsh chemicals can damage surgical instruments and shorten their useful life, increasing both costs and waste. Current, traditional cleaners are widely used but have several disadvantages: poor substrate compatibility, ineffective cleaning performance, and ingredients that are not environmentally friendly.

STERIS developed and introduced Prolystica® Ultra Concentrate cleaning chemistries in 2006. This product line includes a neutral pH enzymatic presoak and cleaner, a neutral detergent, and an alkaline detergent with lower alkalinity. Whereas many traditional cleaners contain surfactants that are biodegradable, Prolystica® Ultra Concentrate cleaning chemistries also contain biodegradable corrosion inhibitors and chelating/sequestering agents. All three formulations are free of phosphate, nonylphenol ethoxylates, and other such ingredients with negative environmental impact. Therefore, the small amount of cleaning chemicals in the effluent after the wash cycle is expected to have minimal impact. These 10-fold concentrated cleaning chemistries provide leading cleaning and protection for surgical instruments and are also environmentally friendly. The smaller product containers of the Prolystica® Ultra Concentrate products reduce the amount of waste generated for disposal and increase staff safety. Overall, Prolystica® Ultra Concentrate products with biodegradable formulas reduce shipment fuel costs, plastic packaging consumption, and chemicals used per wash cycle.

An Alternative to Aldehyde-Based Liquid Chemical Sterilants and High-Level Disinfectants for Reprocessing Heat-Sensitive, Semi-Critical Medical Instruments

High-level disinfectants (HLDs) are used to decontaminate semi-critical medical instruments. Currently, aldehyde-based HLD solutions such as glutaraldehyde and ortho-phthalaldehyde are widely used to reprocess heat-sensitive, semi-critical medical instruments, such as flexible endoscopes and imaging probes, primarily because they are compatible, reusable up to 14 days, and cost-effective. Aldehydes have a number of disadvantages, however; they are skin and respiratory allergens, they are not easily rinsed from treated instruments, and some organisms are resistant to them.

Resert™ XL HLD High Level Disinfectant is a 21-day, reusable liquid chemical sterilant and high-level disinfectant for safely reprocessing heat-sensitive, compatible medical

STERIS Corporation

**STERIS Corporation;
Virox Technologies**

devices. STERIS developed Resert™ XL HLD solution from Virox's activated hydrogen peroxide (AHP™) platform technology, a patented combination of 93-percent water, 2-percent hydrogen peroxide, hydrotropes, pH buffering agents to maintain pH 2.4, and other inert ingredients that optimize the hydrogen peroxide stability during storage and use. The rather mild, nonreactive nature of the components in the mixture and the low levels at which they are formulated make the solution ideal both for processing flexible medical devices and for ensuring complete disinfection, even in the presence of organic matter.

The Resert™ solution overcomes all of the negative characteristics of aldehydes. It is cost-effective, virtually odorless, clear, nonstaining, nontoxic, nonsensitizing, nonflammable, non-combustible, and easily rinsed from instruments. Unlike aldehydes, it requires no treatment to neutralize spent solution prior to disposal. Moreover, the Resert™ solution is very fast-acting, achieving tuberculocidal activity in 8 minutes at 20 °C, as opposed to 12 minutes for ortho-phthalaldehyde and 45 minutes at 25 °C for most glutaraldehyde products.

The U.S. Food and Drug Administration cleared this technology for sale in the United States and STERIS commercialized it under the brand name, Resert™ XL HLD High Level Detergent during 2008.

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

Fouling of surfaces by mineral salts is a major problem in water-bearing systems. Scaling reduces the efficiency of heat transfer and interferes with the operational performance of industrial processes. Similarly, hardness ions hinder the efficiency of detergents and cleaning processes. Scale inhibitors are used to prevent the deposition of inorganic scales on surfaces. Previously, scale inhibitors were either products with poor biodegradability and moderate toxicity but good performance or biodegradable products with limited applicability. Previous products did not use renewable resources.

Carboxymethyl inulin (CMI) is based on inulin, an oligosaccharide harvested from the roots of chicory. Although CMI is a biotic material, it does not compete with the production of food crops. CMI provides an environmentally friendly, cost-effective, safe, and versatile alternative to traditional threshold scale inhibitors that are used in a wide variety of industrial applications. Moreover, CMI has interesting chelation properties (especially for calcium and magnesium) and has excellent dispersant properties, which make it an attractive ingredient for household detergents.

Current commercial applications for CMI include household, industrial, and institutional detergents and cleaners, secondary oil recovery, and pulp and paper processing. Because CMI is stable in the presence of low levels of oxidizing agents like hydrogen peroxide, it can be used as a co-builder and anti-redeposition aid in detergent formulations that contain bleach activator systems. CMI also is a suitable replacement for poorly biodegradable scale inhibitors in water and process water treatment, sugar refining applications, and other industrial applications. CMI neither contains nor releases nitrogen or phosphorus. CMI is not a very strong chelant of transition metals and, therefore, does not contribute to the mobilization of heavy metals.

Solutia developed CMI in collaboration with Royal Cosun. In 2007, Solutia transferred the Dequest® business, including this technology, to Thermphos. During 2008, a Thermphos breakthrough in commercial detergent applications led to a ten-fold increase in U.S. sales.

Vulkem 950NF: A Renewable, Polyol-Based, High-Solids, Low-Odor, Ultra-Low-VOC, “Neighbor-Friendly” Polyurethane Top Coat for Use in Vehicular, Pedestrian, and Specialty Applications

Polyurethane (PU) coatings have been the industry staple for several decades in waterproofing, providing protection to parking garages, pedestrian walkways, and other specialty applications. These coatings are traditionally solvent-based, derived from petroleum, odorous, and high in volatile organic compounds (VOCs). They have a limited product life, especially when exposed to abrasion and common household and institutional chemicals such as motor oil and bleach. In addition, most PU coatings also contain plasticizers such as phthalates, fillers such as fumed silica and titanium dioxide, and catalysts such as organotin complexes or amines. Although coatings across the market have been moving toward lower-odor, lower-VOC, higher-performance versions, the petroleum base of PU chemistry has remained relatively unchanged.

Tremco has developed Vulkem 950NF, a polyurethane top coat that replaces traditional petroleum-based polyols with a proprietary polyol mixture based on castor oil. The replacement polyols have a lower viscosity than others on the market and comprise approximately 45 percent of the Vulkem 950NF formulation. The strong cross-links and intermolecular interactions within the polymeric matrix of Vulkem 950NF produce a harder-curing PU film with unprecedented abrasion resistance. As a result, Vulkem 950NF has twice the lifespan of traditional coatings, and Tremco now offers a ten-year warranty for it, which is double the industry standard. Vulkem 950NF is also less dependent on solvent, allowing for an industry-leading, “Neighbor Friendly”, low-odor product that has a VOC content less than 20 grams per liter, once thought theoretically impossible. Altogether, Vulkem 950NF has raised the bar on an industry staple, providing better wear, very low VOCs, renewable technology, and energy savings.

Tremco commercialized this technology in December 2005. During Tremco’s most recent fiscal year, sales of Vulkem 950NF reached one million dollars. Because Vulkem 950NF performs so well and has been such a financial success, Tremco is currently pursuing additional enhancements to increase the sustainability of this product even more.

Diesel DeNO_x Catalyst

By 2014, EPA will implement more stringent standards restricting emissions from heavy-duty diesel vehicles. These standards are creating a market for products that reduce diesel emissions.

Argonne National Laboratory has developed a technology to remove nitrogen oxides (NO_x) from diesel exhaust gases. The Argonne Diesel DeNO_x Catalyst works by selective catalytic reduction of NO_x to N₂ using diesel fuel hydrocarbons as the reducing agent. The catalyst formulation is based on copper zeolite formulations (Cu-ZSM-5) that can reduce NO_x, but are unstable. Argonne added a cerium oxide coating over the Cu-ZSM-5 formulation, which improved both the catalyst’s long-term stability and its activity at lower temperatures. This catalyst is effective and economical when used with the ultra-low sulfur diesel fuel that is now required for on-highway use. In contrast to other systems, Argonne’s system performs better in the presence of water vapor, making it ideal for automotive and truck exhaust systems, which always contain water. The DeNO_x system can be installed on both existing and new vehicles.

**U.S. Department of
Energy, Argonne
National Laboratory**

Argonne's Diesel DeNO_x Catalyst is a totally passive, easy-to-use system that converts 95–100 percent of NO_x to atmospheric nitrogen (N₂) and meets EPA's standards. It is expected to have lower manufacturing and installation costs than competing technologies. The materials used to produce the system are relatively inexpensive and nontoxic. The catalyst is expected to have a long lifetime.

Integrated Fuels Technology (IFT) is collaborating with Argonne to develop this technology. By combining its own fuel-saving technologies with Argonne's DeNO_x formulation, IFT expects to advance its integrated approach to emissions control and achieve substantial NO_x reduction without adversely affecting other performance-enhancing or emission-reducing technologies. Currently, IFT is refining the design and manufacturing methods for the product. Promising future markets include passenger vehicles and stationary sources including industrial diesel engines, coal-fired power plants, and methane-fueled "peaker" power plants.

Resin Wafer Technology

Resin wafer technology enables electrodeionization (EDI) to be extended well beyond its conventional applications in ultrapure water production to new processes in biobased chemical production, industrial water management, chemical production and purification, carbon dioxide (CO₂) capture, and, potentially, hydrogen production. EDI is an electrically driven process that separates dilute, charged species from process streams at higher efficiency than electrodialysis, its lower-tech counterpart. Resin wafer technology replaces the loose ion exchange resins used for conventional EDI. The performance advantages of resin wafers include (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 loss to waste streams. Resin wafer technology provides new functionalities not available with conventional EDI. These include direct immobilization of biocatalysts, which allows integrated bioconversion and separations; modification of wafer composition and format, which increases ion selectivity and direct pH control; and even in situ catalysis.

Resin wafer technology also offers the following 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 wastewater in power plants. It reduces energy and chemical use during the production of organic acids, esters, and other chemicals. It enables CO₂ capture from flue gases in coal power plants, and it potentially enables enhanced hydrogen production from water.

Argonne has received technical and financial support from Archer Daniels Midland Company for biobased products, Nalco Company for water management, Carbozyme Inc. for CO₂ capture, and the Department of Energy for energy efficiency, renewable energy, and fossil energy. During 2008, Argonne scaled up the technology and demonstrated it successfully on a pilot-plant scale. During the past 18 months, Argonne has been negotiating with commercial entities to commercialize the technology.

Renewable-Resource Industrial Products

Zep has developed and introduced into the marketplace two innovative, high-performance, industry-oriented, chemical-specialty products that are safer for users and have reduced environmental impact. These products are Zep Shell Shock heavy-duty hand cleaner and Zep 70 Liquid penetrating lubricant. Both products incorporate soy methyl ester solvent (methyl soyate) derived from soybean oil, a renewable resource. Methyl soyate is a 100-

percent-biodegradable solvent that contains less than 50 grams per liter of volatile organic compounds (VOCs) and has a flash point above 300 °F. It can replace the nonrenewable, petroleum-derived solvents that are typically used in these types of products.

Shell Shock contains over 87 percent of renewable ingredients. In addition to methyl soyate, Shell Shock also contains sterilized walnut shell abrasive, which is a biodegradable, renewable-resource material that facilitates the removal of heavy soils from the hands. The walnut shell abrasive replaces nonrenewable pumice, which is typically used in heavy-duty industrial hand soaps. Zep's Shell Shock is formulated as an oil-in-water microemulsion that leaves hands clean, soft, and moisturized. Traditional petroleum solvent-based industrial hand cleaners with pumice tend to leave hands dry and chapped, especially during the low-humidity, winter months. The cost of Shell Shock is similar to that of traditional pumice and petroleum-based products.

Zep 70 is a nontraditional, penetrating lubricant that is an excellent alternative to petroleum-based lubricants. It provides equal if not better penetration, corrosion inhibition, and lubrication. It is formulated with more than 80-percent renewable ingredients, including soy methyl esters.

Zep has marketed Shell Shock and Zep 70 for the last 3.5 years and has received commendable feedback from its customers on the performance of both products. Since 2006, the Zep Shell Shock and Zep 70 formulations with soy methyl esters have displaced over 312,000 pounds of petroleum solvents.

Index

Award winners are indicated with *.

3M

Reformulation of 3M™ Neutral Cleaner and 3M™ General Purpose Cleaner for the 3M™ Twist 'n Fill™ Chemical Management System Reduces Air Pollution and Employee Health Hazards 33

Advanced Technology Materials, Inc.

RegenSi™: Low-Carbon-Footprint Wafer Reclaim Solution Extends the Lifecycle of Silicon Test Wafers. 33

Akzo Nobel Functional Chemicals, LLC

Replacement of Phosphates in Automatic Dishwashing Detergents with GLDA, a Readily Biodegradable Chelating Agent Manufactured from a Renewable Feedstock 34

Alvarez, Jessica and Raminderjit (Sonam) Gill, Student Intern LabRATS, University of California, Santa Barbara

The University of California, Santa Barbara Green Chemistry Initiative 9

American Ordnance LLC

Inert Filler TB-1 34

A. S. Trust & Holdings Inc.

A Climate-Friendly Hydrocarbon Refrigerant for Safer, More-Efficient Cooling . . . 19

Ashland Hercules Water Technologies

Pulp Mill Defoamers Based on Vegetable Oil 35

Ashland Inc.

Water-Based Refractory Coatings with Wet/Dry Color Change Indication. 35

Augsburg College, Arlin E. Gyberg; SarTec Corporation

The Mcgyan Process: A Green Synthetic Route for Biodiesel Production. 10

BASF AG; The Dow Chemical Company

Innovative Industrial Process Using Hydrogen Peroxide to Synthesize Propylene Oxide 41

Battelle Memorial Institute

Environmentally Friendly Biobased Plasticizers for Polyvinyl Chloride 36

Bayer MaterialScience, LLC

AURA® Infusion Technology: A Green Method to Incorporate Color and Performance Additives. 37

IMPACT Technology: A Greener Polyether Polyol Process. 37

Bend Research Inc.

Spray-Dried Dispersions Based on Hydroxypropyl Methylcellulose Acetate Succinate for Delivery of Low-Solubility Drugs. 19

***Carnegie Mellon University, Krzysztof Matyjaszewski**

*Chempol®MPS Resins and Sefose® Sucrose Esters Enable High-Performance
Low-VOC Alkyd Paints and Coatings* 3

***CEM Corporation**

*Innovative Analyzer Tags Proteins for Fast, Accurate Results without Hazardous
Chemicals or High Temperatures* 6

Champion Technologies, Inc.

*Lysine Phosphonate Scale Inhibitor: Improved Biodegradation While
Maintaining Performance over Traditional Phosphonates* 38

Clarke Mosquito Control

Natular: Engineering Green Chemistry for Mosquito Control 38

The Clorox Company

*GreenWorks™ Natural Cleaners from the Makers of Clorox: Home
Cleaning Products.* 39

Codexis, Inc.

*Greening Atorvastatin Manufacture: Replacing a Wasteful, Cryogenic Borohydride
Reduction with a Green-by-Design, More Economical Biocatalytic Reduction
for a Higher Quality Product.* 20

*Rapid Enablement of Green, Economic Processes for Chiral Alcohols by the
Codex™ Panel of Recombinant, Robust, Divergent Evolvants of One
Ancestral Ketoreductase* 21

Cognis Corporation; FlyAshDirect Ltd.

Carbon Blocker™ Fly Ash Conditioning Treatment 24

Commercial Fluid Power LLC

Nitro-tuff Tubes: Eliminating Genotoxic Carcinogenic Waste in Cylinder Tubes 21

***Cook Composites and Polymers Company; The Procter &
Gamble Company**

*Chempol®MPS Resins and Sefose® Sucrose Esters Enable High-Performance
Low-VOC Alkyd Paints and Coatings* 7

Cortec Corporation

Corrosion-Control Chemicals Based on Sustainable Resources 22

Cytec Industries Inc.

Sodalite Scale Inhibitor. 40

Cytec Industries Inc.; TDA Research, Inc.

Replacement for Solvent-Based, Chromate-Containing Primer. 40

**Davis, James Hillard, Jr., Department of Chemistry,
University of South Alabama**

*Liquid but Nonvolatile Sulfonic Acids and Amines: Greener Chemicals for
Greening Processes.* 9

Dober Chemical Corporation

Smart Release™ Technology: Intelligent, Green, Water Treatment 22

Doty Energy

Recycling Carbon Dioxide into Carbon-Neutral Liquid Fuels 23

The Dow Chemical Company

Glycerin to Epichlorohydrin Process: How Green is my Epichlorohydrin?. 40

The Dow Chemical Company; BASF AG

*Innovative Industrial Process Using Hydrogen Peroxide to Synthesize
Propylene Oxide 41*

DuPont; Honeywell International, Inc.

*Refrigerant for Automotive Air Conditioning with Low Global
Warming Potential 45*

DuPont Crop Protection

Chlorantraniliprole: Designing Green Chemistry for Insect Control 42

Earth Science Laboratories, Inc.; Linda Schweitzer, Oakland University; Robert Reed, University of Missouri

EarthTec®: Green Water Treatment 15

***Eastman Chemical Company**

A Solvent-Free Biocatalytic Process for Cosmetic and Personal Care Ingredients. 5

Ecolab Inc.

Wash 'n Walk™ Floor Care System 42

Eli Lilly and Company

New Manufacturing Route for Arzoxifene Hydrochloride 43

FlyAshDirect Ltd.; Cognis Corporation

Carbon Blocker™ Fly Ash Conditioning Treatment 24

Foam Supplies, Inc.

Ecomate®: An Environmentally Benign Blowing Agent for Polyurethane Foams . . . 43

Ford Motor Company; Plasmatrete North America Inc.

*Openair™ Plasma Surface Treatment: Reducing Emissions of Volatile Organic
Compounds and Improving Environmentally Sensitive Paint Processes 49*

French Creek Software, Inc.

*Chemical Treatment Modeling and Optimization Software: The French Creek
Software Calculation Engine 24*

Genomatica

*Sustainable Chemicals from Renewable Resources: A Breakthrough for
Biomanufacturing. 25*

Gill, Raminderjit (Sonam) and Jessica Alvarez, Student Intern LabRATS, University of California, Santa Barbara <i>The University of California, Santa Barbara Green Chemistry Initiative</i>	9
GVD Corporation <i>Novel, Solvent-Free, Fluoropolymer Coating Process</i>	25
Gyberg, Arlin E., Augsburg College; SarTec Corporation <i>The Mcgyan Process: A Green Synthetic Route for Biodiesel Production.</i>	10
Henkel Corporation <i>Aquence® Autodeposition Coating: The Smart Coating Solution</i> <i>Bonderite® TecTalis: Next-Generation Coating</i>	44
Honeywell International, Inc.; DuPont <i>Refrigerant for Automotive Air Conditioning with Low Global Warming Potential. .45</i>	
Huntsman Advanced Materials Corporation <i>Manufacturing More Efficient Fuel Cells to Reduce Carbon Dioxide Emissions</i>	46
Ingenuity IEQ, Inc. <i>Green Chemistry for Energy Conservation and Indoor Environmental Quality.</i>	26
JohnsonDiversey, Inc.; Virox Technologies <i>Development of Sustainable Disinfectants.</i>	46
Kansas State University, Department of Grain Science and Industry and Director, Center for Biobased Polymers by Design, Xiuzhi Susan Sun <i>Green Process for Unfolding Soy Protein Polymers for Green Adhesives</i>	16
KTM Industries; Ramani Narayan, Department of Chemical Engineering and Materials Science, Michigan State University <i>Biodegradable, Chemically Modified Starch Polymers for Protective Foam Packaging and Insulation Applications.</i>	13
Liao, James C. , Department of Chemical and Biomolecular Engineering, University of California, Los Angeles <i>Biosynthesis of Higher Alcohols from Renewable Carbon Sources</i>	10
Lipshutz, Bruce H., Department of Chemistry and Biochemistry, University of California, Santa Barbara; Zymes, LLC <i>Getting Organic Solvents Out of Organic Reactions</i>	11
LS9, Inc. <i>Microbial Production of UltraClean™ Diesel</i>	27

**MacGillivray, Leonard R., Department of Chemistry,
University of Iowa**

Template-Controlled Reactivity in the Organic Solid State. 12

**Mascal, Mark, Department of Chemistry, University of
California, Davis**

High-Yield Conversion of Plant Biomass into a New Generation of Biofuels. 12

***Matyjaszewski, Krzysztof, Carnegie Mellon University**

Chempol®MPS Resins and Sefose® Sucrose Esters Enable High-Performance

Low-VOC Alkyd Paints and Coatings 3

Merck & Co.

Green Chemistry in Action: A Remarkably Efficient and Sustainable Synthesis

of the HIV Integrase Inhibitor, Raltegravir™ 47

Method Products

Method Smarty Dish for Fish: An Environmentally Responsible and Effective

Cleaning Solution: No Phosphates, Acrylates, or Ethylenediaminetetraacetic Acid . . 27

**Michigan State University, Department of Chemical
Engineering and Materials Science, Ramani Narayan; KTM
Industries**

Biodegradable, Chemically Modified Starch Polymers for Protective Foam

Packaging and Insulation Applications. 13

Milliken & Company

TractionBack®: Alternative Green Adhesives Solutions for Textile Composites

Used in Commercial Buildings 47

Monsanto Company

Revolutionizing Insect and Weed Control: Bollgard® Insect-Protected

Cotton Technology and Bollgard II® Cotton with Roundup Ready® Flex for

Herbicide Tolerance 48

**Narayan, Ramani, Department of Chemical Engineering and
Materials Science, Michigan State University; KTM Industries**

Biodegradable, Chemically Modified Starch Polymers for Protective Foam

Packaging and Insulation Applications. 13

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

Highly Efficient, Practical Monohydrolysis of Symmetric Diesters 13

**Oakland University, Linda Schweitzer; Robert Reed,
University of Missouri; Earth Science Laboratories, Inc.**

EarthTec®: Green Water Treatment 15

**The Ohio State University, Department of Chemistry,
T. V. (Babu) RajanBabu**

*Ethylene in Catalytic Asymmetric Synthesis: A General Route to Profen
Drugs from Styrene Derivatives and a General Solution to the Exocyclic
Stereochemistry Problem* 14

Ozone International LLC

*Cleaning and Disinfecting with Ozone: Making Green Chemistry with
WhiteWater™ Ozone* 28

Pfizer Global Research and Development

A Green, Energy-Efficient, Biocatalytic Process to Manufacture Pregabalin 49

Plasmatrete North America Inc.; Ford Motor Company

*Openair™ Plasma Surface Treatment: Reducing Emissions of Volatile Organic
Compounds and Improving Environmentally Sensitive Paint Processes* 49

PPG Industries, Inc.

Green Logic™: Chitosan-Enhanced Paint Detackifier 50
Zircobond™ Pretreatment 50

***The Procter & Gamble Company; Cook Composites and
Polymers Company**

*Chempol®MPS Resins and Sefose® Sucrose Esters Enable High-Performance
Low-VOC Alkyd Paints and Coatings* 7

**RajanBabu, T. V. (Babu), Department of Chemistry, The Ohio
State University**

*Ethylene in Catalytic Asymmetric Synthesis: A General Route to Profen
Drugs from Styrene Derivatives and a General Solution to the Exocyclic
Stereochemistry Problem* 14

**Reed, Robert, University of Missouri; Linda Schweitzer,
Oakland University; Earth Science Laboratories, Inc.**

EarthTec®: Green Water Treatment 15

SABIC Innovative Plastics

*Chemical Conversion of Post-Consumer Recycled Polyethylene Terephthalate Waste
into Sustainable Valox iQ™ and Xenoy iQ™ Engineering Thermoplastic Products* . . . 51

SarTec Corporation; Arlin E. Gyberg, Augsburg College

The McGyan Process: A Green Synthetic Route for Biodiesel Production 10

**Savage, Phillip E., Chemical Engineering Department,
University of Michigan**

*Terephthalic Acid Synthesis at High Concentrations in High-Temperature
Liquid Water* 15

**Schweitzer, Linda, Oakland University; Robert Reed,
University of Missouri; Earth Science Laboratories, Inc.**

EarthTec®: Green Water Treatment 15

The Sherwin-Williams Company

<i>High-Solids Hybrid Sucrose Ester Polymer Technology</i>	52
<i>Waterborne Hybrid Cross-linking Dispersion Technology</i>	52

Solazyme, Inc.

<i>Renewable Oil Production from Algae as a Replacement for Petroleum-Based Products</i>	29
--	----

Stanford University, Department of Chemistry, Paul A. Wender

<i>Green Chemistry through Function-Oriented Synthesis, Step Economy, and Ideal Synthesis</i>	16
---	----

STERIS Corporation

<i>An Environmentally Friendly Alternative for Cleaning Surgical Instruments in Healthcare Facilities</i>	53
---	----

STERIS Corporation; Virox Technologies

<i>An Alternative to Aldehyde-Based Liquid Chemical Sterilants and High-Level Disinfectants for Reprocessing Heat-Sensitive, Semi-Critical Medical Instruments</i>	53
--	----

Sun, Xiuzhi Susan, Department of Grain Science and Industry and Director, Center for Biobased Polymers by Design, Kansas State University

<i>Green Process for Unfolding Soy Protein Polymers for Green Adhesives</i>	16
---	----

TDA Research, Inc.; Cytec Industries Inc.

<i>Replacement for Solvent-Based, Chromate-Containing Primer</i>	29
--	----

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

<i>Highly Efficient, Practical Monohydrolysis of Symmetric Diesters</i>	13
---	----

Thermphos USA Corp.

<i>Dequest® PB Carboxymethyl Inulin: A Versatile Scale Inhibitor Made from the Roots of Chicory</i>	54
---	----

Tremco Incorporated

<i>Vulkem 950NF: A Renewable, Polyol-Based, High-Solids, Low-Odor, Ultra-Low-VOC, "Neighbor-Friendly" Polyurethane Top Coat for Use in Vehicular, Pedestrian, and Specialty Applications</i>	55
--	----

U.S. Department of Energy, Argonne National Laboratory

<i>Diesel DeNOX Catalyst</i>	55
<i>Resin Wafer Technology</i>	56

University of California, Davis, Department of Chemistry, Mark Mascal

<i>High-Yield Conversion of Plant Biomass into a New Generation of Biofuels</i>	12
---	----

University of California, Los Angeles, Department of Chemical and Biomolecular Engineering, James C. Liao	
<i>Biosynthesis of Higher Alcohols from Renewable Carbon Sources</i>	10
University of California, Santa Barbara, Department of Chemistry and Biochemistry, Bruce H. Lipshutz, Zymes, LLC	
<i>Getting Organic Solvents Out of Organic Reactions</i>	11
University of California, Santa Barbara, Raminderjit (Sonam) Gill and Jessica Alvarez, Student Intern LabRATS	
<i>The University of California, Santa Barbara Green Chemistry Initiative</i>	9
University of Delaware, Affordable Composites from Renewable Resources (ACRES) Center for Composite Materials, Richard P. Wool	
<i>Biobased Polymers and Composites</i>	17
University of Iowa, Department of Chemistry, Leonard R. MacGillivray	
<i>Template-Controlled Reactivity in the Organic Solid State</i>	12
University of Michigan, Chemical Engineering Department, Phillip E. Savage	
<i>Terephthalic Acid Synthesis at High Concentrations in High-Temperature Liquid Water</i>	15
University of Missouri, Robert Reed; Oakland University, Linda Schweitzer; Earth Science Laboratories, Inc.	
<i>EarthTec®: Green Water Treatment</i>	15
University of South Alabama, Department of Chemistry, James Hillard Davis, Jr.	
<i>Liquid but Nonvolatile Sulfonic Acids and Amines: Greener Chemicals for Greening Processes</i>	9
VeruTEK Technologies, Inc.	
<i>Green Synthesis of Nanometal Catalysts and Plant Surfactant-Based, In Situ Chemical Oxidation for Sustainable Treatment and Remediation</i>	30
*Virent Energy Systems, Inc.	
<i>BioForming® Process: Catalytic Conversion of Plant Sugars into Liquid Hydrocarbon Fuels</i>	4
Virox Technologies; JohnsonDiversey, Inc.	
<i>Development of Sustainable Disinfectants</i>	46
Virox Technologies; STERIS Corporation	
<i>An Alternative to Aldehyde-Based Liquid Chemical Sterilants and High-Level Disinfectants for Reprocessing Heat-Sensitive, Semi-Critical Medical Instruments</i> . . .	53

Water Conservation Technology International, Inc.

Sustainable, Natural Green Chemistry for Cooling Water Treatment 31

Wender, Paul A., Department of Chemistry, Stanford University

Green Chemistry through Function-Oriented Synthesis, Step Economy, and Ideal Synthesis 16

Wool, Richard P., Affordable Composites from Renewable Resources (ACRES) Center for Composite Materials, University of Delaware

Biobased Polymers and Composites. 17

ZeaChem Inc.

Cellulose-Based Fuels and Intermediate Chemicals 31

Zep Inc.

Renewable-Resource Industrial Products 56

Zymes, LLC ; Bruce H. Lipshutz, Department of Chemistry and Biochemistry, University of California, Santa Barbara

Getting Organic Solvents Out of Organic Reactions 11



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