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The Presidential Green Chemistry Challenge Awards Program:

Summary of 2010 Award Entries and Recipients

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Introduction

Each year, chemists, engineers, and other scientists from across the United States nominate their technologies for a Presidential Green Chemistry Challenge Award. This prestigious award highlights and honors innovative green chemistry technologies, including cleaner processes; safer raw materials; and safer, better products. These awards recognize and promote the environmental and economic benefits of developing and using novel green chemistry.

The U.S. Environmental Protection Agency (EPA) celebrates this year's innovative, award-winning technologies selected from among scores of high-quality nominations. Each nomination must represent one or more recently developed chemistry technologies that prevent pollution through source reduction. Nominated technologies are also meant to succeed in the marketplace: each is expected to illustrate the technical feasibility, marketability, and profitability of green chemistry.

This is a special year – 2010 marks the 15th year of the Presidential Green Chemistry Challenge Awards. Throughout the 15 years of the program, EPA has received more than 1,300 nominations and presented awards to 77 winners. By recognizing groundbreaking scientific solutions to real-world environmental problems, the Presidential Green Chemistry Challenge has significantly reduced the hazards associated with designing, manufacturing, and using chemicals. Winning technologies alone are responsible for reducing the use or generation of more than 198 million pounds of hazardous chemicals, saving 21 billion gallons of water, and eliminating 57 million pounds of carbon dioxide releases to air. Collectively, all of the nominated technologies have produced far greater benefits.

This booklet summarizes entries submitted for the 2010 awards that fell within the scope of the program. An independent panel of technical experts convened by the American Chemical Society Green Chemistry Institute judged the entries for the 2010 awards. Judging criteria included health and environmental benefits, scientific innovation, and industrial applicability. Five of the nominated technologies were selected as winners and were nationally recognized on June 21, 2010, at an awards ceremony in Washington, D.C.

Further information about the Presidential Green Chemistry Challenge Awards and EPA's Green Chemistry Program is available at www.epa.gov/greenchemistry.

Note: The summaries provided in this document were obtained from the entries received for the 2010 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 nominations. 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

Recycling Carbon Dioxide to Biosynthesize Higher Alcohols

James C. Liao, Ph.D., Easel Biotechnologies, LLC and University of California, Los Angeles

Innovation and Benefits

Ethanol made by fermentation can be used as a fuel additive, but its use is limited by its low energy content. "Higher" alcohols (those with more than two carbons in the molecule) have higher energy content, but naturally occurring microorganisms do not produce them. Dr. James Liao has genetically engineered microorganisms to make higher alcohols from glucose or directly from carbon dioxide. His work makes renewable higher alcohols available for use as chemical building blocks or as fuel.

Higher alcohols, especially those with 3–8 carbon atoms, are useful as chemical feedstocks and transportation fuels. The efficient biosynthesis of these alcohols directly from carbon dioxide (CO_2) or indirectly from carbohydrates would reduce net carbon emissions. Unfortunately, native organisms do not synthesize these alcohols. Until now, none of these alcohols have been synthesized directly from CO_2, and alcohols above five carbons have never been synthesized in the biosphere.

Dr. Liao, an Easel Biotechnologies board member and professor at the University of California, Los Angeles (UCLA), has developed a microbial technology to produce alcohols with 3–8 carbon atoms from CO_2. His technology leverages the highly active amino acid biosynthetic pathway, diverting its 2-keto acid intermediates toward alcohols. With this technology, Professor Liao and his group have produced isobutanol from glucose in near-theoretical yields with high efficiency and specificity. They also transferred the pathway into a photosynthetic microorganism, *Synechococcus elongatus* PCC7942, which produces isobutyraldehyde and isobutanol directly from CO_2. The engineered strain produces isobutanol at a higher rate than those reported for ethanol, hydrogen, or lipid production by cyanobacteria or algae. This productivity is also higher than the current rate of ethanol production from corn. The technology shows promise for direct bioconversion of solar energy and CO_2 into chemical feedstocks.

Higher alcohols are also good fuels. As fuel substitutes, they have several advantages over ethanol, including higher energy density, lower hygroscopicity, and lower vapor pressure leading to better air quality. After excretion by the cells as aldehydes, the products are readily stripped from the bioreactor, avoiding toxicity to the microbes. Chemical catalysis then converts the harvested aldehydes to alcohols or other chemicals.

If 60 billion gallons of higher alcohols were used each year as chemical feedstocks and fuel (replacing 25 percent of gasoline), Dr. Liao's technology could eliminate about 500 million tons of CO_2 emissions or about 8.3 percent of the total U.S. CO_2 emissions. Easel Biotechnologies is commercializing the CO_2-to-fuels technology under exclusive license from UCLA.

Small Business Award

LS9, Inc.

Microbial Production of Renewable Petroleum™ Fuels and Chemicals

Innovation and Benefits

Industrial microbes usually make single substances, such as triglycerides like those in vegetable oil. Each single substance is then purified and converted into other chemicals, such as biodiesel fuel. LS9, Inc. has genetically engineered a variety of microorganisms to act like refineries. Each microbe makes a specific, final chemical product. Among these products is UltraClean™ diesel. This fuel, produced from biomass, eliminates the benzene, sulfur, and heavy metals found in petroleum-based diesel.

The renewable, scalable fuels and chemicals with the greatest potential for rapid and widespread adoption by consumers are those that are both cost-competitive with petroleum and compatible with the existing distribution and consumer infrastructure. LS9 has developed a platform technology to produce a wide variety of advanced biofuels and renewable chemicals cost-effectively by a simple, efficient, one-step fermentation process. LS9 has engineered established industrial microorganisms to convert fermentable sugars selectively to alkanes, olefins, fatty alcohols, or fatty esters, each in a single-unit operation. The process enables precise genetic control of the molecular composition and performance characteristics of each resulting fuel or chemical product. LS9's technology leverages the natural efficiency of microbial fatty acid metabolism to biosynthesize long hydrocarbon chains. It combines this with new biochemical pathways engineered into microorganisms to convert the long-chain intermediates into specific finished fuel and chemical products that are secreted by the cells. The products are immiscible with the aqueous fermentation medium and form a light organic phase that is both nontoxic to the whole-cell catalyst and easily recoverable by centrifugation. LS9 is actively developing the technology for the production of alkanes (diesel, jet fuel, gasoline), alcohols (surfactants), esters (biodiesel, chemical intermediates), olefins (lubricants, polymers), aldehydes (insulation, resins), and fatty acids (soaps, chemical intermediates). Specific product performance is enabled through the genetic control of each product's chain length, extent of saturation, and degree of branching. Unlike the competing biofuel processes, LS9's process does not require any metal catalysts.

LS9 has successfully scaled up its technology to produce UltraClean™ diesel at the pilot-plant level. UltraClean™ diesel meets or exceeds all of the ASTM 6751 specifications for on-road vehicle use. It eliminates the environmental pollutants benzene, sulfur, and the heavy metals found in petroleum-based diesel and will result in an 85 percent decrease in greenhouse gas (GHG) emissions according to the GREET model for life cycle analysis (LCA). Without subsidy, UltraClean Diesel™ will be competitive in the market with diesel from oil priced at $45–50 per barrel. LS9 is advancing toward commercial scale with its Renewable Petroleum™ facility, which will come on line in 2010. Initially, this facility will produce UltraClean™ diesel; other products will follow. LS9 has achieved some success in direct biomass-to-fuel conversion.

LS9 is applying this technology platform through a strategic partnership with Procter & Gamble to produce surfactants for consumer chemical products. These and other LS9 drop-in, renewable products are on target to facilitate broad environmental benefits through rapid product adoption. The efficiency, affordability, and product performance bodes well for the LS9 technology to become one of the keys to sustainable fuels.

Greener Synthetic Pathways Award

The Dow Chemical Company

BASF

Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide

Innovation and Benefits

Propylene oxide is one of the biggest volume industrial chemicals in the world. It is a chemical building block for a vast array of products including detergents, polyurethanes, de-icers, food additives, and personal care items. Its manufacture creates byproducts, including a significant amount of waste. Dow and BASF have jointly developed a new route to make propylene oxide with hydrogen peroxide that eliminates most of the waste and greatly reduces water and energy use.

Propylene oxide (PO) is among the top 30 largest-volume chemical intermediates produced in the world; its annual worldwide demand is estimated to be over 14 billion pounds. It is a key raw material for manufacturing a wide range of industrial and commercial products, including polyurethanes, propylene glycols, and glycol ethers, which are used in a diverse array of applications including automobiles, furniture, and personal care. Historically, manufacturing propylene oxide either produced significant volumes of coproducts or required recycling of organic intermediates. Traditional PO production uses chlorohydrin or one of a variety of organic peroxides, which lead to coproducts such as *t*-butyl alcohol, styrene monomer, or cumene. In each case, there is a substantial amount of coproduct and waste. Although most of the coproducts are recovered and sold, demand for these coproducts does not necessarily parallel the demand for PO, leading to imbalances in supply and demand.

Dow and BASF have developed the Hydrogen Peroxide to Propylene Oxide (HPPO) process, a new, innovative route to PO based on the reaction of hydrogen peroxide and propylene. It has high yields and produces only water as a coproduct. The Dow–BASF catalyst is a ZSM-5-type zeolite with channels of about 0.5 nm in diameter. In this catalyst, titanium replaces several percent of the silicon of the zeolite in a tetrahedral coordination environment. With this novel catalyst, the HPPO process is relatively straightforward. Propylene is epoxidized by hydrogen peroxide in a fixed-bed reactor at moderate temperature and pressure. The reaction occurs in the liquid phase in the presence of methanol as a solvent. The process is characterized by both high conversions of propylene and high selectivity for propylene oxide. Hydrogen peroxide is completely converted to product. In contrast with processes using organic peroxides, the HPPO process uses substantially less peroxide and eliminates the need to recycle peroxide. Production facilities are up to 25 percent cheaper to build because there is no need for equipment to collect and purify the coproduct.

The HPPO process also provides substantial environmental benefits. It reduces the production of wastewater by as much as 70–80 percent and the use of energy by 35 percent over traditional technologies. BASF performed an Eco-Efficiency Analysis of the various PO processes and found the HPPO process is cheaper and has substantially lower negative impacts than alternative processes. The first commercial process based on this technology was successfully commissioned in 2008 at the BASF production facility in Antwerp, Belgium. A second PO plant based on this technology is scheduled to begin production in Map Ta Phut, Thailand in 2011.

Greener Reaction Conditions Award

Merck & Co., Inc.

Codexis, Inc.

Greener Manufacturing of Sitagliptin Enabled by an Evolved Transaminase

Innovation and Benefits

Merck and Codexis have developed a second-generation green synthesis of sitagliptin, the active ingredient in Januvia™, a treatment for type 2 diabetes. This collaboration has lead to an enzymatic process that reduces waste, improves yield and safety, and eliminates the need for a metal catalyst. Early research suggests that the new biocatalysts will be useful in manufacturing other drugs as well.

Sitagliptin is the active ingredient in Januvia®, an important treatment for type 2 diabetes that is in high demand worldwide. The current manufacturing process includes a novel and efficient asymmetric catalytic hydrogenation of an unprotected enamine. The process has some inherent liabilities however: inadequate stereoselectivity requires a crystallization step, and high-pressure hydrogenation (at 250 psi) requires expensive, specialized manufacturing equipment, and a rhodium catalyst.

Merck and Codexis were independently aware that transaminase enzymes could, in principle, improve the manufacturing process for sitagliptin by converting a precursor ketone directly to the desired chiral amine. Merck's tests of available transaminases failed to identify an enzyme with any detectable activity on the sitagliptin ketone.

Collaboration between Merck and Codexis has lead to an improved, greener route for the manufacture of sitagliptin. Starting from an *R*-selective transaminase with some slight activity on a smaller, truncated methyl ketone analog of the sitagliptin ketone, Codexis evolved a biocatalyst to enable a new manufacturing process to supplant the hydrogenation route. The evolved transaminase had a compounded improvement in biocatalytic activity of over 25,000-fold, with no detectable amounts of the undesired, *S*-enantiomer of sitagliptin being formed. The streamlined, enzymatic process eliminates the high-pressure hydrogenation, all metals (rhodium and iron), and the wasteful chiral purification step. The benefits of the new process include a 56 percent improvement in productivity with the existing equipment, a 10–13 percent overall increase in yield, and a 19 percent reduction in overall waste generation.

Evolved transaminases are proving to be a general tool for the synthesis of *R*-amines directly from ketones, constituting an important new green methodology, one of the key transformations identified by the American Chemical Society Green Chemistry Institute's Pharmaceutical Roundtable. Merck and Codexis have used scientific innovation to benefit the environment, meet the manufacturing demands of an important drug in growing demand, and potentially enable a broad class of chemistry. During 2009, Merck scaled up the new process to pilot scale. Plans to commercialize this technology are moving forward.

Clarke

Natular™ Larvicide: Adapting Spinosad for Next-Generation Mosquito Control

Innovation and Benefits

Spinosad is an environmentally safe pesticide but is not stable in water and so therefore cannot be used to control mosquito larvae. Clarke has developed a way to encapsulate spinosad in a plaster matrix, allowing it to be released slowly in water and provide effective control of mosquito larvae. This pesticide, Natular™, replaces organophosphates and other traditional, toxic pesticides and is approved for use in certified organic farming.

Spinosad, a 1999 Presidential Green Chemistry Challenge Award winner, is an effective insecticide with excellent control in many terrestrial applications. Its instability in water, however, renders it ineffective for extended application in aquatic environments.

Clarke has created a "sequential" plaster matrix that protects the spinosad molecule from water and releases it slowly, allowing extended performance of spinosad formulations for up to 180 days. This matrix is insoluble calcium sulfate hemihydrate plaster and water-soluble polyethylene glycol (PEG) binders fine-tuned for varying durations of insecticide release. The PEG dissolves slowly, exposing the spinosad and calcium sulfate to water. The calcium sulfate takes up the water to form the mineral gypsum and releases spinosad. Clarke formulated the plaster matrix for Natular™ larvicide entirely with approved pesticide inerts that also meet the U.S. Department of Agriculture's (USDA's) National Organics Standard (NOS). The resulting formulations of Natular™ larvicide provide excellent control of mosquito larvae in a range of aquatic environments from catch basins to salt marshes. Clarke manufactures the dustless, extended-release tablets with a solventless process that increases the environmental benefits.

Natular™ larvicide is effective at application rates 2–10-fold lower than traditional synthetic larvicides. It is 15-fold less toxic than the organophosphate alternative, does not persist in the environment, and is not toxic to wildlife. Its manufacture eliminates hazardous materials and processes. Natular™ is the first new, chemical larvicide for mosquito control in decades; it meets the highest standards for environmental stewardship and offers a new choice for Integrated Pest Management (IPM). It is especially useful in environments with intermittent water, such as tidal pools and flood plains. These intermittently wet areas provide excellent, short-term pools for mosquito breeding; the transient nature of the pooling makes traditional mosquito control difficult. The Natular™ larvicide can be applied in dry or wet conditions, however, and only releases the active ingredient when water is present.

The benefits of using Clarke's new formulations extend beyond the reduced environmental impact. Traditional larvicides require up to three applications per season. In contrast, Natular™ tablets require just one or two applications.

Altogether, Natular™ larvicide demonstrates green chemistry innovation through the development and design of its controlled-release matrix. With the projected adoption of Natular™ larvicide by local and federal agencies, Clarke anticipates a shift in the mosquito-borne disease management industry toward reduced overall synthetic load in the environment and improved health and quality of life in treated areas. In 2009, Clarke began commercial-scale production of Natular™ larvicide in the United States. This patent-pending formulation has been accepted for use domestically and abroad. Clarke also expects its slow-release matrix will enable controlled release of other active ingredients, including herbicides and veterinary drugs.

Entries from Academia

Template-Controlled Reactivity in the Organic Solid State

Professor Leonard R. MacGillivray, Department of Chemistry, University of Iowa; University of Iowa Research Foundation

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

Professor MacGillivray has developed a general method to control organic chemical reactivity in the solid state. He uses small organic molecules as templates to assemble olefins into position for chemical reactions. The templates, not long-range crystal packing, control the solid-state arrangements of the olefins. The templates assemble the olefins via hydrogen bonds within stoichiometric solids known as co-crystals. The olefins then undergo intermolecular [2+2] photodimerizations. This pioneering work has the potential to open new avenues of organic synthesis because the solid-state medium allows molecules to react in geometries and orientations that can be inaccessible in solution.

Professor MacGillivray has used his solid-state method to synthesize molecules known as ladderanes with regiospecificity, 100-percent yield, and no byproducts. Ladderane structures are building blocks for many natural products that previously had presented a major synthetic challenge for chemists. Recently, Professor MacGillivray received a patent for his solid-state preparation of ladderanes; he and the University of Iowa Research Foundation are working toward commercialization.

In 2008, Professor MacGillivray discovered that the co-crystals used for his solid-state reactions can form via solvent-free, mortar-and-pestle dry grinding. Previously, co-crystal formation had required solvent. In addition to synthesizing unique organic molecules, he has used his methods to synthesize ligands in inorganic chemistry. Specifically, his molecules can be used as building blocks for self-assembled metal–organic architectures and porous materials with structures akin to zeolites. His work opens the solid state as a general solvent-free medium in synthetic organic chemistry with applications in inorganic chemistry and materials science. Professor MacGillivray received the highly prestigious Arthur C. Cope Scholar Award of the American Chemical Society in 2007 in recognition of his solid-state methodology.

High-Yield Conversion of Biomass into a New Generation of Biofuels and Value-Added Products

Professor Mark Mascal, Department of Chemistry, University of California, Davis; Nevada Institute for Renewable Energy Commercialization

The prevailing, worldwide petroleum-based economy is making way for alternative technologies. This transformation is creating an extraordinary need for bioenergy research. Consequently, researchers have developed several schemes to exploit lignocellulose, the most abundant organic material on the planet. Although these schemes vary considerably, each one has the basic objectives of cleaving the glycan into its monosaccharide components and deriving useful products from them efficiently and inexpensively. Researchers are continually developing new schemes, but the most successful will be those that produce the highest yields, minimize capital and operating expenses, and allow the most feedstock flexibility.

In 2008, Professor Mascal described a process to convert cellulose into a mixture of 5-(chloromethyl)furfural (CMF) and three minor furfural-derived products in a remarkable 85-percent overall yield. The method involved acidic digestion of cellulose in a biphasic aqueous–solvent reactor in which the organic products, once formed, could be separated from the acid before they decomposed. Subsequently, Professor Mascal discovered that his method works equally well on raw biomass: it produces not only CMF in high yield from the cellulose of biomass, but also furfural itself from the C_5-sugar (hemicellulose) fraction. Thus, it uses all of the carbohydrate of biomass.

Recently, Professor Mascal and his group have refined their process so that the only products they obtain from cellulose are CMF (84 percent) and levulinic acid (LA) (5 percent) in an overall 89-percent yield. From sucrose their process gives CMF and LA in a combined 95-percent yield. Their method also works well on biodiesel feedstocks to produce a hybrid lipidic–cellulosic biodiesel that increases the yield of fuel from oil seeds by up to 25 percent. No other known process gives simple organic products from cellulose in comparable yields. Professor Mascal is currently partnering with an experienced biofuels developer to commission a 2 million gallon per year production facility by 2011.

Professor Satomi Niwayama, Department of Chemistry and Biochemistry, Texas Tech University; Wako Chemicals USA, Inc.; Kishida Chemical Co., Ltd.

Highly Efficient and Practical Monohydrolysis of Symmetric Diesters

Water is among the most environmentally friendly solvents because it generates no hazards during chemical conversion processes. Desymmetrization of symmetric compounds is one of the most cost-effective synthetic conversions 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.

Monohydrolysis of symmetric diesters produces half-esters, which are highly versatile building blocks in organic synthesis and have considerable commercial value. They are frequently applied to the synthesis of polymers, dendrimers, and hyper-branched polymers. 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 reactivity. Ring-opening reactions of cyclic acid anhydrides require hazardous organic solvents.

Professor Niwayama pioneered water-mediated desymmetrization and has been developing monohydrolysis of symmetric diesters to form half-esters 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 with or without a small amount of a cosolvent such as THF at 0 °C. The reaction produces pure half-esters in high to near-quantitative yields without producing dirty waste and without hazardous organic solvents. This reaction, which is anticipated to contribute significantly to green chemistry and be useful in both industry and academia, has been licensed by Wako Chemicals USA and Kishida Chemical Company. Several half-esters produced by this reaction have been commercialized.

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

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

Terephthalic acid (TPA) is a monomer used to produce polyethylene terephthalate (PET), 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 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 45,000 pounds of methyl bromide annually.) Water is a byproduct of terephthalic acid synthesis. Separating the water byproduct from the acetic acid solvent for recycling requires an expensive, energy-intensive distillation. Further, acetic acid oxidizes during the reaction so that approximately 4 billion pounds of makeup acetic acid are required each year. Manufacturing this makeup 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 require make-up acetic acid. Because water is both the byproduct and the 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 his greener reaction conditions would accommodate the high concentrations needed for a commercial process. The University of Michigan has filed a provisional patent application for this technology.

Green Process of Unfolding Soy Protein Polymers for Green Adhesives

Professor Xiuzhi Susan Sun, Department of Grain Science and Industry, Kansas State University; SoyResin, LLC

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, the 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. Hydrophobic regions are often buried inside the complicated protein molecule, however.

Professor Sun's technology unfolds protein molecules with 0.5–5 percent nonhazardous agents such as urea, detergents, organic–inorganic salts, and pH-adjustment agents such as sodium hydroxide (NaOH) and hyrdrochloric acid (HCl). As the proteins unfold, some of their covalent and hydrogen bonds break and form individual polypeptides. Because hydrophobic groups are now exposed on their surfaces, the resulting polypeptides become surface-active and interact with other hydrophobic polymers, cross-linking agents, and chemicals. Potential applications include adhesives; surfactants; coatings; medical materials such as tissue engineering, drug delivery, and pharmaceuticals; thickeners and binders for food and animal feed; and cosmetic products. This technology makes high-value products from the coproducts of biofuel production and, thus, can have great impacts on bioenergy and the environment. It will replace at least 6 billion pounds of hazardous materials including adhesives based on formaldehyde, vinyl acetate, isocyanine, and acrylic acid. 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; others are evaluating samples for a variety of uses.

Professor Yi Tang, Department of Chemical and Biomolecular Engineering, University of California, Los Angeles

An Efficient, Biocatalytic Process for the Semisynthesis of Simvastatin

Statins are important drugs for treating cardiovascular diseases. Lovastatin, a secondary metabolite produced by *Aspergillus terreus,* was the first FDA-approved statin. Simvastatin is an important semisynthetic derivative of lovastatin; it has two methyl groups (not one) at the C2′ position of the side chain. Simvastatin has become the second-highest-selling generic drug since 2007 when it went off-patent as Merck's Zocor®. In 2008, simvastatin had sales of approximately $2 billion.

Adding the methyl group to convert lovastatin into simvastatin requires a multistep chemical synthesis that includes protecting then deprotecting other functionalities in the lovastatin molecule. Two main routes have been described. In the first route, lovastatin is hydrolyzed to the triol, monacolin J, followed by protection by selective silylation, esterification with dimethyl butyryl chloride, and deprotection. The other route involves protection of the carboxylic acid and alcohol functionalities, followed by methylation of C2′ with methyl iodide and deprotection. Both routes are inefficient: they have less than 70 percent overall yield despite considerable optimization. Both are mass-intensive as a result of protection and deprotection. Variations on these routes have been patented, but none have overcome the limitations of the current multistep process.

Professor Tang and his group have developed a route that circumvents protection and deprotection, is more efficient, and results in greater atom economy, reduced waste, and overall less hazardous reaction conditions. First, they cloned and identified LovD, a natural acyltransferase in *Aspergillus terreus* that is involved in the synthesis of lovastatin and can accept low-cost, non-natural acyl donors. They recognized that LovD might be a type of simvastatin synthase and a starting point for developing a biocatalytic process. They then evolved this enzyme toward commercial utility. Codexis has licensed the technology, engineered the enzyme further, and optimized the process to accomplish pilot-scale simvastatin manufacture in 100 kilogram batches. Commercial-scale manufacturing is planned in 2010.

Professor Robert M. Waymouth, Department of Chemistry, Stanford University; Dr. James L. Hedrick, IBM Almaden Research Center

Organic Catalysis: A Broadly Useful and Environmentally Benign Strategy to Synthetic Polymer Materials

The discovery of highly active, environmentally benign, catalytic processes is a central goal of green chemistry. The team of Dr. Hedrick and Professor Waymouth has developed a broad class of highly active, environmentally benign organic catalysts for the synthesis of biodegradable and biocompatible plastics. Their technology applies metal-free, organic catalysts to the synthesis and recycling of polyesters. The team has discovered several new families of organic catalysts that rival or exceed metal-based alternatives for polyester synthesis in both activity and selectivity. These new synthetic strategies provide an environmentally attractive, atom-economical, low-energy alternative to traditional metal-catalyzed processes. This technology includes organocatalytic approaches to a variety of polymerization techniques such as ring-opening, anionic, zwitterionic, group transfer, and condensation polymerization. Their mechanistic and theoretical investigations have provided new insights into the diversity of mechanistic pathways for organocatalytic polymerization reactions and opportunities for the synthesis of well-defined macromolecular architectures. The novel mechanisms of enchainment of their catalysts provide access to polymer architectures that are difficult to access by conventional approaches.

Their monomer feedstocks focus primarily on those from renewable resources such as lactides derived from biomass, but also include those from petrochemicals. Dr. Hedrick and Professor Waymouth have designed and implemented organic catalysts to depolymerize petrochemical-based polymers such as poly(ethylene terephthalate) (PET) quantitatively, allowing a bottle-to-bottle recycling of PET to mitigate the millions of pounds of PET that plague landfills. Their catalysts are tolerant to a wide variety of functional groups, enabling them to synthesize well-defined biocompatible polymers for biomedical applications. Because these catalysts do not remain bound to polymer chains, they are effective at low concentrations. These results, coupled with cytotoxicity measurements in biomedical applications, highlight the environmental and human health benefits of their approach. The team has received eight patents on this work; since 2002, their work has received over 1,000 citations in the scientific literature.

Entries from Small Businesses

Safer, Sustainable, Biodegradable, Solid-State Chemistry for Treating Cooling Water Systems

APTech Group, Inc.

Scale and corrosion inhibitors for liquid cooling water typically contain 10–15 percent active ingredients in an aqueous solution. Because many of the active ingredients are insoluble at neutral pH at these concentrations, sodium hydroxide (NaOH) is added to increase the pH and stabilize the solution. Typical formulations contain 10–30 percent NaOH.

APTech Group has developed chemistry so that only the active ingredients are mixed, heated, filled into recyclable containers, cooled, and allowed to cure, resulting in a unique, noncorrosive, solid-state concentrate. At the point of use, the solid-state product is reconstituted with system makeup water into a dilute solution (approximately 0.5 percent or less). NaOH is not needed because the low concentrations of the active ingredients in the dilute solution are below the solubility limits for these chemicals.

The solid-state product is not a compressed series of raw materials or physical mixtures, but a true homogenous solid state comprised of both liquids and powders blended in a proprietary process. When made into solution on demand, the product contains the same reproducible ratio of active ingredients needed to prevent scale and corrosion in water systems. This technology not only eliminates the discharge of NaOH into wastewater streams but also eliminates the potential for spills of this corrosive chemical. At present sales levels, this technology is eliminating the use of almost 280,000 pounds of NaOH each year. It is also saving 462,000 gallons of production water and 660,000 gallons of rinse water annually.

APTech Group has recently improved its technology so that its products consist of totally biodegradable materials. Potentially, this could eliminate the 106 million pounds per year of non-biodegradable materials. Finally, new energy-efficient eductor dosing systems can reduce energy consumption by 90 percent over conventional pumping systems. APTech Group has filed a patent for its eductor system.

HCR-188C1: An All-New, High-Efficiency Hydrocarbon Refrigerant with No Impact on Global Warming or the Ozone Layer

A.S. Trust & Holdings, Inc.

Chlorofluorocarbons (CFCs) have been used as refrigerants in air conditioners and refrigerators since the 1930s. Although CFCs have the advantages of incombustibility, high stability, and low toxicity, they contribute heavily to ozone-layer depletion, languishing as chlorine atoms in the stratosphere for up to a century. As a result, the production and use of CFCs have been virtually abolished. CFCs have been systematically replaced by various hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Although HCFCs and HFCs are less destructive to the ozone layer, they are powerful greenhouse gases with their own environmental risks.

A.S. Trust & Holdings has developed HCR-188C1, a substitute hydrocarbon (HC) formulation that has been independently shown to have zero ozone depletion potential (ODP) and zero global warming potential (GWP). HCR-188C1 is a proprietary blend made strictly from naturally occurring substances approved for common use and available from any gas manufacturer: propane, butane, isobutene, and ethane. This blend can be used independently of CFCs, HFCs, and HCFCs. It cools so effectively that the mass of HCR-188C1 needed in a refrigerator or automotive air-conditioning system is only one-quarter that needed for CFC R-12 or the high-GWP formula, HFC R-134a. HCR-188C1 is the only approved alternative refrigerant that can substitute in systems designed for both CFC R-12 and HFC R-134a.

HCR-188C1 also features major safety improvements over other HCs, including reduced charge rates. It solves the problem of decomposition upon leakage that causes HFCs to become less efficient and require more frequent replacement. The higher molecular weight of HCR-188C1 makes it less apt to leak through joints or o-rings; HCR-188C1 also retains its cooling properties longer, which extends the lifetimes of units that run on it. A.S. Trust has been successfully using its original HCR-188C formulation for automotive and refrigerator cooling for more than ten years. The company launched HCR-188C1 in the summer of 2009.

BCR Environmental LLC; SABIC Innovative Plastics

Recovering and Using a Formerly Incinerated Sodium Nitrite Waste Stream to Disinfect and Stabilize Municipal Biosolids

Municipal wastewater treatment plants use biological processes to break down human waste. Sewage sludge, the residue left after biological treatment, contains innumerable pathogens that can harm humans, animals, and the environment. The treatment and disposal of sewage sludge has become an increasing problem. Municipal landfill space is limited; alternatively, applying sludge to land may restrict the land use for years, depending on how the sludge was treated.

BCR Environmental developed its Neutralizer® process as an effective, safe, verifiable, and economical solution to disinfect and stabilize municipal sludge, making it safe for use as a fertilizer. The Neutralizer® process destroys the pathogens in sewage sludge and stabilizes the sludge so that it does not attract vectors. This process generates its two principal chemicals, chlorine dioxide and nitrous acid, onsite at the wastewater treatment plant. During the process, sludge at up to 4-percent solids is treated with chlorine dioxide. Next, sodium nitrite and an acid are added; at pH 2.3, the sodium nitrite is converted to nitrous acid, which destroys any remaining pathogens and their eggs. Finally, the pH is returned to near-neutral and the treated sludge is dewatered for use as a fertilizer.

BCR collaborated with SABIC Innovative Plastics to use a waste stream from SABIC's production of thermoplastic resin as the source of sodium nitrite for the Neutralizer® process. The resulting commercially viable, biologically safe fertilizer frees up landfill space, offsets the production of commercial fertilizer, reduces the production of greenhouse gasses, and saves the energy required to incinerate millions of gallons of SABIC's nitrite-bearing waste stream. In December 2009, EPA notified BCR that it had successfully completed the process for approval of its Neutralizer® Process, the first process to receive this approval in the last sixteen years.

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 water solubility. Indeed, approximately 40 percent of all new drug candidates and 70 percent of new anticancer drug candidates in development are not well-absorbed orally, principally due to low water solubility. These candidates frequently have low oral bioavailability and require high doses to achieve therapeutic effects.

Bend Research has developed a novel, green, drug-delivery technology using hydroxypropyl methylcellulose acetate succinate (HPMCAS), a low-toxicity, renewable material. Spray-dried dispersions (SDDs) of low-solubility drugs and HPMCAS dissolve rapidly. They disperse in the body to enhance the bioavailability of low-solubility drugs by 10-fold or more and to reduce the dose of active pharmaceutical ingredients required for therapeutic results. Currently, the pharmaceutical industry generates an estimated 25–100 kilograms of waste per kilogram of product. If all low-solubility drugs were formulated as HPMCAS SDDs, the enhanced bioavailability could eliminate more than 27,000 tons of toxic pharmaceutical waste annually.

The HPMCAS SDD manufacturing process uses green chemistry and renewable materials. Typically, only the drug and HPMCAS are dissolved in an organic solvent, such as acetone, methanol, or mixtures of these with water. The dispersion is spray-dried and the solvent is recovered for reuse.

HPMCAS is an amphiphilic polymer. Its hydrophobic regions interact with low-solubility drug molecules and its hydrophilic regions allow the drug–HPMCAS structures to form stable colloids in aqueous solution. HPMCAS forms amorphous dispersions with a broad range of structurally diverse low-solubility drugs for use in solid, oral dosage forms. Bend's technology can enable the development of many promising drug candidates that would otherwise be halted due to low solubility. Over 400 candidate drug compounds have been successfully formulated as HPMCAS SDDs; 28 have advanced to human clinical testing, including one to Phase 3. In 2007, Bend constructed a $90 million commercial SDD production facility.

Supercritical–Solid Catalyst Reaction Process for Converting Waste Fats, Oils, and Greases into Premium Biodiesel

BioFuelBox, Inc.

BioFuelBox has developed and successfully operated a process for continuous-flow production of ASTM-quality biodiesel without using toxic consumable catalysts or post-reaction purification reagents. The technology, patented by Idaho National Laboratory and licensed by BioFuelBox, uses heat and pressure in a closed system with heterogeneous catalysis and nontoxic gaseous cosolvents at supercritical conditions. The simplistic combination of these factors allows the use of historically unsuitable lipid feedstocks, including those containing microbial degradation products, heavy metals, organic sulfur, extreme fatty acid levels, and water, to produce 100-percent biodiesel (B100). The continuous-flow supercritical–solid catalyst (NovoStream™) process does not require added acid or base catalyst or the subsequent neutralization and water-washing steps typical of traditional biodiesel production.

By implementing this technology at its American Falls, Idaho facility over the past year, BioFuelBox has demonstrated the feasibility of converting over 10,000 liters per day of previously landfilled lipid waste (such as grease trap sludge) to quality, consumer-ready methyl ester fuels in high yields. Further, the NovoStream™ process makes fuel without the significant chemical waste and massive water use that are typical of traditional biofuel synthetic processes.

The BioFuelBox technology reduces environmental impacts not only by the chemistry involved, but also by using the lowest grades of municipal and industrial waste as feedstocks. These materials, with volumes of nearly 4 billion gallons annually in the United States alone, are currently destined for disposal in landfills, where they subsequently undergo microbial degradation to form potent greenhouse gases. The patented technology has proven successful in the energy-efficient, rapid conversion of these wastes to fuels. The benefits include eliminating this portion of our nation's waste burden as well as reducing the use of food-oil seeds for non-food uses. In August 2009, BioFuelBox produced 50,000 gallons of B100 biodiesel fuel.

Chemguard Ltd.

Elimination of Perfluorinated Alkyl Surfactants from Fire-Fighting Foams

Traditional fire-fighting foams for use on Class B (i.e., flammable liquid) fires, known as Aqueous Film-Forming Foams (AFFFs), typically contain perfluorinated alkyl surfactants, which extinguish fires quickly and resist re-ignition. Foams are used extensively in a wide variety of fire-fighting applications, including fixed systems (fuel loading docks, aircraft hangers, fuel storage tanks, etc.) and hand-line applications (municipal fire fighting trucks, airport emergency response, etc.). In general, fire-fighting foams are applied to quickly extinguish an ongoing fuel fire and to suppress re-ignition. Water alone cannot accomplish this.

When possible, containment systems capture residual foam liquid to prevent its release. Often, however, foam is applied to an unignited fuel spill as a safety precaution to prevent a flash fire while rescue workers perform their duties in and near the flammable fuel. In many cases, it is not feasible to contain the foam once applied. It is well-known that perfluorinated alkyl chains used in AFFFs are persistent in nature. There is an ongoing debate as to the human health and environmental effects of such chemicals released into the environment during normal use.

Chemguard developed ECOGUARD and its principle surfactant component in response to market requests for an organofluorine-free, alternative AFFF. ECOGUARD uses a novel hydrocarbon polymer surfactant (Chemguard HS-100) to substitute for and eliminate perfluorinated alkyl surfactants. The convergent, three-step synthesis of HS-100 has no byproducts and produces only water from the condensation polymerization. Because the properties of HS-100 eliminate the need for polysaccharide thickeners, the ECOGUARD formulation does not require a biocide. ECOGUARD is readily biodegradable and has a "low concern" for toxicity. ECOGUARD is registered by Underwriters Laboratories (UL) for hand-line operations and for use in sprinkler systems. Among organofluorine-free foams, only ECOGUARD has passed the UL sprinkler test. Chemguard was recently awarded two patents related to its organofluorine-free fire-fighting foam formulations.

Commercial Fluid Power LLC

Elimination of Hexavalent Chromium from Hydraulic and Pneumatic Tubing

The fluid power market relies heavily on chrome-plated tubes to produce pneumatic and hydraulic cylinders. Chrome plating provides an excellent wear surface, great lubricity, and good corrosion resistance; it is economical, time-tested, and readily available. The plating process is problematic. Plating produces a mist containing hexavalent chromium (Cr(VI)) ions that are carcinogenic. Although most large chrome-plating facilities currently meet or exceed EPA, OSHA, and other government standards for air quality, disposal, and containment of waste, the trend toward tighter controls will continue. Stringent regulations will continue to drive up the cost of chrome plating.

Commercial Fluid Power is taking steps to reduce the use of industrial hard chrome or engineered chrome in the fluid power market. The company is developing and marketing Nitro-tuff tubes as safe, environmentally friendly replacements 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-Fe_3N) 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 $Fe_3NO_{3\text{-}4}$. The iron nitride layer is the basis for the steel's extraordinary wear and corrosion resistance. Advances in mechanical properties, size, and finish control now allow Nitro-tuff tubes to substitute for chrome-plated tubes without loss of quality or strength. These efforts are reducing the use of hexavalent chromium and its release into the environment.

In conjunction with MACSTEEL's NitroSteel Division, Commercial Fluid Power continues to strive to bring an eco-friendly, cost-effective solution to the fluid power market. Recent research, development, and testing have overcome past challenges and opened new markets for Nitro-tuff tubes and bars. The journey for safer, more environmentally friendly replacement products at Commercial Fluid Power is ongoing. During 2009, Commercial Fluid Power developed a process for nitriding stainless steel.

Corrosion Control with a Greener Pathway

Cortec Corporation

Several years ago, a survey commissioned by the Federal government estimated the cost of corrosion in the United States at $275 billion annually. Corrosion of metals is a natural process during which metals oxidize. Selected chemicals can prevent, control, and slow down the corrosion of metals. Traditional chemicals used for corrosion control include cyclohexyl ammonium benzoate and other amine salts.

Cortec Corporation (derived from <u>cor</u>rosion <u>tec</u>hnology) began to evaluate sugar beet glucoheptonate as an anti-icing road additive in 1994 when electrochemical screening indicated it could prevent metal corrosion in salt water. Cortec hypothesized that gluconic acid derivatives could protect rebar in concrete from corrosion; after tests were successful, the company began to develop this product. Cortec now sells eleven corrosion-control products based on natural oils, six based on gluconates, one based on soy protein, and three films 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 by salt.

An independent study by American Engineering Testing concluded that MCI 2005, a product derived from gluconates, delayed the onset of corrosion in steel embedded in concrete beams; when corrosion developed, MCI 2005 reduced the corrosion current and the extent of corrosion. The study involved 56 cycles of 3-percent sodium chloride (NaCl) ponding, drying the concrete beams for two weeks, and repeating the 3-percent NaCl ponding. The test measured corrosion by electrochemical measurements on the embedded rebar in the concrete blocks midway through each cycle.

Cortec has been awarded six patents covering the use of gluconates to protect rebar in concrete and has been successful in selling these products worldwide. In 2008, sales of these products were 6 percent of Cortec's total sales; this figure increased to over 7 percent in 2009.

Safer, Less Toxic, Sustained Release Chemistry: Green Water Treatment with Smart Release® Technology

Dober Chemical Corporation

Smart Release® Technology is a patented, controlled-release coating process for chemistries used to treat water in cooling towers to prevent corrosion, scale, and fouling. It takes advantage of existing nontoxic, water-based suspension chemistries that are free of volatile organic compounds (VOCs) and creates a semipermeable membrane coating that can be used to control the release of neutralized water-treatment chemistries. The polymeric coating includes poly(vinyl acetate), vinyl versatate, and others. Smart Release® Technology has demonstrated that it can improve cooling tower efficiency; this promotes more reliable cooling and saves energy.

Because the solid, Smart Release® product contains 95-percent active ingredients compared with 10-percent active ingredients for liquid products, Smart Release® requires less packaging and shipping, which reduces its carbon footprint by 74 percent. It reduces energy consumption during application because it uses a feeder made of recycled material that has no moving parts, uses no energy, and requires no maintenance. Smart Release® provides safer handling because workers handle tablets with an inert outer coating that prevents contact with active chemistry. Primarily because it is a pH-neutral solid, the active Smart Release® chemistry is less toxic than competing liquid products. Smart Release® Technology also reduces accident potential because solids are less prone to spills than are liquids.

Smart Release® has applications in other aqueous treatment applications including potable water, biocides, biodispersants, and reverse osmosis membranes. Cool-N-Save®, Dober's recent retail product line, provides safe, effective precooling water treatment for both light industrial and private cooling units, permitting maintenance-free precooling. This technology has been shown to reduce air conditioning costs by as much as 30 percent with a corresponding reduction in energy consumption. A case study showed reductions of 15,000–50,000 kWh per month in light industrial applications. In 2009, Dober sold more than 40,000 pounds of Smart Release® Technology for industrial cooling towers, which eliminated 1.5 million metric tons of carbon dioxide (CO_2) releases.

FRX Polymers Inc.

Green Chemistry to Replace Bromine-Based Flame Retardants

Flame-retardant materials are a legal requirement globally for many plastics in electrical, building, construction, fiber, and textile applications. Flame-retardant plastics and additives comprise a worldwide materials market of over $15 billion with annual growth rates of 5–6 percent. Over 60 percent of all current plastic formulations include a class of flame-retardant additives known as brominated hydrocarbons. This popular class of flame retardants is, however, being shown to have severe, undesirable effects including persistence in the environment, bioaccumulation, and toxicity in rodent studies. In addition, the burning or thermal disposal of these additives can result in highly toxic dioxins and furans. These problems combine to place great pressure on companies to eliminate brominated agents as flame retardants.

FRX Polymers has developed green chemistry that allows diphenyl methyl phosphonate to polymerize effectively with an aromatic diol into either an oligomer or polymer with a phosphorus content of greater than 10 percent. This unique polymer has the highest limiting oxygen index measured for a thermoplastic material. FRX Polymers has also developed a low-cost, green synthesis for the diphenyl methyl phosphonate monomer. Yields from both the monomer and polymer processes are essentially quantitative. The phenol coproduct of polymerization is reused, so that little or no waste (less than 5 percent) is generated from the production of FRX polymers and copolymers. Eliminating bromine in favor of phosphorus in flame-retardant additives is expected to allow greater recovery and recyclability of plastics after use.

FRX Polymers is currently scaling up its synthesis of this material and plans to reach 1,000 metric tons per year by the end of 2010. Customers have reported favorable results in several applications including biobased polymers in carpeting, transparent flame-retardant lenses in LED lighting, electrical connectors and switches, and electronic and electrical housings. To date, FRX Polymers has commercialized applications for two customers.

Genomatica

Sustainable Chemicals from Renewable Resources: A Breakthrough for Biomanufacturing

Genomatica develops and commercializes novel biomanufacturing processes to produce industrial chemicals that impact all major industry sectors. The company produces sustainable chemicals through proprietary technology that transforms the way in which natural processes can be used to convert low-cost, renewable feedstocks into high-value chemicals. It defines sustainable chemicals as those that are designed and manufactured using efficient, effective, safe, and more environmentally benign raw materials and processes. Petrochemical processes generally are not sustainable because they are energy- and capital-intensive. They also use nonrenewable, hydrocarbon-based raw materials and solvents that are often toxic. Finally, they release large amounts of harmful waste and greenhouse gases.

Genomatica's breakthrough process uses an engineered microorganism (*E. coli*) and 100-percent-renewable materials (i.e., sugar and water) in an anaerobic fermentation to produce 1,4-butanediol (BDO), a large-volume chemical used in many polymer applications. Genomatica's technology platform combines computational modeling and design with experimental engineering of microorganisms and overall processes. Genomatica used proprietary metabolic models and simulation algorithms to test all possible pathways to produce BDO from sugar inside microorganisms. It selected optimal paths and implemented them in the laboratory to produce a microorganism and fermentation process for BDO.

Compared to petroleum-based BDO processes, this new bio-BDO process will produce less waste and lower emissions, use less energy, and reduce per-unit capital investment. A preliminary life cycle analysis (LCA) indicates that Genomatica's process to convert sucrose to BDO will require at least 59-percent less fossil energy and emit up to 68 percent less carbon dioxide (CO_2) than do current, petrochemical BDO processes. The most recent analysis shows that biobased BDO will compete economically against petrochemical BDO if oil prices are as low as $50 per barrel. Genomatica has established a complete, cost-effective downstream process and recovered BDO from 30-liter fermentation broths at greater than 99.5-percent purity.

Zequanox™, an Environmentally Safe Solution for Controlling Invasive Zebra and Quagga Mussels

Marrone Bio Innovations, Inc.

Invasive mussels have a billion-dollar impact on the North American economy. Because there are no environmentally responsible pesticides on the market for selective control of invasive mussels, power generation and industrial facilities are treated regularly with chlorine or other nonselective biocides. Although these chemicals are approved for this use, their nonspecificity and toxicity raise concern for worker safety and the environment.

Zequanox™ is a microbial pesticide comprised of *Pseudomonas fluorescens* CL145A (*Pf* CL145A) discovered in North American soil. It represents the first selective, environmentally friendly product to control invasive zebra and quagga mussels (*Dreissena polymorpha* and *Dreissena rostriformis bugensis*). In earlier work, the New York State Museum found that *Pf* CL145A was highly selective and efficacious for killing dreissenid mussels. Extensive nontarget ecotoxicity testing shows that it does not harm other species.

Recently, Marrone Bio Innovations (MBI) has been working to realize the commercial potential of *Pf* CL145A. MBI isolated, identified, and quantified some of the novel chemicals in *Pf* CL145A responsible for its selective activity against invasive mussels. These novel chemicals have potential as a new family of specific molluscicides. MBI optimized its fermentation process to produce high concentrations of active compounds within *Pf* CL145A. Now, they are developing stable formulations of killed *Pf* CL145A cells that are cost-effective and user-friendly.

In 2009, MBI began manufacturing Zequanox™ for field trials at hydropower facilities. MBI is working with its customers to guide product development. Zequanox™ meets EPA's criteria for registration as a reduced risk pesticide; MBI expects EPA registration in June 2010. Although product development is continuing, MBI is prepared to provide Zequanox™ to initial customers after EPA registration to replace current, less-selective molluscicides. In early 2010, MBI will provide Zequanox™ to the U.S. Bureau of Reclamation to treat its facilities along the Colorado River under an EPA FIFRA Section 18 Emergency Use Exemption registration.

Modular Genetics, Inc.

An Acyl Amino Acid Surfactant Produced by Sustainable Chemistry

Surfactants are generally composed of both hydrophobic and hydrophilic regions. Their amphiphilic nature enables them to reduce either the surface tension of a liquid or the interfacial tension between two liquids. These properties enable wide commercial use of surfactants as foaming agents, emulsifiers, and dispersants. Globally each year, petroleum is the feedstock for about 7.4 million metric tons of surfactants; seed oils such as palm or coconut oil are feedstocks for about 3.3 million metric tons. Manufacturing surfactants from petroleum releases approximately 31.6 billion kilograms of carbon dioxide (CO_2) into the atmosphere annually. Manufacturing them from seed oil releases less CO_2, but rainforest preservation limits the available amounts of palm and coconut oils. Sustainably manufactured surfactants have the potential to reduce rainforest destruction and eliminate annual emissions of atmospheric CO_2 equivalent to combusting 3.6 billion gallons of gasoline.

One of the most powerful known biosurfactants is surfactin, a lipopeptide produced by some strains of the soil bacterium *Bacillus subtilis*. Surfactin has only limited use in consumer products, however, because it is not water-soluble. Using genetic techniques, Modular Genetics engineered a *B. subtilis* strain and its peptide synthetase enzyme. The engineered bacterium now produces a novel acyl amino acid surfactant by fermentation of cellulosic carbohydrates such as soybean hulls, an abundant agricultural waste. The new surfactant is a fatty acid-glutamate (FA-Glu) that is very similar to myristoyl glutamate, a commercial surfactant widely used in consumer product formulations. FA-Glu has higher water solubility and a lower critical micelle concentration (CMC) than myristoyl glutamate. Like surfactin, FA-Glu is secreted into the fermentation broth, enabling partial purification by foam fractionation. This novel approach should enable the sustainable manufacture of many new useful surfactants.

During 2009, Modular Genetics distributed samples to potential customers and filed a patent application for its technology.

Orono Spectral Solutions

Device and Method for Analyzing Oil and Grease in Wastewaters without Solvent

Oil and grease are grouped together as one of five conventional pollutants covered by the 1974 Clean Water Act. They rank second only to pH as the most-enforced-against pollutant. All National Pollution Discharge Elimination Systems (NPDES) permits, all pretreatment permits, and all Industrial Effluent Guidelines require measurements of oil and grease. Millions of analyses for oil and grease are done each year in the United States alone.

As a result of the Montreal Protocol in 1989, EPA moved from a Freon extraction method (EPA 413) to an *n*-hexane extraction mass-based determination method (EPA 1664 in 1995; EPA 1664a in 1999). This created several new problems: (1) *n*-hexane methods require personal exposure, handling, and transportation of a hazardous, flammable liquid; (2) *n*-hexane is a known neurotoxin; (3) each analysis takes longer; and (4) millions of liters per year of *n*-hexane waste now require disposal. Thus, the current methodology is inconsistent with the intent of the Clean Air Act and Clean Water Act, both of which consider *n*-hexane a hazardous pollutant.

The “solid phase infrared amenable extractor” technology developed by Orono Spectral Solutions (OSS) solves the problems above by eliminating solvents from oil and grease analysis. It also provides more economical, accurate analyses. OSS’s extractor unit is small, economical, robust, and disposable (or partially recyclable). It contains no toxic substances. It includes a polymeric membrane that captures and concentrates oil and grease from water, a metal-membrane support, and a polypropylene housing designed for pressurized water samples. The polymeric membrane does not absorb IR light in the spectral regions of interest; after drying, the device can be put into an IR spectrophotometer to determine the amount of oil and grease.

This patent-pending technology has successfully completed ASTM multi-laboratory validation studies and has been assigned ASTM method number D7575. OSS is actively commercializing this technology for worldwide markets.

2-Methyltetrahydrofuran: A Green Alternative to Oil-Derived Ethers and Chlorinated Solvents

Pennakem LLC

2-Methyltetrahydrofuran (2-MeTHF) is the only aprotic solvent derived from renewable resources. The pentoses from agricultural waste such as corncobs cyclize to furfural in aqueous solution; furfural is further dehydrogenated to 2-MeTHF. As the largest producer of corn in the world, the United States provides a dependable supply of corncobs as waste from the food and bioethanol industries.

Pennakem initiated and developed the global market for 2-MeTHF as a green alternative to petroleum-derived ethers and volatile chlorinated solvents. Pennakem's proprietary technology produces 2-MeTHF with hydrogen from natural gas and water as the solvent. 2-MeTHF can reduce process mass intensity (PMI) to facilitate greener processes in chemical manufacturing. Substituting 2-MeTHF for tetrahydrofuran (THF) can lead to (1) higher reaction yields (reducing PMI for organometallics by 15–30 percent); (2) increased solubility of organometallic reagents (reducing PMI by 30–50 percent); (3) higher extraction yields during workup (reducing PMI by 15–30 percent); (4) one-pot reactions due to cleaner reactions, increased solvent stability, and easy phase separation (reducing PMI by 50 percent for 2 steps); and (5) elimination of hydrophobic cosolvents (reducing PMI by 30 percent). Switching to 2-MeTHF could eliminate 30,000 metric tons of THF per year along with 30,000 metric tons of hydrophobic cosolvents from Grignard workups. Because THF and cosolvent mixtures are often incinerated, substituting 2-MeTHF may reduce carbon dioxide (CO_2) emissions up to 90 percent.

2-MeTHF is easier to dry and recycle due to its rich azeotrope with water (10.6 percent) and simple distillation at atmospheric pressure. The energy savings for 2-MeTHF recycling are approximately 70 percent compared to THF. Other advantages for 2-MeTHF are improved process safety, lower chemical oxygen demand (COD) in effluent waters, and lower emissions of volatile organic compounds (VOCs).

Recently, CPS-Chirotech in the United Kingdom reported the first industrial application that substitutes 2-MeTHF for dichloromethane; this expands the potential for 2-MeTHF to substitute for chlorinated solvents.

PRE-TEC 3000®: An Environmentally Friendly Wood Treatment

Preventive Technology, Inc.

Preventive Technology developed PRE-TEC 3000® to protect wood products against fire, termites, mold, fungus, and moisture without using toxic or dangerous chemicals. PRE-TEC 3000® contains a silicate–borate mixture that forms an insoluble borosilicate gel upon drying. This treatment protects against termites and fire at the usual levels in borate-treated wood. The insoluble silica gel combats leeching. The carbonates, silicates, and borates in the treatment provide exemplary fire retardation, termite repulsion, mold inhibition, and decay prevention. PRE-TEC 3000® contains no metals. The disposal of wood treated with PRE-TEC 3000® will pose no threat to the environment.

Various species of trees produce vastly different types of lumber. Unfortunately, traditional wood-treatment technology is not effective for all types of lumber such as red pine, the preferred lumber in the Midwest. PRE-TEC 3000® has successfully treated many wood products that had previously been untreatable. This allows the opening of new markets to the building industry.

PRE-TEC 3000® will work with the system of "green" pressure-treating wood that is already established. It is currently being tested and cleared by the International Code Council (ICC) using their "green" process for approval of treated lumber for the building industry. If PRE-TEC 3000® replaces only one billion board feet of copper-based wood treatments next year, over 7,000 tons of copper would not contaminate the environment through leeching or eventual disposal of copper-treated wood. PRE-TEC 3000® is currently undergoing further testing by independent certified test laboratories.

Solazyme, Inc.

Renewable Oil Production from Algae

Certain species of algae produce lipids, mainly triglyceride oils, as a way to store energy. These algae can store more than 75 percent of their total cell mass as lipids. Using proprietary strains of heterotrophic algae, Solazyme has, for the first time, created a practical bridge from carbohydrates, sugars, and cellulosic biomass to the production of low-carbon lipids and hydrocarbons, compounds critically important to humankind's need for fuels and chemicals. Solazyme developed its algal strains through a combination of strain selection, screening, classical mutagenesis, and metabolic engineering.

Solazyme has pioneered the development and commercialization of renewable algal oil to replace conventional petroleum-based products. Solazyme has used 100-percent algal oil to produce a broad range of renewable, green fuels including (1) Soladiesel BD™ fuel, a fatty acid methyl ester biodiesel that meets the ASTM D6751 and EN14214 standards; (2) Soladiesel RD™ fuel, a hydrotreated diesel fuel that meets the ASTM D-975 standard; and (3) SolaHR$_{Jet}$™ fuel, a jet fuel that meets the most-challenging specifications for aviation turbine fuel, ASTM D1655. In addition, Solazyme algal oils and biomass have been incorporated into a variety of food products and converted into important chemicals such as polyols and soaps.

Solazyme's algal oils provide a number of environmental and human health benefits including efficient use of land and water resources, reduced air pollution, compatibility with the existing infrastructure, and reduced greenhouse gas emissions. An outside analysis of the total life cycle greenhouse gas emissions of Solazyme's fuel technology using the GREET model yielded estimated 89- and 169-percent reductions in global warming index (GWI) for Soladiesel™ fuels made from sugarcane and municipal green waste, respectively. Solazyme is currently operating continuously in commercial facilities to produce over 2,200 gallons (15 tons) of algal oil per week. During 2009, Solazyme established plans and obtained funds for an integrated biorefinery to produce renewable fuel and chemical feedstocks.

SoyResin, LLC; Professor Xiuzhi Susan Sun, Department of Grain Science and Industry, Kansas State University

Green Process of Unfolding Soy Protein Polymers for Green Adhesives

NOTE: This project is the result of a partnership between Professor Xiuzhi Susan Sun of Kansas State University and SoyResin, LLC. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 11.

Development and Commercial Application of SAMMS®: A Novel Adsorbent for the Removal of Mercury and Other Toxic Heavy Metals

Steward Advanced Materials

Mercury contamination poses a serious threat to the environment and human health. Many technologies that remove mercury, however, also produce harmful byproducts or secondary waste. The technology using SAMMS® successfully adsorbs and removes toxic metals (e.g., mercury, cadmium, lead) and replaces less-effective adsorbents currently used in the chemical industry (e.g., activated carbon, IX resins). Specifically developed to form strong chemical bonds with targeted toxic heavy metals, SAMMS® has superior adsorption capacity; it also provides superior cost-effectiveness by significantly reducing the volume of hazardous waste.

SAMMS® is a mesoporous ceramic substrate with a single layer of functional sorbent molecules chemically anchored to the substrate surface. The functional molecules are tailored to have high affinity for specific cations or anions. Originally, the manufacture of SAMMS® required a functionalization process using flammable organic solvents including toluene. The resulting waste stream consisted of water, methanol, toluene, and traces of mercaptan. This mixture required disposal as hazardous waste.

Steward Advanced Materials dramatically improved the SAMMS® synthesis using nonflammable, nontoxic supercritical carbon dioxide ($SCCO_2$). With this patented, commercially viable, green-chemical process, SAMMS® manufacturing is faster and more efficient; it also yields a higher-quality product. The $SCCO_2$ process results in a defect-free silane monolayer with virtually no residual silane. Consequently, the only byproducts are carbon dioxide (CO_2) and the alcohol resulting from the hydrolysis of the alkoxysilane. The CO_2 and alcohol are readily separated, allowing the CO_2 to be captured and recycled. The pure alcohol can then be captured as a recyclable feedstock, rather than becoming waste as in the traditional synthesis. The SAMMS® materials emerge from the reactor clean, dry, and ready for reuse. The benefits of the green manufacturing process for SAMMS®, coupled with the superior adsorption characteristics of SAMMS® materials currently deployed in the chemical industry, result in substantial reductions in toxic metals being released to the environment.

Bioil Technology: One-Pot, Catalytic Hydrolysis of Lignocelluloses

Sun Pharmaceuticals, Inc.

One of the biggest challenges society faces is the depletion of fossil fuels. Replacing these fuels with renewable feedstocks such as lignocelluloses can address this challenge. During the last three years, Sun Pharmaceuticals has developed a technology to change biomass refining from time- and energy-consuming multiple steps to a simple, one-step catalysis. This technology uses every organic polymer of lignocelluloses including cellulose, hemicellulose, and lignin; in contrast, other biomass-refining technologies use only carbohydrates. The new technology hydrolyzes lignocellulose polymers into small organic compounds in one step under mild conditions without hydrogen. No gas or black tar forms during hydrolysis, suggesting that no organic carbon is lost. The product is "Bioil", a mixture of about sixty major organic compounds including four groups: cyclopentanones and cyclopentanols, α-hydroxyl carboxylic acids and amino acids, substituted phenols and catechols, and monosaccharides.

The major advantages of Bioil technology over other biomass-refining technologies are its efficient use of materials and energy. Bioil technology saves more than 70 percent of the organic carbon and 60 percent of the energy consumed by ethanol fermentation. Current biomass-refining technologies have difficulty becoming profitable, due to the limited products (e.g., ethanol or gasoline) that they can make from lignocellulose. The Sun Pharmaceuticals technology will make commercialization more practical by producing green, high-value-added chemical products, as well as hydrocarbon liquid fuels, food, and food additives. Residues left after isolating pure compounds from Bioil are easy to convert to gasoline or diesel fuel.

During 2009, Sun developed isolation methods for some of these sixty compounds and successfully completed a pilot run for the Bioil technology and isolation process under a joint venture in China. The first demonstration plant with a commercial-scale, annual consumption of 50,000 tons of biomass is being initiated. It can be modified to produce ten million gallons of gasoline per year in addition to food and food additives.

Terrabon, Inc.

Conversion of Municipal Solid Wastes to Drop-In Fuels and Chemicals

Terrabon's MixAlco™ process converts any anaerobically biodegradable material (e.g., proteins, cellulose, hemicellulose, fats, and pectin) into a wide array of chemicals (e.g., ketones, secondary alcohols) and fuels (e.g., drop-in biofuels such as gasoline, diesel, and jet fuel). The conversion occurs by nonsterile, anaerobic fermentation of biomass into mixed carboxylic acids and salts by a mixed culture of naturally occurring microorganisms, followed by the conversion of the mixed acids and salts into the desired chemicals or fuels by conventional chemistry.

Terrabon uses municipal solid waste (MSW), which typically ends up in landfills, as the feedstock for the MixAlco™ process to make ketones, secondary alcohols, and gasoline. This process will increase landfill life and replace nonrenewable petroleum resources. According to a life cycle analysis (LCA) using the GREET model, it will reduce greenhouse gas emissions by over 180 percent compared to conventional gasoline. This process may also use other waste products of environmental concern such as leachate from landfills, raw sewage, and sewage sludge. When high-water effluents are used as the water sources along with MSW, this process can export up to 25 gallons of distilled water for every gallon of fuel it produces.

Terrabon has built a pilot plant and a semiworks plant in Bryan, TX to confirm the scalability of this process. The semiworks plant processes the equivalent of about 5 dry tons of biomass per day and generates enough fermentation products to produce 100,000 gallons of biogasoline per year. The conversion to biogasoline at the plant includes dewatering the fermentation salt product by evaporation and drying, thermally converting it into ketones, and finally catalytically converting the ketones into alcohols and hydrocarbons. Terrabon successfully completed testing this process at the semiworks plant, producing good-quality gasoline. In 2010, it plans to start designing and constructing a 220 dry ton per day plant to make 5 million gallons of gasoline per year.

Troy Corporation

Source Reduction and Sustainability through Use of Mergal® 753 Antimicrobial Preservative

Product innovation is standard with high-volume agricultural products, but is less frequent with antimicrobial and biocidal preservatives. Troy developed Mergal® 753 in response to market concerns over green chemistry initiatives, sustainability, and release of volatile organic compounds (VOCs). Mergal® 753 is a concentrated aqueous dispersion of 1,2-benzisothiazolin-3-one (BIT), a widely known biocidal active ingredient; it contains no VOCs and is compatible with water-based production processes. Typical applications for industrial biocides like Mergal® 753 include adhesives, paints, coatings, and metalworking fluids.

Mergal® 753 meets basic green chemistry parameters. Troy assessed the carbon footprint of its product using the methods and tools developed by the Greenhouse Gas Protocol Initiative, a joint project of the World Business Council for Sustainable Development and the World Resources Initiative. The basic calculation used to develop its carbon footprint included the “functional unit”: comparing the amount of product needed by a customer for a given application. Troy’s conventional, dilute product requires 4.5 times the volume as the concentrated product (Mergal® 753) to treat the same amount of material at the customer’s facility. The primary comparison assumed that Mergal® 753 is diluted by the customer to the same final concentration as the dilute product and that the use rate per functional unit is equivalent for the two products. With this approach, Troy estimated that the potential energy savings through replacement of its dilute product with Mergal® 753 results in a carbon dioxide (CO_2) reduction equivalent to taking 5.3 passenger cars off the road each year. Additional savings would occur with increased product use, which effectively reduces worker exposure to hazardous workplace substances. Troy optimized the formulation of its product to ensure suitability with current application systems, and EPA formally registered Mergal® 753 on October 31, 2008.

Highly Efficient and Practical Monohydrolysis of Symmetric Diesters

Wako Chemicals USA, Inc.; Professor Satomi Niwayama, Department of Chemistry and Biochemistry, Texas Tech University; Kishida Chemical Co., Ltd.

NOTE: This project is the result of a partnership between Professor Satomi Niwayama of Texas Tech University, Wako Chemicals USA, Inc., and Kishida Chemical Co., Ltd. The project was judged in both the academic and small business categories. The abstract appears in the academic section on page 10.

RegenSi™: A Wafer Reclaim Solution with a Low Carbon Footprint that Extends the Life Cycle of Silicon Test Wafers

Advanced Technology Materials, Inc.

Because a prime silicon wafer costs approximately $300, semiconductor manufacturers use test wafers, at over $100 apiece, to optimize their manufacturing processes. One large fabricator might spend $2 million monthly on test wafers. The industry uses more than 27 million prime and test wafers annually. Because silicon is the greatest material expense for fabricators, they are eager to improve their reclamation and reuse of test wafers.

Traditional wafer reclamation processes involve chemically stripping unwanted films from the wafer surface, surface planarization (i.e., mechanical polishing to remove damage or impurities), and cleaning. Wafer reclamation has been limited because each cycle of stripping and polishing reduces the thickness of the wafers; eventually, they become too thin and are discarded. Traditional processes have very low reclaim yields because they cannot remove unwanted films completely.

RegenSi™ is a novel, all-wet, single-step process that strips away most films from test wafers and limits damage to the underlying silicon. This eliminates or reduces the need for wafer surface planarization, which is energy-intensive, requires a large volume of consumables, and is expensive. RegenSi™ chemicals also have a much longer bath life, which reduces both chemical waste and worker exposure. The RegenSi™ process eliminates sulfuric, nitric, and hydrochloric acids. It reduces hydrofluoric acid 24-fold. The process has a carbon footprint 28-fold lower than the traditional three-step process and consumes 85-percent less energy. One Taiwanese manufacturer using RegenSi™ increased reclaim yields to 85 percent and reduced silicon loss by 75 percent, increasing the life of each test wafer fourfold. Another RegenSi™ customer saved 20 tons of deionized rinse water per day in each facility.

This combination of higher yields, fewer resources, greater productivity, and increased reuse leads to significant overall cost savings, energy savings, and waste reduction. Both IBM and Texas Instruments are using RegenSi™; many others are using or testing it.

Bipolar Membrane Electrodialysis for Greener Processing of Chelates

AkzoNobel Functional Chemicals, LLC

Chelates are chemical agents that interact or complex with metal ions, often increasing their solubility. Liquid redox sulfur recovery (LRSR) uses chelates to remove poisonous hydrogen sulfide (H_2S) from gas streams. A chelate called *N*-hydroxyethyl ethylenediamine triacetic acid (HEDTA) is conveniently used in LRSR to complex iron and to keep it in solution, where it reacts with H_2S.

Several years ago, AkzoNobel developed two novel products containing HEDTA for use in this LRSR process. At that time, the manufacturing process for these novel products included treating the sodium salt of HEDTA (HEDTA-Na_3) with ion exchange (IE) technology where Na^+ ions are exchanged with H^+ ions. Although IE offers favorable exchange of Na^+ for H^+, it does so at the expense of generating a significant waste stream during regeneration of the IE resin. The Na^+ ions present on the resin combine with the regeneration acid, forming a waste salt solution. In addition, IE is inherently a dilution step: energy is required to boil and concentrate the HEDTA product streams after IE processing.

AkzoNobel has now developed and implemented a greener manufacturing technology to replace IE. Bipolar Membrane Electrodialysis (BMED) is a technology that uses ion-permeable membranes and electricity to exchange Na^+ for H^+. Unlike IE, the BMED technology does not generate a waste stream of salt; rather, it generates a stream of useable sodium hydroxide (NaOH) and requires no regeneration acid. BMED actually concentrates the processed HEDTA chelate solution and eliminates IE's energy-intensive concentration step, saving approximately 360 kilograms of steam per metric ton of HEDTA products.

AkzoNobel believes the BMED technology, implemented at its plant in the United States, is the first major, if not the only, commercial use of this technology to process chelates. Since the technology's introduction, AkzoNobel has identified other opportunities for BMED, allowing greener processing of chelates and other electrolyte products.

AkzoNobel Surface Chemistry, LLC

Novel, Greener, Water-Soluble, Hybrid Polymer Technology for Fabric and Cleaning, Industrial Water Treatment, and Oil Recovery Applications

Many consumer and industrial applications require the control and prevention of scales such as calcium carbonate. Among these applications are automatic dishwashing and laundry; maintaining equipment for industrial water treatment; and facilitating oil production, drilling, and stimulation. Synthetic polycarboxylates created from acrylic acid and other monomers derived from petrochemicals have been used traditionally to manage water hardness and prevent deposition of scale and other solids in these applications.

AkzoNobel Surface Chemistry (ANSC), a global supplier of synthetic polycarboxylates for over three decades, has created a new class of polymers called hybrid polymers. These polymers have traditional synthetic functionality, but use plant-based feedstocks for half or more of the polymer backbone. The resulting products reduce ANSC's dependence on petrochemicals and increase its use of agricultural products, resulting in better environmental sustainability. Prototypes of the hybrid products show excellent cost- and weight-performance in automatic dishwashing, laundry, water treatment, and oil drilling and production, making it feasible to switch to the new hybrid polymers.

Life cycle analysis (LCA) shows that replacing traditional, petrochemical-based polymers with the ANSC hybrid polymers reduces energy use by 44 percent, petrochemical depletion by 43 percent, carbon dioxide (CO_2) emissions by over 35 percent, acid rain by 10 percent, and ground-level ozone by 40 percent. These benefits result from the sustainable, plant-based materials in the hybrid polymers. Incorporating polysaccharides into the hybrid polymers gives them substantial biodegradability; purely synthetic polymers are not biodegradable.

Current hybrid prototypes based on 65-percent polysaccharide, for example, can be manufactured in existing equipment with water as the solvent. The aquatic and human toxicity profiles of the hybrids are equal to or better than their synthetic counterparts. ANSC first used this technology in cleaning and oilfield drilling applications. The company is exploring commercial extensions into petrochemical, personal care, and water treatment applications. ANSC expects to begin commercialization in 2010.

An Environmentally Friendly Process for Upcycling Plastic Waste into Advanced Carbon Nanotubes and Carbon Spheres

Argonne National Laboratory

Left unchecked, the escalating volume of plastic waste that requires hundreds of years to degrade will cause severely negative environmental and human health effects on life on earth. Current recycling technology is only a partial solution; it often results in downcycling plastics rather than making new, high-quality products. Thus, innovative approaches for upcycling or remediating plastics are needed in addition to conventional recycling facilities.

Argonne has developed an original, solventless, solid-state, controlled pyrolysis process that uses mixed plastic waste in a one-pot, closed system. This reproducible, environmentally friendly process presents an opportunity to use plastic waste as a feedstock to produce carbon spheres (CSs) and carbon nanotubes (CNTs), which are industrially significant, value-added products. Argonne's approach for fabricating CNTs is inexpensive and innovative relative to other current methods. This technology also eliminates the air and water pollution caused by incinerating plastic waste or burying it in a landfill. It also uses less energy than do typical recycling methods for plastic waste.

Argonne has successfully tested as-prepared dry CSs and CNTs in lithium, Li-ion, and Li–air batteries. The CSs and CNTs acted as superior anode materials, improving the electrochemical performance in Li-ion batteries. Cobalt-encapsulated CNTs also showed promising performance as an air cathode in Li–oxygen batteries. The micrometer-sized, smooth, carbon spheres are pure, conducting, and paramagnetic. They have potential applications in toners, printers, lubricants, and the tire industry.

Argonne designed a prototype reactor with a 40 cubic centimeter (cc) capacity to upcycle plastic waste; it optimized the reaction conditions (e.g., temperature, effect of single or mixed plastic waste, selection and amounts of catalysts, autogenic pressure measurements). It is working to elucidate the mechanism of CS and CNT formation. Argonne is systematically characterizing the atomic structure, composition, and morphology of the CSs and CNTs with advanced structural, spectroscopic, and imaging techniques. Argonne is seeking licensees for this technology.

BioBased Tile® with BioStride®: A Revolutionary New Flooring Made with Rapidly Renewable Resources

Armstrong World Industries, Inc.

Today, more than three-quarters of a billion feet of vinyl composition tile (VCT) is installed annually. Historically, resilient VCT flooring has been manufactured with binders derived from fossil fuel. Typical binders for VCT include poly(vinyl chloride) (PVC), polyolefins, ethylene acrylic resins, and synthetic rubbers. These binders combine plasticizers, processing aids, stabilizers, limestone, and pigments.

In 2008, Armstrong commercialized Migrations® BioBased Tile® flooring, a revolutionary plasticizer-free, biobased flooring product. Armstrong is the first manufacturer in over 100 years to develop a biobased polymer as a binder for a hard-surface flooring product. Linoleum is the only other such flooring available. The new binder, BioStride®, created a new category of composition tile. Branded by Armstrong as BioBased Tile®, it couples indoor air quality and environmental benefits with improved performance.

The BioStride® polymer binder contains ingredients from rapidly renewable, domestic crops, resulting in reduced reliance on fossil fuels and a lower carbon footprint. The development of the BioStride® binder and BioBased Tile® flooring followed important principles of green chemistry, life cycle assessment, and Design for the Environment (DfE). The consumer product made from the BioStride® binder contains 10-percent preconsumer recycled limestone. Replacing VCT with BioBased Tile® flooring could save 108 million pounds of virgin materials, eliminate 259,000 pounds of volatile organic compounds (VOCs) from manufacturing, capture 34 million pounds of carbon dioxide (CO_2) from the atmosphere in biobased components, reduce energy consumption by 365 billion Btu (equivalent to 43 million pounds of CO_2), and improve indoor air quality. BioBased Tile® flooring is certified by Floor Score with no detectable levels of total VOCs; it contains no materials listed in the table of Chronic Reference Exposure Levels (CRELs) established by the California Office of Environmental Health Hazard Assessment (OEHHA). BioBased Tile® is helping customers qualify for LEED certification and other green building initiatives.

Baker Hughes Incorporated

Highly Water-Dispersed Oilfield Corrosion Inhibitors Eliminate over One Million Pounds of Nonrenewable Solvents Annually

Corrosion-induced leaks in hydrocarbon-producing equipment threaten safety, health, and the environment. Only recently, however, has anyone focused on safer corrosion inhibitors with reduced environmental impacts. Extensive product development by Baker Hughes has led to an innovative line of corrosion management chemicals that is free of hydrocarbon solvents, but contains active inhibitors that historically could only be formulated with these flammable solvents. The new, highly water-dispersed products exhibit better dispersibility and water partitioning in use than traditional products and, therefore, deliver the active inhibitors to metal surfaces more efficiently. The net result is significantly reduced field-level chemical use rates that do not compromise corrosion inhibitor performance.

This innovative technology entails much more than simply making water-soluble formulations. What truly distinguishes the new technology is its use of the inhibitors themselves as dispersing agents, both eliminating the need for hydrocarbon solvents and limiting or eliminating the need for additional additives or surfactants. The chemistry is based on formulated fatty acid amide–imidazoline technology. Careful adjustments of pH, hydrophilic-lipophilic balance, and levels of active ingredients produce stable dispersions of the inhibitors with no or only minimal added surfactants. As a result, oilfield operators can reap the benefits of the powerful chemicals commonly found in hydrocarbon-based, corrosion-inhibiting products in safer, water-based formulas that have less impact on the environment. The water-based products contain no naphthalene; they have higher flash-points than traditional, solvent-based products, so they are safer to store and handle.

Since 2006, Baker Hughes has commercialized five of these products. Based on 2009 sales, the net direct environmental impact of this technology is the elimination of at least 1 million pounds of hydrocarbon solvents annually. With continuing development and as oilfield deployment of this technology grows, the direct and indirect positive impacts of the technology are expected to increase several-fold in the very near term.

Battelle Memorial Institute

ReFlex™ 100 Bioderived Green Bioplasticizers for Poly(vinyl chloride)

Global production of plasticizers is over 13 billion pounds annually. Ninety percent of all plasticizers are used with poly(vinyl chloride) (PVC) to make it softer or more flexible for applications including vinyl flooring, films, blood bags, wallpaper, inks, plastisols, and shoes. Eighty percent of all plasticizers are phthalates, but some phthalates have come under severe regulatory scrutiny as suspect endocrine disruptors. For example, President George W. Bush signed the Consumer Product Safety Improvement Act (CPSIA) in August 2008, which led to banning three phthalate ester plasticizers in toys.

Consequently, the PVC industry has an immediate need to replace phthalates with cost-effective, safe, green plasticizers. Replacing 25 percent of the U.S. plasticizer production with biobased products derived from renewable resources offers energy savings of approximately 5 trillion Btu per year. In addition, each pound of bioplasticizer consumed reduces carbon dioxide (CO_2) emissions by about one pound.

Battelle's technology addresses the need for a safe, cost-effective alternative to phthalates. Battelle has developed several novel plasticizers based on extensive modeling studies to identify those chemical structures derived from renewable feedstocks that exhibit optimal compatibility with PVC resin and enhance both thermal stability and plasticization efficiency. One such plasticizer is epoxidized propylene glycol disoyate.

In 2008, Battelle licensed its patented technology to PolyOne, based in Ohio, and Nexoleum, based in Brazil. In 2009, PolyOne and Archer Daniels Midland successfully scaled up and commercialized reFlex™ 100, a first-generation, bioderived, green plasticizer for PVC. ReFlex™ has superior solvation, higher thermal stability, and increased plasticization efficiency. It can replace butyl benzyl phthalate across a range of applications, particularly plastisols and inks. Nexoleum has sold several hundred tons of its bioderived Nexo E1™ plasticizer in Brazil. These new bioplasticizers are proving to be drop-in replacements for phthalates in many applications; they require minimal, if any, changes to current practices in the PVC industry.

IMPACT Technology: A Greener Polyether Polyol Process

Bayer MaterialScience, LLC

The Bayer MaterialScience (BMS) IMPACT technology for polyether polyol (PET) production couples a breakthrough catalyst invention with an equally innovative process design. The IMPACT process includes modifying the double metal cyanide (DMC) catalyst to increase its reactivity more than 10-fold and exploiting 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 new process generates less waste, eliminates process steps, and is inherently safer.

A gate-to-gate life cycle assessment (LCA) of the continuous process in comparison with conventional technology shows reductions of 76–80 percent in energy consumption, carbon dioxide (CO_2) generation, acidification, eutrophication potential, and smog. Moreover, the BMS Channelview, TX plant eliminates over 34 kilotons of wastewater annually at typical run rates and reduces over 32 kilotons of CO_2 equivalents at full capacity. Recently, total production in the United States using the continuous process reached a billion pounds, and BMS completed licensing its technology to major competitors. These milestones have established IMPACT as the industry standard in environmental savings and productivity. Worldwide, plants will be converted or constructed for IMPACT technology, increasing the positive effects on the environment. Polyethers for use in polyurethanes have a multi-billion-pound worldwide market with applications spanning nearly every market segment including insulation, coatings, elastomers, and flexible foams such as bedding, furniture, and automotive seating. BMS has a 23-percent market share with a global capacity of over 1,100 kilotons. Around 50 percent of BMS's PET production can be manufactured using the IMPACT technology. BMS has converted about half of this volume to the new processes. BMS has used this technology to double PET production at the Channelview plant within four years to 200 kilotons and has lowered its variable production costs by 40 percent.

Berry Plastics; Flame Chk Inc.; Chemische Fabrik Budenheim KG

Nonhalogenated Flame Retardant for Use in High-Performance Adhesives and Coatings

Deaths due to fire claim thousands of lives every year all over the world. The challenge is to make products that will burn more slowly or not at all when exposed to fire, allowing occupants to escape and giving firefighters a chance to save lives and property. For decades, fire-retardant systems were made up of halogenated materials including bromine, chlorine, and antimony. These materials have recently come under scrutiny, however. They have been found to accumulate in the environment and in humans. This has led many domestic and international organizations to regulate and phase out these materials, as is the case with decabromodiphenyl ether (decaBDE). Many customers are requiring their suppliers to provide products that are halogen-free. The challenge is finding effective, nonhalogenated replacements.

Berry Plastics has shown that melamine borate (i.e., Budit 313 made by Chemische Fabrik Budenheim and distributed by Flame Chk) is an effective replacement in the pressure-sensitive adhesives it manufactures. Melamine borate is not expected to harm humans or aquatic environments. In contact with heat, it decomposes, acts as a heat sink, and releases inert nitrogen gases, which dilute the oxygen and flammable gases. It inhibits burning, prevents fire from spreading, and reduces the emission of toxic fumes by building a char barrier. The char barrier greatly diminishes the fuel available to fire.

The current challenge with nonhalogenated flame retardants is that more of the material is required to produce the same effect as the halogenated flame retardants. Thus, each application being made flame retardant requires a unique formula to balance flame retardancy with product functionality. The technology is not a one-to-one replacement and will require more research, but the cost is expected to be competitive with the halogenated systems. In November, 2009, Flame Chk submitted a Premanufacture Notification and Low Volume Exemption for melamine borate to EPA.

Cargill Incorporated

The Development and Commercialization of a Low-pH, Lactic Acid Process for Renewable Plastics

Lactic acid is a commodity-scale fermentation product, ranking among the highest-volume chemicals produced by fermentation. Greater than 95 percent of the world's 370,000 metric tons of lactic acid is produced by submerged fermentation of sugar. This fermentation has traditionally been carried out by lactic acid bacteria maintained near neutral pH (pH 5–7). At this pH, however, the fermentation product is a lactic acid salt that requires neutralization. One of the primary limitations of the bacterial lactic acid process is the cost and environmental footprint of the recovery and subsequent disposal of the waste salt caused by the neutralizing agent used during purification.

Cargill, in an effort cofunded by the Department of Energy (DOE), has developed and commercialized a metabolically engineered yeast biocatalyst that efficiently produces free lactic acid at low pH (significantly below the pK_a of lactic acid). The lactic acid production attributes (rate, titer, and yield) of this yeast biocatalyst are near those of a bacterial lactic acid producer, but the low pH of the fermentation produces free lactic acid as the product, not a lactate salt. This technology improves product quality and reduces production costs by roughly 50 percent. It also reduces the use of sulfuric acid and calcium hydroxide and formation of the calcium sulfate byproduct by approximately 85 percent. Finally, it leads to a 35-percent reduction in greenhouse gas emissions (GHG) over the bacterial process.

Cargill uses lactic acid as the monomer to produce NatureWorks LLC Ingeo™ poly(lactic acid) (PLA). Ingeo™ biopolymer is the world's first and only performance plastic made from 100-percent annually renewable resources. Ingeo™ biopolymer is clear and strong like petroleum-based plastic, yet can be commercially composted. Plant-based Ingeo™ biopolymer offers the cost and performance necessary to compete with traditional petroleum-based materials in the packaging and serviceware markets. Cargill commercialized its new yeast-based process in 2008.

Codexis, Inc.

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

Chiral secondary alcohols are intermediates in the syntheses of numerous chiral active pharmaceutical ingredients (APIs). They are commonly produced from the corresponding ketones using hazardous, boron-based reducing agents or, more recently, asymmetric catalytic reduction. Because these reduction methods typically produce inadequate stereoselectivity, additional processing is required to upgrade stereopurity, and product yields are low. Greener, more economical alternatives to such hazardous reagents and their energy- and mass-intensive processes are required to produce the increasing volumes of chiral alcohols needed for current and future drugs.

Biocatalytic reduction of ketones has long been recognized as an attractive, green alternative for making chiral alcohols. This promise went largely unfulfilled, however, because the available ketoreductase (KRED) biocatalysts were hampered by narrow substrate-specificity, low activity, poor in-process stability, inadequate stereoselectivity, and productivity-limiting product inhibition.

Codexis's widely applicable platform of diverse KREDs pre-evolved from a common wild-type ancestor successfully addresses these long-unmet needs for practical, greener processes to manufacture chiral alcohols. The Codex™ KRED Panel comprises diverse variants of one KRED that are pre-evolved for in-process stability and efficient manufacture. The variants contain combinatorial mutations that, as a population, confer activity on a wide structural variety of ketones and selectivity to either alcohol stereoisomer. The variants are arrayed on microtiter plates for rapid screening to find the desired activity on any new ketone substrate and to obtain Protein Sequence Activity Relationship (ProSAR) data for rapid enzyme optimization if needed. Codexis developed processes for chiral alcohol intermediates of four generic APIs with variants identified from KRED panel screens and transferred them to contract manufacturers. Codexis has used panel variants to synthesize material for more than 15 drug candidates in development. Building on its success, Codexis has since developed Codex™ panels for other generally useful biocatalytic conversions including panels of transaminase, nitrilase, acylase, halohydrin dehalogenase, and ene reductase biocatalysts.

Cytec Industries Inc.

Saturated Polyester–Phenolic Resin Systems Eliminate Bisphenol A and Epoxy from Interior Can Coatings for Food Packaging

Recent studies of bisphenol A (BPA) in animals have revealed potential endocrine-disrupting effects. BPA, however, is a key raw material for the binders used in interior coatings for food cans. Because these coatings are an important source for consumer exposure to BPA, the food industry is demanding coatings that are free of BPA. Although U.S. regulatory agencies have not yet made a final regulatory decision about BPA, the use of this monomeric substance in interior can coating systems has become a matter of public interest and scientific discussion.

Cytec has developed a new generation of saturated polyester resins for use as the main binder in conjunction with phenolic resins. Together, these two resins can be used in interior can coatings for the metal packaging goods industry. Coating systems based on these resins exhibit comparable performance to conventional high-molecular-weight epoxy systems, with the additional advantage of being completely free of residual epoxy resin monomers and their byproducts (e.g., BPA; bisphenol A diglycidyl ether and its derivatives).

Cytec's saturated polyester resin, DUROFTAL PE 6607/60BGMP, has a predominantly linear structure and a molecular weight of approximately 10,000. All monomers used in its synthesis comply with food contact laws. It does not contain any significant levels of free solvent if properly cured; in this and other features, it complies with FDA 21 CFR §175.300. It is more flexible than conventional systems based on high-molecular-weight epoxy resins. Although DUROFTAL PE 6607/60BGMP is compatible with most existing cross-linkers (predominantly phenolic resins and amino resins), Cytec designed a new, tailor-made phenolic resin for this special application so that the system can be completely free of BPA and have comparable performance to existing systems. DUROFTAL PE6607/60GMP does not have the estrogenic properties of BPA. It has been on sale in the United States since 2008.

Cytec Industries Inc.

MAX HT™ Bayer Sodalite Scale Inhibitor

The Bayer process converts bauxite ore to alumina, the primary raw material for aluminum. The heat exchangers and interstage piping in the process build up sodalite scale (i.e., aluminosilicate crystals), which reduces the efficiency of the heat exchangers. The equipment must be taken off line periodically and cleaned with sulfuric acid.

Cytec developed its MAX HT™ Bayer Sodalite Scale Inhibitor products for the Bayer process. There are no other scale inhibitors on the market for this application. The active polymeric ingredient contains silane functional groups that inhibit crystal growth by incorporation into the crystal or adsorption onto its surface. Dosages range from 20 to 40 ppm. Assessments of these polymers under EPA's Sustainable Futures Program indicated low overall concern for human health and the aquatic environment.

Eliminating sodalite scale from heater surfaces produces many benefits. Heat recovery from the steam produced in various unit operations is more efficient. Increased evaporation makes the countercurrent washing circuit more efficient and reduces caustic. Reducing the use of steam reduces emissions from burning carbon-based fuels. Lastly, reducing the sulfuric acid used to clean heaters reduces both worker exposure and waste.

There are about 45 operating Bayer process 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, 11 Bayer process plants worldwide have adopted it; 14 more plants are testing it. Each plant using MAX HT™ saves $2–20 million annually. Per ton of alumina produced, each plant saves 0.25–1.25 million Btu, the equivalent of about 29–202 pounds of carbon dioxide (CO_2) not released to the atmosphere depending on the energy savings and fuel used. Fewer cleaning cycles and less acid per cycle allow a typical 1.5-million-ton alumina plant to reduce its waste by 1,500–4,500 tons of 5-percent acid annually.

Cytec Industries Inc.

UV-Curable Pressure Sensitive Adhesive

UV-curable Pressure Sensitive Adhesives (PSAs) have attracted the attention of the PSA market due to their major advantages over the traditional waterborne and solventborne products. These advantages include (1) lower conversion costs because less energy is required, (2) smaller space requirements due to the compact equipment necessary for processing, (3) lower shipping costs and inventory needed because UV-curable PSAs are 100-percent active, (4) more efficient processing because a thick film can be made in a single pass, and (5) environmental friendliness because these products have low volatile organic compounds (VOCs). UV-cured products are attractive to PSA coaters seeking lower capital investment and operational costs as well as those facing footprint constraints. Although UV-curable PSA formulations have been studied since the 1970s, problems with their performance and cost have hindered their acceptance by the market.

Through numerous experiments with synthesis and formulation, Cytec has created new UV-curable PSA polymers with reasonable raw material costs, specially designed blocks of microstructure domains, optimized molecular weights, and efficient UV-curing properties. Cytec's UV-curable PSA technology involves the formation of a unique, acrylated urethane hybrid that combines soft segments to provide flexibility and adhesion with hard segments to give the film cohesive strength, high temperature resistance, and chemical resistance. Cytec's technology solves the five performance challenges faced by other UV-curable PSA technologies. This acrylated urethane hybrid provides good adhesion to substrates of both low and high surface energy coupled with excellent high-temperature shear performance. In addition, Cytec's technology achieves consistent performance over a broad UV curing range and good through-cure for thick PSA films at a reasonable cost to the general PSA market. It is a 100-percent-active PSA with no solvent or water, requiring much less energy for curing than traditional waterborne or solventborne PSA formulations. Currently, nine locations globally are evaluating this technology.

Accelerated Solvent Extraction with Solvent Saver Mode™: Reducing Organic Solvent Consumption and Waste in Laboratories

Dionex Corporation

Accelerated Solvent Extraction (ASE®) is a sample preparation system that uses organic solvents at elevated temperatures and pressures to extract analytes of interest from solid or semisolid matrices prior to analysis. Higher temperatures increase the capacity of solvents to solubilize analytes; they also enable analytes to move faster from the boundary layer near the surface of the matrix from which they are extracted into the bulk solvent. Elevated pressures speed up the extractions overall. They also make it possible to keep solvents in a liquid state at temperatures above their boiling points, which is critical for efficient extraction. Dionex developed ASE® to replace traditional extraction techniques such as Soxhlet that require large volumes of solvent. The company's intent was to develop a technique that was faster, safer, and more cost-efficient. Early results for the ASE® technology allowed extraction of a 10 g sample in 15 minutes with only 15–25 mL of solvent; a typical Soxhlet extraction requires 500 mL of solvent.

The end result, ASE® 350, is an automated system that greatly reduces the amount of organic solvent required to extract analytes. ASE® technology significantly reduces solvent waste, solvent vapors, and solvent exposure to laboratory personnel. With the introduction of the ASE® 350 system, users can reduce the amounts of solvent even further by activating the Solvent Saver Mode™. This mode can save up to an additional 33 percent of solvent during each extraction. As one example, the amount of solvent required to analyze a year's worth of 10 g samples is 49 L for the ASE® 350 system in the Solvent Saver Mode™ and 3,120 L for the traditional Soxhlet method. This is a significant decrease in the amount of organic solvent waste generated and the amount of solvent vapors released into the environment. Dionex introduced its ASE® 350 system in 2008.

Energy Savings from a New Manufacturing Route for Vinyl Methyl Ether

The Dow Chemical Company

Glutaraldehyde is a broad-spectrum antimicrobial agent. Glutaraldehyde formulations address the antimicrobial needs of a variety of applications including agriculture, metalworking fluids, heat-transfer systems, oil and gas operations, water treatment, paper manufacturing, and medical and dental facilities. A key raw material in the production of glutaraldehyde is vinyl methyl ether (VME). Historically, VME has been produced using a two-step chemical process. The energy associated with the steam needed for this process is approximately 15,000 Btu per pound of VME or approximately 300 billion Btu per year.

Seeking more sustainable process conditions, Dow Process Research and Development identified the synthesis of VME as a prime candidate for reactive distillation technology. Reactive distillation combines chemical reaction and distillation in a single step. This technology is part of the separations roadmap supporting Vision 2020 for the U.S. chemical industry because it can significantly reduce the energy consumption of separation processes.

Applying reactive distillation to the VME process meant replacing one reactor and four distillation columns with a single reactive distillation column. The new process requires less steam, leading to energy savings equivalent to 54,000,000 kWh each year. This is enough energy to provide electricity for approximately 4,800 homes per year based on average 2007 household consumption reported by the Department of Energy. The primary aqueous waste stream from the VME process using reactive distillation contains much less byproduct and is efficiently cleaned by a wastewater treatment plant, eliminating chemical pretreatment. In addition, careful selection of plant location reduced the transit distance between the VME plant and its sister derivatization plant from 1,200 to 500 miles, which lowered fuel use per transported railcar by 60 percent as an added benefit. A VME plant based on reactive distillation was built at a contract manufacturing facility in early 2009; the conventional VME plant closed later that year.

The Dow Chemical Company

An Innovative Approach to Texturizers without Hydrofluoric Acid or Nitric Acid for Multicrystalline Silicon Photovoltaics

Solar cell fabrication includes a texturizing step. A flat surface reflects energy away from the cell, but raised structures on the surface reflect energy into the cell, increasing its energy output. The texturizing step for multicrystalline photovoltaic cells reduces reflectance and improves the efficiency of the cell; it is critical to the cell's ultimate performance.

Current texturizing technologies for multicrystalline silicon wafers require several hazardous chemicals. The photovoltaic industry currently dilutes concentrated 49-percent hydrofluoric acid (HF) and 69-percent nitric acid in an exothermic reaction to a make a bath that contains 10-percent HF and 35-percent nitric acid. The nitric acid oxidizes the silicon and the HF does the bulk etching. The handling, storage, use, and disposal of these hazardous solutions require extreme care and can contribute significant expense depending on local and regional treatment requirements.

Dow's new technology uses an alkaline hydroxide solution with an added oxidant, which behaves isotropically like the HF–nitric acid bath and delivers equivalent or better performance while significantly reducing the health, safety, and environmental negatives of the current technology. This alkaline texturizer is compatible with existing equipment configurations. The process also reduces the cost of ownership by reducing operational costs including process energy and waste treatment. The makeup chemistry for the new solution requires about 8-percent active ingredients compared to 45-percent for the HF–nitric acid bath. The HF system requires replenishment with three times more reagents than does the new system. The new technology consumes substantially fewer materials, which results in significant cost savings and less chemical waste. Dow will be alpha-testing its new, multicrystalline texturizer in January 2010 and expects to make it available commercially later in 2010. There are no other suitable replacements for HF–nitric acid on the market today or described in the literature.

Cerenol® Polyol Technology Platform for a Sustainable, Biobased Economy

E. I. du Pont de Nemours and Company

With its vision for a sustainable, biobased economy, DuPont has developed an innovative technology platform based on renewably sourced polyols. This platform integrates biology, chemistry, materials science, and engineering to develop renewably sourced products with performance equal to or better than the petrochemical products they replace.

DuPont Cerenol® is a family of high-performance poly(ether diols) made in a sustainable, unconventional, self-condensation polymerization process that primarily uses a renewably sourced ingredient, 1,3-propanediol (Bio-PDO™). The process uses a soluble acid catalyst at less than one percent by weight that is subsequently removed during purification. The benefits of the Cerenol® platform include (1) a large number of polymers and products from renewably sourced polyols, (2) high-value uses for agricultural feedstocks, and (3) manufacturing processes that not only eliminate hazardous chemicals and process conditions but are also more energy-efficient and generate reduced levels of greenhouse gas emissions versus competing petroleum-based products. Although it has no in-kind competitors, Cerenol® has a significantly lower environmental footprint than does the related petroleum-based compound, poly(tetramethylene ether glycol), as determined by an ISO 14000-compliant life cycle analysis (LCA). From cradle-to-gate, Cerenol® provides 30-percent savings in nonrenewable energy and a 40-percent reduction in greenhouse gas (GHG) emissions.

The exceptional properties of Cerenol® make it attractive for a variety of end-use applications, including performance coatings, inks, lubricants, functional fluids, plasticizers, and personal care products. Cerenol® polymers are also ideal building blocks for several value-added thermoplastic elastomers such as polyurethanes, spandex, copolyether esters, and copolyether ester amides. DuPont's Cerenol® products include two high-performance industrial Imron® polyurethane coating products and Hytrel® RS thermoplastic elastomers for the automotive and sporting goods markets. Over the last two years, more than 20 customers have adopted Cerenol® polyols in their product development with guidance and technology licensed from DuPont; six customer products are in the marketplace today.

Chlorantraniliprole: Designing Green Chemistry for Insect Control

E. I. du Pont de Nemours and Company

Historically, developers of pesticide active ingredients focused primarily on the effectiveness of their pesticides against target pests. Now, however, new pesticide active ingredients must also work by new modes of action to minimize the development of resistance and meet societal demands for safety to humans and the environment. Consumers expect affordable, high-quality food that is produced with minimal impact on the environment. These expectations are reflected in higher regulatory hurdles.

To meet these demands and expectations, DuPont redesigned its discovery process to include early optimization of key health and environmental characteristics along with biological efficacy. For its new insecticide, DuPont evaluated over 2,000 candidate analogs to find one with the right balance in the complex dynamic of pesticidal efficacy, low toxicity to mammals and other nontarget species, and environmental attributes. The result, chlorantraniliprole, is one of the most active and least toxic chemical insecticides ever discovered. It is a replacement for organophosphate insecticides such as azinphos-methyl, pyrethroids, and neonicotinoids. Chlorantraniliprole is effective at lower application rates and requires fewer applications per growing season than other pesticides. It is effective against several pests that have developed resistance to other pesticides.

Known by the trade names Rynaxypyr® and Calteryx™, for crop and turf applications respectively, chlorantraniliprole controls insect pests through a new mode of action: activation of insect ryanodine receptors (RyRs). Chlorantraniliprole is remarkably selective for insect over mammalian RyRs; this selectivity is a key attribute of its low toxicity and high margins of exposure. In 2008, EPA registered Rynaxypyr® as a reduced-risk pesticide for several major uses. It was the first anthranilic diamide insecticide registered for use in the United States. After less than 20 months of sales, products containing chlorantraniliprole have achieved significant adoption by growers, approaching 10 percent of the total insecticide market on key target crops.

Foam Supplies, Inc.

Ecomate® Environmentally Benign Blowing Agent for Polyurethane Foams

For many years, chlorofluorocarbons (CFCs) were the preferred 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 are scheduled for phaseout in the United States in 2010. A related problem is that some foam blowing agents, including CFCs, HCFCs, and hydrofluorocarbons (HFCs), have very high global warming potentials (GWPs). HCFCs and HFCs have GWPs of 725–1810, compared to 1.00 for carbon dioxide (CO_2).

Foam Supplies developed ecomate® (its trade name for methyl formate) blowing agent to replace CFCs, HCFCs, and HFCs as blowing agents for polyurethane foams. Ecomate® blowing agent has zero ODP and zero GWP. Because it does not contribute to smog formation, ecomate® blowing agent is also volatile organic compound (VOC)-exempt. Each pound of ecomate® blowing agent replaces about two pounds of alternatives, so one million pounds of ecomate® blowing agent could eliminate 1.4–3.4 billion pounds of carbon dioxide equivalents (CO_2e) or 0.6–1.5 million metric tons of CO_2e. Ecomate® blowing agent costs substantially less than HFCs, and there are usually no significant expenses associated with implementing the ecomate® technology. Using ecomate® foaming systems allows manufacturers to help the environment without increasing costs.

Ecomate® technology has outstanding properties and low environmental impact. It has been demonstrated in pour-in-place, boardstock, and spray insulation systems as well as boat flotation foam. Ecomate® foaming systems have been introduced widely into refrigeration applications. Using ecomate® blowing agent in polyurethane foams has saved close to 1 million metric tons per year of high-GWP compounds such as HFC-134a and HFC-245fa.

Henkel Technologies

A Safer, Environmentally Superior, High-Performance Acid Inhibitor Designed to Protect Metallic Infrastructure during Industrial Cleaning

Since the early 1900's, additives have been used to prevent base-metal attack by acids during industrial cleaning. These additives have made cleaning highly efficient through reductions in acid use, base-metal attack, and hydrogen generation, but early acid inhibitors were very toxic. Typical current products include heterocyclic amines and sulfur compounds, benzyl sulfonium salts, formaldehyde, naphthalene and pyridine derivatives, thioureas, propargyl alcohol, and alkylphenol ethoxylate surfactants (APEs), combined with solvents isopropanol or methanol and water.

Henkel has recently developed safer inhibitors including a new hydrochloric acid (HCl) inhibitor for steel mills that is free of propargyl alcohol and flammable solvents and is an inhibitor for a variety of acids used in food processing equipment cleaning. This invention involves high-performance inhibition that matches the high performance of the best current product. Henkel's best inhibitor, Rodine® 213, is based on a sustainable raw material derived from pine tree waste. Rodine® 213-SF uses dehydroabietylamine solubilized with glycolic acid. For safety, paraformaldehyde replaces uninhibited 37-percent formaldehyde. The inhibitor reaction takes place in one step with zero waste. The use of poly(alkoxylated propargyl alcohol) and elimination of coproducts including vinyl methyl ketone and several chlorinated organics eliminates flammability and toxicity. Residual formaldehyde is reduced by 90 percent. Finally, alkoxylated natural fatty alcohols replace APE surfactants, which are estrogen mimics.

Replacing all of Henkel's current sales of acid inhibitors with its new product would eliminate 27,300 pounds of propargyl alcohol, 94,680 pounds of alkylphenol alkoxylated surfactants, 68,750 pounds of isopropanol, 30,000 pounds of hydrochloric acid, 74,430 pounds of acetone, 13,480 pounds of vinyl methyl ketone, 28,640 pounds of 37-percent formaldehyde, 2,130 pounds of residual formaldehyde, and 630 pounds of chlorinated organics.

Henkel has completed final formulation improvements, testing, and reviews for full-scale manufacturing. Rodine® 213-SF is currently being advertised and sampled to potential customers.

Tru-Core® Protection System for Wood

Kop-Coat, Inc.

Wood is the most widely used building material in the United States. Its environmentally positive characteristics include low embodied energy and sustainability, but its susceptibility to decay and insect attack can limit its durability. For over 100 years, people have used chemical treatments to improve wood's resistance to destructive organisms and extend its service life. Many traditional preservative chemicals had relatively poor health, safety, and environmental profiles, however. A newer generation of wood preservatives has addressed some of the drawbacks of the older chemicals, but delivering these preservatives into the wood is still largely based on 19th-century technologies.

The Tru-Core® Protection System rapidly delivers globally accepted wood preservatives and insecticides deep into the core of wood substrates without high pressure, vacuum treatment, or volatile organic solvents such as mineral spirits. The Tru-Core® system embodies a unique chemical infusion process that uses nonvolatile, polar, bonding carriers (amine oxides) in a minimal amount of water to penetrate the cellular structure of wood and to deposit and bind wood-protecting preservatives and insecticides deep within the substrate. Buffers (e.g., borates) bring the pH to 7 or 8 to control the penetration and binding. Unlike conventional treatments, the Tru-Core® process uses very little water to carry the preservatives; thus, it eliminates the costly, energy-consuming redrying of wood after treatment. The Tru-Core® treatment is applied to the wood surface by dipping or inline spraying. The preservatives typically require a 12–24 hour activation period for full penetration. Afterwards, the wood can be used or subjected to further processing or painting without drying.

The Tru-Core® technology has recently been granted a U.S. patent. This process is in commercial use in three plants in the United States and eleven plants in New Zealand, where it has largely replaced a vacuum-treatment process requiring large amounts of petroleum-based solvents that emitted volatile organic compounds (VOCs).

NEXAR™ Polymer Membrane Technology for Water Purification and Moisture Management

Kraton Polymers LLC

The global production of desalinated water is currently 11 billion gallons per day and is growing each year. Sixty percent of desalination capacity is based on membrane technology. Current membranes are limited, however, by their poor resistance to chlorine. Typical desalinization plants chlorinate water to prevent biofouling. They then dechlorinate it before passing it through the desalination membrane, and, finally, rechlorinate it prior to its entry into the drinking water system. With current technology, capital equipment and energy account for 70–80 percent of the cost of producing desalinated water and, typically, energy costs alone account for up to 40 percent of operational costs.

Kraton Polymers addressed these problems by developing NEXAR™ polymer membrane technology for applications requiring high water and ion flux. Reverse osmosis and electrodialysis are two of the key market segments in which NEXAR™ technology will increase water flux and save energy. High water-transport materials like NEXAR™ polymers offer a solution to reduce energy consumption. The system increases flux at a given pressure, thus allowing greater efficiency of the overall process. NEXAR™ polymers exhibit good chlorine resistance that could allow processes that do not require a pretreatment to remove chlorine.

Kraton's NEXAR™ polymers are sulfonated pentablock copolymers, a new family of ionomeric polymers. The unique pentablock structure allows regiospecific sulfonation of the midblock, which is poly(styrene-co-styrene sulfonate); nonionic endblocks provide strength and toughness in dry and wet conditions. Kraton Polymers improved the synthesis of sulfonated block copolymers by eliminating halogenated hydrocarbons; this has significant environmental and human health benefits. In addition, the synthesis of this unique structure uses as little as half the amount of aliphatic hydrocarbon.

NEXAR™ technology brings performance enhancements to numerous commercial applications including liquid separation, humidification control, breathable textiles, and advanced batteries. During 2009, Kraton completed initial field efficacy trials and began commercial sales.

Pfizer Inc.

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 including the United States. Pfizer's new route to Pregabalin is an innovative biocatalytic process that is more sustainable than the chemical process it replaced. Pfizer has implemented exceptional innovation in green chemistry by 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. Key innovations were overcoming product inhibition in the biocatalytic step to allow exceptionally high substrate concentrations and designing, building, and validating a new continuous plant to allow recycling of the undesirable enantiomer. The revised route dramatically improves environmental performance, worker safety, and process efficiency. Now, 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 successfully implemented its new biocatalytic process in a production facility at a 10 metric ton batch size. Between 2007 and 2020, Pfizer estimates that the new process will eliminate 185,000 metric tons of solvent, 4,800 metric tons of mandelic acid, 11,000 metric tons of the starting cyanodiester, and 2,000 metric tons of Raney® nickel. The biocatalytic process also uses 83 percent less energy than the classical resolution process and reduces the E factor of the process from 86 to 9. In the current chemoenzymatic route, the enzyme is less expensive than the resolving agent, (*S*)-mandelic acid, used in the first-generation route. Pfizer believes it has brought an important pain-relieving medicine to the patient in the most environmentally responsible manner.

Waterborne, Low-VOC, Alkyd Acrylic Dispersion Technology

The Sherwin Williams Company

The high cost and uncertain availability of petroleum- and oil-based raw materials makes dependence on these 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) are necessitating VOC-compliant waterborne technologies that perform like solventborne coatings.

Responding to this challenge, Sherwin Williams developed a novel, waterborne, low-VOC, alkyd acrylic dispersion (LAAD) that incorporates sustainable and naturally occurring materials. Poly(ethylene terephthalate) (PET) is commonly used in beverage bottles. Sherwin Williams depolymerizes post-industrial, recycled, or virgin PET with soy fatty acids and then repolymerizes it with trimethylol ethane. This soy–PET liquid polyester is grafted with hydrophobic and hydrophilic acrylic monomers in soybean oil (a reactive diluent) instead of solvent. The anionic prepolymer is dispersed in water using triethylamine under high-shear conditions; the resulting dispersion is formulated into coatings. The polymer dispersion has hard PET segments of 1–2 microns for hardness; acrylic functionality for improving dry times and barrier properties; and soya functionality to help in film formation, gloss, flexibility, and cure.

Coatings formulated from LAAD technology perform like the conventional, solvent-based alkyd paints with high gloss and excellent adhesion, moisture resistance, and hydrolytic (shelf) stability. This surfactant-free technology enables alkyd-like properties with water cleanup and less odor than currently available conventional and high-solids alkyd and latex coatings. Replacing all solventborne coatings (500 million gallons in 2007) with LAAD technology would use about 250 million pounds of recycled PET and about 320 million pounds of soybean oil, replace over a million barrels of crude oil, and eliminate 800 million pounds of VOCs. The LAAD technology could also provide a secondary binder for conventional latex paints. Sherwin Williams commercialized its LAAD technology in industrial maintenance coatings in 2009 and will launch waterborne products for interior and exterior architectural products in 2010.

Green Chemistry Process for the Large-Scale Manufacture of Polyamino Acids

Sigma-Aldrich

Polyamino acids have properties that mimic proteins, making them ideal for targeted drug delivery. They are water-soluble, selective, biodegradable, low-toxicity molecules. Their production involves both unstable intermediate amino acid *N*-carboxyanhydrides (NCAs) and polymer processing. These two steps involve large quantities of hazardous chemicals including phosgene, hydrogen bromide–acetic acid, acetone, and dioxane.

Sigma-Aldrich developed novel manufacturing processes for polyamino acids that minimize hazardous chemicals while improving quality and efficiency. For NCA production, they removed uncertainty in quality and yield, which is critical for targeted drug delivery. They also eliminated repeated NCA recrystallizations and minimized manufacturing runs by over 30 percent, consequently reducing phosgene and tetrahydrofuran by 30 percent and ethyl acetate and hexane by 50 percent.

Sigma-Aldrich also applied green practices to manufacturing poly-L-glutamic acid, a major drug-delivery polymer, which requires hazardous operations with highly flammable solvents and hydrogen bromide–acetic acid or hydrogenation. By replacing a benzyl protecting group with an ethyl group, they were able to replace hazardous chemicals with water-based chemicals, decrease cycle time by more than half, and improve the scaleup potential 10-fold.

The production of polylysine polymers and polyamino acid copolymers achieved similar savings with manufacturing processes that reduce hazardous chemicals and improve product yield and quality. For polylysine polymers, the yield increased from 10–30 percent to 43–53 percent with half the hazardous chemicals (dioxane, hydrogen bromide–acetic acid, and acetone). Production runs were halved, saving hundreds of gallons of hazardous chemicals, generating less waste, and saving energy. Polyamino acid copolymer production was switched to water-based systems, eliminating generation of the hazardous lachrymator byproduct, benzyl bromide, and saving hydrogen bromide–acetic acid and acetone.

Sigma-Aldrich believes that its scientific contributions will lead to efficient chemotherapeutic treatments for serious human diseases such as cancer and diabetes and pave the way for greener chemical industry practices.

STERIS Corporation

An Environmentally Friendly Alternative for Cleaning Surgical Instruments in Healthcare Facilities

Cleaning is the single most important step in processing a surgical instrument for reuse. 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." Inorganic and organic soils that are not removed from surgical instruments during cleaning can negatively compromise subsequent disinfection and sterilization of surgical instruments, leading to patient infection. If surgical instruments are repeatedly exposed to harsh chemicals, their useful life may be shortened, leading to increases in both cost and waste for the healthcare facility. Current, traditional chemistries have several disadvantages: poor substrate compatibility, ineffective cleaning performance, packaging that is not ergonomic, and ingredients that are not environmentally friendly.

STERIS developed Prolystica® Ultra Concentrate cleaning chemistries and introduced them in 2006 as an innovative, green alternative. The product line includes a neutral pH enzymatic presoak and cleaner, a neutral pH detergent, and an alkaline detergent with lower alkalinity. All three formulations are phosphate-free. They contain surfactants that are biodegradable, as well as biodegradable corrosion inhibitors (biodegradable polycarboxylic acid), chelating agents (an iminodisuccinate and a methyl glycine diacetate), and sequestering agents (including inulin derived from chicory). These 10-fold-concentrated cleaning products provide industry-leading cleaning and protection for surgical instruments and are 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. Prolystica® Ultra Concentrate products are now in use at 1,442 healthcare facilities in the United States and Canada.

Thermphos USA Corp.

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

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

Carboxymethyl inulin (CMI), developed by Solutia in collaboration with Royal Cosun, provides an environmentally friendly, cost-effective, safe, and versatile alternative to traditional scale inhibitors in a wide variety of industrial applications. Moreover, CMI is a good chelator and an excellent dispersant, which makes it an attractive ingredient for household detergents. Recent research has shown that CMI can be formulated in lower amounts than can polyacrylates and polyaspartates. Unlike polyaspartate, CMI is stable in the presence of low levels of oxidizing agents like hydrogen peroxide. Thermphos has discovered synergistic effects between CMI and other chelants and has filed patents.

Phosphorous in detergents is a growing environmental concern. Many commercial detergents include CMI because it can be used in phosphorus-free formulas at much lower concentrations than other co-builders. CMI is based on inulin, an oligosaccharide harvested from the roots of chicory. It does not compete with food production. Current commercial applications include household, industrial, and institutional detergents and cleaners, secondary oil recovery, and pulp and paper processing. CMI can also replace poorly biodegradable scale inhibitors in water and process water treatment, sugar refining, and other industrial applications. It performs well on sulfate scales, especially under high total dissolved solids and high iron conditions. CMI is not a strong chelator of transition metals and, therefore, does not contribute to the unintended mobilization of heavy metals. CMI is the first inulin derivative to reach the market.

Diesel and Jet Fuels from Renewable Resources That Are Fungible with Petroleum Fuels

UOP LLC

Two roadblocks preventing the widespread use of renewable sources in transportation fuel are compatibility with the existing fuel distribution infrastructure and blending compatibility with current petroleum-based fuels. The primary components of current renewable transportation fuel are ethanol and fatty acid methyl ester (FAME; biodiesel). Because neither of these components is compatible with the existing infrastructure, they must be splash-blended at fuel distribution terminals. Also, they are limited to about 10 percent by volume because they are incompatible with current gasoline, jet, and diesel engines. This presents a huge hurdle for their commercial acceptance.

Scientists and engineers at UOP have developed the innovative approach of hydroprocessing biofeedstocks into transportation fuels. Using new catalysts and process-flow schemes, UOP can produce both diesel and jet fuels from a broad range of biofeedstocks including jatropha, camelina, algal oil, animal fats, and used cooking oil. Their products are compatible with the existing refinery infrastructure, technology, and distribution network. More importantly, the bioproducts resulting from the UOP processes can be blended directly into current fuels without modifying the jet or diesel engines or the delivery infrastructure.

UOP took these inventions through full process design leading to the UOP/Eni Ecofining™ process for green diesel, which it licensed to four refiners. UOP has extended its technology to jet fuel and produced commercial quantities of green jet fuel. Five commercial demonstration flights by major international airlines have used the fuel successfully. Although the diesel and jet processes are similar, the detailed flow schemes and catalysts are different because of the differing specifications for the two fuels. A life cycle analysis (LCA) estimates greenhouse gas (GHG) savings to be 84 percent for green jet fuel and 89 percent for green diesel. UOP has filed a total of 28 U.S. patent applications for the Ecofining™ diesel and jet fuel technologies.

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