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Presidential Green Chemistry Challenge Awards Program:

Summary of 2012 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.

Throughout the 17 years of the awards program, EPA has received 1,492 nominations and presented awards to 88 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.

Each year our 88 winning technologies are together responsible for:

- Reducing the use or generation of 825 million pounds of hazardous chemicals
- Saving 21 billion gallons of water
- Eliminating 7.9 billion pounds of carbon dioxide releases to air

And adding the benefits from the nominated technologies would greatly increase the program's total benefits.

This booklet summarizes entries submitted for the 2012 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 2012 awards. Judging criteria included health and environmental benefits, scientific innovation, and industrial applicability. Six of the nominated technologies were selected as winners and were nationally recognized on June 18, 2012, 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 2012 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 based on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.

Academic Award

Synthesizing Biodegradable Polymers from Carbon Dioxide and Carbon Monoxide

Professor Geoffrey W. Coates, Department of Chemistry, Cornell University

Innovation and Benefits

Carbon monoxide and carbon dioxide derived from biomass or other carbon sources are ideal feedstocks for chemicals, but there had been no efficient way to make them into valuable polymers. Professor Coates developed a family of catalysts that convert carbon dioxide and carbon monoxide into polymers. Novomer, Inc. is using his discoveries to develop a range of innovative, high-performance products, including can and coil coatings, adhesives, foams, and plastics.

Plastics improve our lives in countless ways, but they also pose a serious threat to our environment. Virtually all plastics are derived from scarce fossil fuels that pose their own danger, including oil well leaks and global warming induced by carbon dioxide (CO_2). Of the 150 million tons of plastics made each year worldwide, only a small fraction is recycled. The rest end up in landfills or worse as litter.

CO_2 and carbon monoxide (CO) are ideal feedstocks for polymer synthesis. They can be derived from many low-cost sources including biorenewable agricultural waste, abundant coal, or even from industrial waste gas. The challenge with using them, however, lies in converting them into useful products efficiently. Professor Geoffrey Coates has developed innovative processes to synthesize plastics from inexpensive, biorenewable substances including carbon dioxide, carbon monoxide, plant oils, and lactic acid.

Professor Coates has developed a new family of catalysts over the last decade that can effectively and economically turn CO_2 and CO into valuable polymers. These catalysts have high turnover frequencies, turnover numbers, and selectivities. As a result, only a small amount of catalyst is required leading to cost-effective commercial production for the first time. These catalysts can also be used in highly efficient continuous flow processes.

Professor Coates has invented active and selective catalysts to copolymerize CO_2 and epoxides into high-performance polycarbonates. Professor Coates also invented a class of catalysts that can insert one or two molecules of CO into an epoxide ring to produce β-lactones and succinic anhydrides. Both of these products have many uses in synthesizing pharmaceuticals, fine chemicals, and plastics. Polymers made from CO_2 and CO contain ester and carbonate linkages. These polymers exhibit unique performance in current commodity plastic applications and in some cases are ultimately biodegradable.

Professor Coates's work forms the scientific foundation of Novomer Inc., a start-up company backed by venture capital. In 2010, Novomer and DSM announced an agreement to develop coatings using the new polycarbonates made with Coates's catalysts. Prototype high-performance industrial coil coatings are moving from development toward commercialization. There is potential to develop a coating system to replace the bisphenol A (BPA) epoxy coatings that line most food and drink cans worldwide. This discovery is important, as BPA is a suspected endocrine disrupter that can migrate out of coatings over time. The novel polymer is currently sold to companies that manufacture electronics because the thermally degradable nature of the polymer allows more efficient production of electronic components. The new polycarbonate coating is expected to require 50 percent less petroleum to produce and will sequester up to 50 weight percent CO_2. Lifecycle analysis shows that at full market penetration, Novomer's materials have the potential to sequester and avoid approximately 180 million metric tons of annual CO_2 emissions.

Academic Award

Professor Robert M. Waymouth, Department of Chemistry, Stanford University

Dr. James L. Hedrick, IBM Almaden Research Center

Organic Catalysis: A Broadly Useful Strategy for Green Polymer Chemistry

Innovation and Benefits

Traditional metal catalysts required to synthesize polyesters and other common plastics end up trapped in the plastic, raising human health and environmental concerns. Professor Waymouth and Dr. Hedrick discovered an array of alternatives—metal-free catalysts—that are highly active and able to make a wide variety of plastics. Their discoveries include catalysts that can depolymerize plastic and enable cradle-to-cradle recycling.

Catalysis is a foundation for sustainable chemical processes, and the discovery of highly active, environmentally benign, catalytic processes is a central goal of green chemistry. Conventional routes to polyesters rely on metal catalysts such as those derived from tin complexes, even though the residual metal catalysts used for high-volume plastics can have negative environmental impacts in solid waste. For this reason, the European Union recently phased out many organotin compounds. As a result, research on organic catalysts to replace the tin-based workhorse catalysts has gained significant prominence in industrial settings related to important commodity polymers such as siloxanes, urethanes, nylons, and polyesters.

Dr. James L. Hedrick and Professor Robert M. Waymouth have developed a broad class of highly active, environmentally benign organic catalysts for synthesizing biodegradable and biocompatible plastics. Their technology applies metal-free organic catalysts to the synthesis and recycling of polyesters. They discovered new organic catalysts for polyester synthesis whose activity and selectivity rival or exceed those of metal-based alternatives. Their approach provides an environmentally attractive, atom-economical, low-energy alternative to traditional metal-catalyzed processes. Their technology includes organocatalytic approaches to ring-opening, anionic, zwitterionic, group transfer, and condensation polymerization techniques. Monomer feedstocks include those from renewable resources, such as lactides, as well as petrochemical feedstocks. In addition to polyesters, Dr. Hedrick and Professor Waymouth have discovered organocatalytic strategies (1) to synthesize polycarbonates, polysiloxanes, and polyacrylates, (2) to chemically recycle polyesters, (3) to use metal-free polymers as templates for inorganic nanostructures for microelectronic applications, and (4) to develop new syntheses for high-molecular-weight cyclic polyesters. This team has shown that the novel mechanisms of enchainment brought about by organic catalysts can create polymer architectures that are difficult to synthesize by conventional approaches.

The team also developed organic catalysts to depolymerize poly(ethylene terephthalate)(PET) quantitatively, allowing recycling for PET from bottles into new bottles as a way to mitigate the millions of pounds of PET that plague our landfills. Dr. Hedrick and Professor Waymouth also demonstrated that their organic catalysts tolerate a wide variety of functional groups, enabling the synthesis of well-defined biocompatible polymers for biomedical applications. Because these catalysts do not remain bound to the 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 this approach. Professor Waymouth and Dr. Hedrick have produced over 80 manuscripts and eight patents on the design of organic catalysts for polymer chemistry with applications in sustainable plastics, biomedical materials, and plastics for recycling.

Small Business Award

Using Metathesis Catalysis to Produce High-Performing, Green Specialty Chemicals at Advantageous Costs

Elevance Renewable Sciences, Inc.

Innovation and Benefits

Elevance employs Nobel-prize-winning catalyst technology to break down natural oils and recombine the fragments into novel, high-performance green chemicals. These chemicals combine the benefits of both petrochemicals and biobased chemicals. The technology consumes significantly less energy and reduces greenhouse gas emissions by 50 percent compared to petrochemical technologies. Elevance is producing specialty chemicals for many uses, such as highly concentrated cold-water detergents that provide better cleaning with reduced energy costs.

Elevance produces high-performance, cost-advantaged green chemicals from renewable oils. Its processes use Nobel Prize-winning innovations in metathesis catalysis, consume significantly less energy, and reduce greenhouse gas (GHG) emissions by 50 percent compared to petrochemical technologies. The processes use a highly efficient, selective catalyst to break down natural oils and recombine fragments. The core technology is based on the work of Nobel Laureate Dr. Robert H. Grubbs. In 2011, Elevance expanded its proprietary technology with a licensing agreement with XiMo AG to use proprietary molybdenum and tungsten metathesis catalysts based on the work of Nobel Laureate Dr. Richard Schrock.

The resulting products are high-value, difunctional chemicals with superior functional attributes previously unavailable commercially. These molecules combine the functional attributes of an olefin, typical of petrochemicals, and a monofunctional ester or acid, typical of biobased oleochemicals, into a single molecule. Conventional producers have to blend petrochemicals and biobased oleochemicals in attempts to achieve these functional attributes simultaneously, which when possible, increase their production costs. Elevance's difunctional building blocks change this paradigm by creating specialty chemical molecules which simultaneously include desired attributes enabled by both chemical families, such as lubricant oils with improved stability or surfactants with improved solvency.

Elevance's low-pressure, low-temperature processes use a diversity of renewable feedstocks that yield products and byproducts with low toxicity. Elevance's processes result in lower source pollution, production costs, and capital expenditures than petrochemical refineries. Currently, Elevance is the only company that can produce these difunctional chemicals. The company's ability to manufacture biochemicals for multiple products reduces reliance on petrochemicals and provides more effective, sustainable products to consumers.

The company makes difunctional molecules as part of its specialty chemical business. Elevance's products enable novel surfactants, lubricants, additives, polymers, and engineered thermoplastics. For instance, Elevance is producing specialty chemicals to enable cold water detergents that have more concentrated formulations and improved solvency for better cleaning, to improve sustainability metrics, and to reduce energy costs for customers and consumers. Other examples include biobased anti-frizz and shine additives for leave-in hair care products to replace petroleum-based petrolatum, alternatives to paraffin for high performance waxes, novel plastic additives for poly(vinyl chloride) (PVC) and unique monomers for biobased polymers and engineered plastics.

Elevance has completed validation in toll manufacturing. It is building world-scale facilities in Gresik, Indonesia, and Natchez, Mississippi, with combined annual production capacity over 1 billion pounds and exploring sites in South America. Elevance has also secured strategic partnerships with value chain global leaders to accelerate rapid deployment and commercialization for these products.

Greener Synthetic Pathways Award

Codexis, Inc.

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

An Efficient Biocatalytic Process to Manufacture Simvastatin

Innovation and Benefits

Simvastatin, a leading drug for treating high cholesterol, is manufactured from a natural product. The traditional multistep synthesis was wasteful and used large amounts of hazardous reagents. Professor Tang conceived a synthesis using an engineered enzyme and a practical low-cost feedstock. Codexis optimized both the enzyme and the chemical process. The resulting process greatly reduces hazard and waste, is cost-effective and meets the needs of customers. Some manufacturers in Europe and India use this process to make simvastatin.

Simvastatin, a leading cholesterol lowering drug, was originally developed by Merck under the brand name Zocor®. In 2005, Zocor® was Merck's best selling drug and the second-largest selling statin in the world with about $5 billion in sales. After when Zocor® went off patent in 2006, simvastatin became the most-prescribed statin, with 94 million prescriptions filled in 2010, according to IMS Health.

Simvastatin is a semisynthetic derivative of lovastatin, a fungal natural product. Simvastatin contains an additional methyl group at the C2' position of the lovastatin side chain. Introduction of this methyl group in lovastatin using traditional methods requires a multistep chemical synthesis. In one route, lovastatin is hydrolyzed to the triol, monacolin J, which is protected by selective silylation, esterified with dimethylbutyryl chloride, and deprotected. Another route involves protecting the carboxylic acid and alcohol, methylating the C2' with methyl iodide, and deprotecting. Despite considerable optimization, these processes have overall yields of less than 70 percent, are mass-intensive due to protection/deprotection, and require copious amounts of toxic and hazardous reagents.

Professor Yi Tang and his group at UCLA conceived a new simvastatin manufacturing process and identified both a biocatalyst for regioselective acylation and a practical, low-cost acyl donor. The biocatalyst is LovD, an acyltransferase that selectively transfers the 2-methylbutyryl side chain to the C8 alcohol of monacolin J sodium or ammonium salt. The acyl donor, dimethylbutyryl-*S*-methylmercaptopropionate (DMB-SMMP), is very efficient for the LovD-catalyzed reaction, is safer than traditional alternatives, and is prepared in a single step from inexpensive precursors. Codexis licensed this process from UCLA and subsequently optimized the enzyme and the chemical process for commercial manufacture. Codexis carried out nine iterations of in vitro evolution, creating 216 libraries and screening 61,779 variants to develop a LovD variant with improved activity, in-process stability, and tolerance to product inhibition. The approximately 1,000-fold improved enzyme and the new process pushed the reaction to completion at high substrate loading and minimized the amounts of acyl donor and of solvents for extraction and product separation.

In the new route, lovastatin is hydrolyzed and converted to the water-soluble ammonium salt of monacolin J. Then a genetically evolved variant of LovD acyltransferase from *E. coli* uses DMB-SMMP as the acyl donor to make the water-insoluble ammonium salt of simvastatin. The only coproduct of simvastatin synthesis is methyl 3-mercaptopropionic acid, which is recycled. The final yield of simvastatin ammonium salt is over 97 percent at a loading of 75 grams per liter of monacolin J. The nominated technology is practical and cost-effective. It avoids the use of several hazardous chemicals including *tert*-butyl dimethyl silane chloride, methyl iodide, and *n*-butyl lithium. Customers have evaluated the simvastatin produced biocatalytically and confirmed that it meets their needs. Over 10 metric tons of simvastatin have been manufactured using this new process.

Greener Reaction Conditions Award

MAX HT® Bayer Sodalite Scale Inhibitor

Cytec Industries Inc.

Innovation and Benefits

The "Bayer process" converts bauxite to alumina, the raw material for making aluminum. Mineral scale deposited on the heat exchangers and pipes in Bayer process plants increases energy use. Removing the scale requires stopping production and cleaning with sulfuric acid. Cytec's product hinders scale growth. Eighteen plants worldwide are using MAX HT® inhibitor, saving trillions of Btu (British thermal units) annually. Fewer cleaning cycles also reduce hazardous acid waste by millions of pounds annually.

The Bayer process converts bauxite ore to alumina, the primary raw material for aluminum. The process involves extracting alumina trihydrate from bauxite ore using hot caustic solution. After separating out the insoluble solids, the alumina trihydrate is precipitated and the spent liquor is recycled. Heat exchangers re-concentrate the liquor to the optimum concentration of caustic and then heat it to the proper temperature for digestion. Silica present as silicates, primarily clay materials, dissolves quickly in typical Bayer liquor used to digest alumina, resulting in the liquor being supersaturated in silica, particularly after precipitation of the alumina trihydrate. The silica in the liquor reacts with the caustic and alumina on the hot surfaces of the heat exchangers; as a result, sodalite scale (i.e., crystalline aluminosilicate) builds up on the heat exchangers and interstage piping in the process. This reduces the efficiency of the heat exchangers. Periodically, Bayer process plant operators must take the equipment off line for cleaning that involves removing the scale with sulfuric acid. The used acid is a waste stream that requires disposal. In addition to the acid cleaning, much of the interstage piping requires cleaning with mechanical means such as jackhammers to remove the scale.

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. The polymers have molecular weights in the range 10,000 and 30,000. Their synthesis involves polymerizing a monomer containing a silane group or reacting polymer backbone with a reagent containing the silane group. Dosages range from 20 to 40 ppm. Assessments of these polymers under EPA's Sustainable Futures Program indicate low overall concern for human health and the aquatic environment.

Eliminating sodalite scale from heater surfaces has 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 losses. Reducing the use of steam reduces emissions from burning carbon-based fuels. Finally, reducing the sulfuric acid used to clean heaters reduces both worker exposure and waste. Typically, MAX HT® inhibitor increases the on-stream time for a heater from 8–10 days to 45–60 days for digestion and from 20–30 days to over 150 days for evaporators.

There are about 73 operating Bayer process plants worldwide with annual capacities of 0.2–6 million tons of alumina per plant; most plants are in the 1.5–3 million ton range. Eighteen Bayer process plants worldwide have adopted this technology; seven more plants are testing it. Each plant using MAX HT® saves $2 million to $20 million annually. The realized annual energy savings for all plants together are 9.5 trillion to 47.5 trillion Btu, which is the equivalent of about 1.1 billion to 7.7 billion pounds of carbon dioxide (CO_2) not released to the atmosphere. Fewer cleaning cycles and less acid per cycle result in a realized annual hazardous waste reduction of 76 million to 230 million pounds for all plants together.

Buckman International, Inc.

Enzymes Reduce the Energy and Wood Fiber Required to Manufacture High-Quality Paper and Paperboard

Innovation and Benefits

Traditionally, making strong paper required costly wood pulp, energy-intensive treatment, or chemical additives. But that may change. Buckman's Maximyze® enzymes modify the cellulose in wood to increase the number of "fibrils" that bind the wood fibers to each other, thus making paper with improved strength and quality—without additional chemicals or energy. Buckman's process also allows papermaking with less wood fiber and higher percentages of recycled paper, enabling a single plant to save $1 million per year.

The paper and packaging industry is an important part of the U.S. economy, with product sales of $115 billion per year and employment of about 400,000 people. Previously, papermakers who needed to improve paper strength were limited to adding costly pulps, increasing mechanical treatment that expends significant energy, or using various chemical additives such as glyoxalated polyacrylamides and polyacrylamide copolymers.

Enzymes are extremely efficient tools for replacing conventional chemicals in papermaking applications. Buckman's Maximyze® technology consists of new cellulase enzymes and combinations of enzymes derived from natural sources and produced by fermentation. These enzymes were not previously available commercially. Wood fibers treated with Maximyze® enzymes prior to refining (a mechanical treatment unique to papermaking) have substantially more fibrils that bind the wood fibers to each other. Maximyze® enzymes modify the cellulose polymers in the wood fiber so that the same level of refining produces much more surface area for hydrogen bonding, which is the basic source of strength in paper. As a result, Maximyze® treatment produces paper and paperboard with improved strength and quality.

Maximyze® improves strength so the weight of the paper product can be reduced or some of the wood fiber can be replaced with a mineral filler such as calcium carbonate. Maximyze® treatment makes it possible to use higher percentages of recycled paper. Maximyze® treatment uses less steam because the paper drains faster (increasing the production rate) and uses less electricity for refining. Maximyze® treatment is less toxic than current alternatives and is safer to handle, manufacture, transport, and use than current chemical treatments. These and other benefits are produced by Maximyze® treatment, a biotechnology that comes from renewable resources, is safe to use, and is itself completely recyclable.

The first commercial application began with the production of fine paper within the past two years. In 2011, a pulp and paper manufacturer in the Northwest began to add Maximyze® enzymes to the bleached pulp used to produce paperboard for food containers. This change increased machine speed by 20 feet per minute for a 2 percent increase in production. It also reduced the level of mechanical refining by 40 percent for a substantial savings in energy. Finally, it reduced the basis weight (density) of the paper by 3 pounds per 1,000 square feet without changing the specifications for quality. Overall, Maximyze® treatment reduced the amount of wood pulp required by at least 1 percent, which reduced the annual amount of wood needed to produce the food containers by at least 2,500 tons. Buckman estimates that using Maximyze® technology for this one machine can save wood pulp equivalent to 25,000 trees per year. Another large mill producing fine paper has used Buckman's technology since January 2010 and saved over $1 million per year. Since introducing this new technology, Buckman has expanded it and is now applying it successfully in over 50 paper mills in the United States and beyond.

Entries from Academia

Ethyl L-Lactate as a Tunable Solvent for Greener Synthesis of Diaryl Aldimines

Professor Jacqueline Bennett, Department of Chemistry & Biochemistry, State University of New York Oneonta and SUNY Research Foundation

Imines are essential intermediates in many pharmaceutical syntheses. For example, diaryl aldimines are feedstocks for blockbuster drugs such as Taxol® (used for chemotherapy) and Zetia® (used to reduce cholesterol). Diaryl aldimines added to polyethylene increase its photodegradation in the environment. Unfortunately, traditional syntheses of diaryl aldimines often require hazardous solvents and include energy-intensive, multihour reflux steps. Although some imine syntheses use more benign solvents or conditions, they still require long reaction times, recrystallization, or other environmentally unfriendly procedures.

Recently, Professor Bennett found that ethyl L-lactate, an FDA-approved food additive, can replace the hazardous solvents commonly used to synthesize imines. Her method is extremely efficient under ambient conditions and requires less solvent than published methods. It has a median yield of over 92 percent and a median reaction time of less than 10 minutes. The resulting imines are usually pure enough without recrystallization, avoiding additional waste. Professor Bennett's method "tunes" the polarity of ethyl L-lactate by adding water. The starting materials remain dissolved, but the imine crystallizes out of solution as it forms. Although traditional methods often drive reactions forward by removing water, Professor Bennett's method drives the reaction forward by removing the product through crystallization. To date, she and her undergraduate research students have synthesized nearly 200 imines using this method; her students in teaching labs have made more than half of these in a green chemistry project. In summary, the ethyl L-lactate method is faster, usually results in higher purity and yield, uses less energy, uses less solvent, generates less waste, and uses a more benign solvent than published methods.

A patent application for this method was published in 2011. Professor Bennett is now studying these imines in biological and other applications. All are fluorescent and some are photochromic. Several show promise as fluorescent cell markers and antibacterial agents.

Sustainable Molecular Design through Biorefineries: Biomass as an Enabling Platform for Safe Oil-Thickening Agents (Amphiphiles)

Professor George John, Department of Chemistry, The City College of the City University of New York

Non-polymeric amphiphiles can form molecular gels or viscoelastic materials when they self-assemble by noncovalent interactions such as surface tension and capillary action. Amphiphiles can immobilize a large pool of organic or aqueous solvent into a gel. A wide variety of amphiphiles are currently derived, at least in part, from nonrenewable resources. In addition, their synthesis frequently requires multiple steps, energy-intensive purifications, and complex, expensive catalysts. Structuring an amphiphile such as vegetable oil into a gel alters its physical properties with or without altering its chemical properties. Current structuring agents and methods used for food tend to increase the content of saturated fatty acids and *trans*-fatty acids in oils, which may increase the risk of vascular and heart disease.

Professor John and his group have developed potent amphiphiles from biobased resources using enzyme-mediated transesterification of sugar alcohols with fatty acid donors. Upon self-assembly, these amphiphiles produce soft materials in aqueous and organic solvents. These amphiphiles exhibit superior ability to structure vegetable oils without increasing their saturated fatty acids. They are also nontoxic and biodegradable. The ease of synthesis and cheap raw materials translate into low-cost production of efficient sugar-based amphiphilic gelators. In addition, these self-assembled gels have a remarkable ability to trap highly volatile pheromones and release them slowly, so they remain effective longer. Another application is environmentally benign oil spill recovery: when added to an oil-water mixture, Professor John's amphiphiles can selectively partition into the oil phase and convert it to a gel. This technology offers the potential to replace current oil structuring agents with safe, biobased amphiphiles resulting in enhanced performance at lower cost.

Currently, Professor John is developing next-generation, biobased amphiphiles to structure hydrophobic liquids such as vegetable oils and related compounds for food and cosmetic applications. Several food and personal care companies have expressed interest in licensing this technology.

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

Chemical Conversion of Biomass into New Generations of Renewable Fuels, Polymers, and Value-Added Products

The gradual decline of the prevailing, worldwide petroleum economy is creating an extraordinary need for alternative technologies and, hence, bioenergy research. Consequently, researchers are developing schemes to exploit lignocellulose, the most abundant organic material on the planet. These schemes vary considerably, but each aims to cleave lignocellulose into its monosaccharide components, then derive useful products from the monosaccharides efficiently and inexpensively. The most successful schemes will be those that (1) produce the highest yields, (2) minimize capital and operating expenses, and (3) allow feedstocks from the most sources.

In 2008, Professor Mascal and his group described a process that meets all three objectives. Their method involves digestion of cellulose in a biphasic aqueous acid–organic solvent reactor to give remarkably high yields of the novel organic platform chemical, 5-(chloromethyl) furfural (CMF). The method works equally well on raw biomass, producing not only CMF from the cellulose of the feedstock, but also furfural itself from the C5 sugar fraction (i.e., hemicellulose). It uses all of the carbohydrate in the biomass without requiring that lignin first be stripped from the lignocellulose.

Recently, Professor Mascal has upgraded his technology: it now produces an overall 89 percent yield from cellulose consisting of CMF (84 percent) and levulinic acid (LA, the well-known carbohydrate breakdown product) (5 percent) . The new process requires 20-fold less solvent and recycles solvent after use. The same method processes sucrose into CMF and LA in a remarkable 95 percent overall yield. The method also works well on oil seed feedstocks and leads to a 25 percent increase in biodiesel production from safflower seeds. No other method produces simple organic products directly from cellulosic materials with comparable yields. Important CMF derivatives include biofuels, renewable polymers, agrochemicals, and pharmaceuticals. The green tech companies Micromidas and Incitor have adopted the technology with backing from major chemical and energy company partners.

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

Highly Efficient, Practical Monohydrolysis of Symmetric Diesters to Half-Esters

Half-esters have considerable commercial value: they are highly versatile building blocks for polymers, dendrimers, and hyperbranched polymers that have applications in many industrial products. Because the two ester groups in the symmetric diesters are equivalent, however, the statistically expected yield of half-esters is only 50 percent. Classical saponification usually produces complex mixtures of dicarboxylic acids, half-esters, and the starting diesters, which are difficult to separate and therefore, generate a large amount of undesirable waste. Alternate ring-opening reactions of cyclic acid anhydrides to half-esters are also undesirable because they require hazardous organic solvents.

Among various synthetic conversions, the desymmetrization of symmetric compounds is one of the most atom-economical, cost-effective reactions. The symmetric starting compounds are typically available commercially at low cost or easily made from inexpensive precursors. Water is among the most environmentally friendly solvents and is the least expensive of all solvents. Water-mediated desymmetrization of symmetric organic compounds is, therefore, of tremendous synthetic value and can make a significant contribution to creating greener reaction conditions.

Professor Niwayama pioneered an environmentally safe, highly efficient, practical ester monohydrolysis of symmetric diesters to half-esters. In this reaction, aqueous sodium hydroxide (NaOH) or potassium hydroxide (KOH) is added to a symmetric diester suspended in water at 0 °C that may also contain a small amount of an aprotic cosolvent such as tetrahydrofuran (THF). Monohydrolysis occurs at the interface between the aqueous phase and the organic phase containing the diester. The reaction produces pure half-esters in high to near-quantitative yields without hazardous organic solvents or dirty waste products. Wako Chemicals USA and Kishida Chemical Company have licensed the technology and 10 resulting half-esters are now available commercially.

Improved Resource Use in Carbon Nanotube Synthesis via Mechanistic Understanding

Professor Desirée L. Plata, Department of Civil and Environmental Engineering, Duke University

Carbon nanotube (CNT) production by catalytic chemical vapor deposition (CVD) currently exceeds 300 tons per year and is growing. The current CVD process has very low yields (3 percent or less) and high energy requirements. Emissions from ethene- and H_2-fed CVD reactors contain over 45 distinct chemicals including: the potent greenhouse gas, methane; toxic and smog-forming compounds, such as benzene and 1,3-butadiene; and trace quantities of polycyclic aromatic hydrocarbons. Eliminating thermal treatment of the feedstock gases may prevent the formation of unwanted byproducts, reduce energy demands, and improve overall control of the synthesis, but heating the feedstock gas is necessary to generate the critical, previously unidentified, CNT precursor molecules required for rapid CNT growth.

Using in situ CNT height measurements and gas analysis, Professor Plata and her group identified the heat-generated compounds correlated with rapid CNT formation (e.g., propyne and but-1-en-3-yne). She then mixed each of these chemicals with typical feedstock gases (C_2H_4 and H_2) without preheating and tested them with a heated metal catalyst. She found that several alkynes (e.g., ethyne, propyne, and but-1-en-3-yne) accelerate CNT formation. This new mechanism for CNT formation features C–C bond formation between intact chemical precursors, similar to polymerizations. It challenges the accepted hypothesis that precursors must completely dissociate into C or C_2 units before "precipitating" from the metal.

Using these mechanistic insights, Professor Plata can form high-purity CNTs rapidly. Her technology improves yields by 15-fold, reduces energy costs by 50 percent, and reduces the ethene and H_2 starting materials by 20 and 40 percent, respectively. It also reduces unwanted byproducts by over 10-fold (translating to ton-sized reductions in toxic and smog-forming chemicals and greenhouse gases). The reduced starting materials and energy requirements also lower the cost of CNTs without sacrificing product quality. A commercial CNT manufacturer has licensed this patent-pending work.

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

Ethylene: A Feedstock for Fine Chemical Synthesis

New carbon–carbon bond-forming processes have been responsible for significant advances in organic synthesis. Practical methods using feedstock carbon sources as starting materials to form enantioselective carbon–carbon bonds are rare, however. Ideally, any new reaction must: (1) use abundantly available, carbon-neutral sources; (2) produce a functional intermediate for other common organic functional groups; (3) be highly catalytic, generating little or no waste including toxic metals; (4) provide high, reagent-dependent selectivity to produce all isomers including enantiomers; and (5) include easy product recovery. A broadly applicable reaction using ethylene to install highly versatile vinyl groups enantiomerically could thus have significant impact in organic synthesis.

Professor RajanBabu and his group have developed highly catalytic (substrate–catalyst ratio up to 7,412:1) protocols for nearly quantitative (isolated yields can be over 99 percent) and highly selective (approximately 100 percent regioselectivity; enantiomeric ratios of over 99:1) co-dimerization of ethylene and various functionalized vinylarenes, 1,3-dienes, and strained alkenes. These reactions proceed under mild conditions (-52 °C to 25 °C; 1 atmosphere of ethylene) to produce intermediates such as 3-arylbutenes, which can be transformed to nonsteroidal anti-inflammatory drugs (NSAIDs) in two steps. These reactions consume both starting materials, leaving no side products. Successes include highly enantioselective syntheses of common NSAIDs, such as ibuprofen, naproxen, flurbiprofen, and fenoprofen, from the corresponding styrenes and ethylene.

Cyclic and acyclic 1,3-dienes also undergo efficient enantioselective addition of ethylene. Syntheses of several 1-vinylcycloalkenes and 1-substituted-1,3-butadienes achieve yields up to 99 percent. Professor RajanBabu has found expeditious routes to biologically relevant classes of compounds including bisabolanes, herbindoles, trikentrins, steroid D-ring 20*S*- or 20*R*-derivatives, (-)-desoxyeseroline, pseudopterosin A–F, G–J, and K–L aglycones, and helioporins. These syntheses require fewer steps than traditional methods and produce uncommon configurational isomers. In 2010 and 2011, Professor RajanBabu published five papers on this work.

Professor Bala Subramaniam, Department of Chemical and Petroleum Engineering, University of Kansas

A Truly Green Process for Converting Ethylene to Ethylene Oxide

The LeFort process, the only industrial process currently used to make ethylene oxide (EO), emits huge amounts of carbon dioxide (CO_2, about 3.6 million tons/year). This venerable gas-phase technology also presents safety hazards due to the explosive potential of heated ethylene and oxygen gases.

At the Center for Environmentally Beneficial Catalysis (CEBC), Professor Subramaniam and his colleagues are developing an alternative green technology for EO manufacture. In the CEBC process, a highly reactive oxidation catalyst, methyltrioxorhenium (MTO), transfers an oxygen atom from hydrogen peroxide (H_2O_2) to ethylene with total selectivity, high conversion, no substrate or solvent burning (to cause CO_2 emissions), and no explosion hazard.

Despite requiring an H_2O_2 oxidant and rhenium-based catalyst that cost more than the LeFort system's O_2 oxidant and silver catalyst, the CEBC process can potentially compete economically if it has reliable in-service lifetimes of 2–3 months. Experiments indicate that the CEBC system should be capable of this critical in-service lifetime. Mechanistic studies with isotopic tracers identified only one detectable mechanism for catalyst destruction and conditions necessary to avoid it. CEBC will soon attempt long-term, continuous process operations.

The CEBC process has relatively high productivity (40–50 percent versus LeFort 10–15 percent) because it exploits the critical properties of ethylene to greatly increase its solubility. For similar production capacities, the carbon footprint of the CEBC process is net

23 percent lower than the LeFort process; thus, the additional carbon emissions from manufacturing H_2O_2 are considerably less than the emissions eliminated by not burning substrate or product. The CEBC process is the first economically competitive alternative to the LeFort process. The new EO process excels in conversion, selectivity, safety and sustainability, and the two processes appear to be comparable in manufacturing costs and productivity. A U.S. patent for this process was allowed in 2011.

A Novel Bacteriophage-Based Test to Identify MRSA/MSSA Acquired Infections

Professor Kent Voorhees, Department of Chemistry and Geochemistry, Colorado School of Mines and MicroPhage, Inc.

At the Colorado School of Mines (CSM), Professor Voorhees and his colleagues have developed a bacteriophage (phage) amplification platform that rapidly identifies *Staphylococcus aureus* and determines whether it is methicillin resistant (MRSA) or methicillin susceptible (MSSA) without extensive bacterial culturing. CSM licensed the technology to MicroPhage, which was founded in 2002 by Professor Voorhees and Mr. Jack Wheeler to provide medical devices. These point-of-care devices fulfill needs such as determining *S. aureus* susceptibility while reducing the nonrenewable materials used in manufacturing and the generation of medical waste.

Phages are viruses that infect bacteria in a species-specific fashion and then multiply rapidly. The amplification process can generate up to a 10^5 increase in phage and reduce incubation times to 1–5 hours down from 24–48 hours for traditional microbiological culture assays. The MicroPhage and CSM KeyPath™ test is conducted with modern chemical detection methods on a milliliter scale. The test resembles a typical immunoassay whereby a blood culture containing a suspected pathogen is added to two reaction tubes: one containing phage and a nutrient media; and the second containing phage, media, and methicillin. The test samples are mixed with the tube contents and incubated, followed by analysis on a dual-track lateral flow immunoassay strip. A positive result on the first track shows the presence of *S. aureus*. A positive result on the second track shows that the *S. aureus* is also methicillin-resistant. The manufacturing and use of the KeyPath™ kit address several of the 12 principles of green chemistry.

This phage amplification platform is the first and only rapid in vitro diagnostic test approved by the U.S. Food and Drug Administration (FDA) to identify bacteria directly and determine their antibiotic resistance or susceptibility. During 2011, the FDA gave 501(k) approval for the sale of these human diagnostic devices and sales began in the United States.

Biobased Polymers and Composites

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

Professor Richard Wool's research has shown that recent advances in green chemistry, genetic engineering, composite science, and natural fiber development offer significant opportunities for new, improved materials from renewable resources that are recyclable, biocompatible, and biodegradable, thereby enhancing global sustainability. He typically makes composite resins from highly saturated plant oils such as soy or linseed oils and makes pressure-sensitive adhesives, coatings, and elastomers from high oleic oils. When he combines his biobased resins with natural plant and poultry fibers, starch, and lignin, he can produce new low-cost composites, pressure-sensitive adhesives, elastomers, and foams that are economical in many high-volume applications. These high-performance composites are designed for use in energy-efficient solar integrated roofs, wind-foil blades, hurricane-resistant housing, sub-aqua hydro turbines, and hydrogen storage, in addition to agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, electronic materials, and sports equipment.

Professor Wool makes foams, usually from various mixtures of oils depending on the required rigidity, using carbon dioxide (CO_2) as the blowing agent. Recently, he developed a biobased foam to replace polyurethane and its toxic precursors, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). Professor Wool developed it in collaboration with Crey Bioresins; currently, several packaging and automotive suppliers are exploring this foam.

In collaboration with Crey Bioresins and Dixie Chemical TX, Professor Wool developed biobased composite resins that have been in worldwide distribution since 2011. Also in 2011, Professor Wool invented eco-leather, made from natural fibers including chicken feathers, flax, and plant oils. This breathable leather substitute can potentially replace 50 billion pounds of toxic waste currently generated by the leather industry. Nike and Puma are exploring this technology.

Entries from Small Businesses

Geothermal Heat Pumps: A Greener and More Energy-Efficient Renewable Energy Resource

ACTA Technology, Inc.

Because buildings account for nearly 40 percent of U.S. energy consumption and greenhouse gas emissions, they are a prime target for energy conservation. Although geothermal heat pumps (GHPs) save energy in the range of 30–60 percent compared to typical heating and air conditioning units, their high initial cost and long payback period hamper their adoption. Today's GHPs use propylene glycol–water or ethylene glycol–water mixtures as circulating fluids in their ground source loops. Ethylene glycol is a toxic chemical that presents environmental risks and disposal problems.

ACTA Technology has developed fluids containing nanoparticles (i.e., nanofluids) with improved heat-transfer efficiency that can reduce the lifecycle cost of GHPs by 17 percent. Adding nanoparticles to propylene glycol–water mixtures improves their heat transfer by 48 percent. ACTA also improves the heat transfer of Paratherm® LR (a food-grade, heat-transfer oil) by adding alumina nanoparticles at 2 percent by weight and a surfactant. The nanofluid Paratherm® LR is a better heat-transfer fluid than either ethylene or propylene glycol mixtures. Because ACTA's nanofluids increase the heat transfer rate of the ground loop in a GHP, the ground loop can be smaller and the GHP can pump less fluid. This technology reduces both the initial and lifecycle costs.

ACTA manufactures nanoparticles by a pyrogenic (flame) process. The resulting fumed nanoparticles have large surface-area-to-volume ratios that increase the heat-transfer rate and decrease the thermal response time. They are hydrophilic, with hydroxyl groups over approximately 40 percent of their surfaces. They are easily removed from nanofluids for recycling.

ACTA's technology offers circulating fluids for GHPs without the harmful effects of ethylene glycol. These greener nanofluids could also improve the fuel economy of automobiles because radiators could be smaller with less fluid to pump. ACTA applied for a U.S. patent for their technology in 2011.

Producing Chemicals and Carbon from Waste Tires, Plastics, Carpet, and Biomass

BCD Group-II, Inc.

Vast amounts of waste tires, plastics, and biomass have been discarded in landfills because there was no practical way to depolymerize them for reuse. BCD Group-II has developed catalytic transfer hydrogenation (CTH), a modified base-catalyzed decomposition (BCD) process that depolymerizes plastics, tires, rubber, other polymers, and biomass into chemicals or solid products with carbon contents of at least 84 percent. The CTH process is non-oxidative. Unlike pyrolysis and liquefaction processes that require temperatures of 450–700 °C, the CTH process converts polymers into reusable chemicals and carbon at 130–300 °C within 30–90 minutes. The proprietary reaction medium is composed of an alkali metal carbonate or hydroxide, a hydrocarbon donor/solvent (usually a high-boiling aliphatic hydrocarbon), and a proprietary catalyst/water absorption agent. Reactive hydrogen from the hydrogen donor breaks bonds between heteroatoms to produce monomers, oligomers, polymers from copolymers, and sodium salts of anions. Products are also easily converted into syngas. Depolymerization of polyester, polyurethane, polycarbonates, or carpets by existing technologies requires much higher temperatures, higher pressures, and more expensive reagents.

CTH technology can replace coke, a traditional fuel in solid oxide fuel cells (SOFCs). Coke production from coal requires processing for 16–24 hours at temperatures of around 2,000 °C. The CTH technology produces carbon from tires and biomass that is useful as SOFC fuel.

A U.S. patent application describing this technology was submitted (Provisional Application # 61/571,383) on July 7, 2011. In 2011, BCD Group-II and C-4 Polymer Inc., of Chagrin Falls, OH, completed laboratory-scale studies to depolymerize and recover polypropylene from copolymer waste generated by the food packaging and auto industries. BCD Group-II expects to complete pilot-scale tests and initiate commercial development during 2012. Licensees of the original BCD process and an India chemical firm have expressed interest in CTH technology; the Environmental Business Cluster in Silicon Valley, California, will present this technology to venture capitalists.

Blue Marble Biomaterials LLC

Greening the Design of Chemical Production with Microbes

Currently, chemical synthesis using energy-intensive processes and fossil-based materials produces the majority of fine chemicals. In contrast, the biosynthesis of fine chemicals from biobased feedstocks has demonstrated feasibility and promise, however, over the past few years. Blue Marble Biomaterials is developing microbial systems to lower the carbon intensity and improve the lifecycle sustainability of fine chemical production.

Blue Marble has developed a proprietary combination of microbes that produce a wide variety of fine chemicals and chemical intermediates including carboxylic acids, esters, thiols, and other organosulfur compounds in a single batch. Blue Marble's unique polyculture fermentation uses no genetically modified organisms and resists environmental stress. This fermentation can process low-cost, nonsterile lignin, cellulose, and protein-based waste byproducts from food, forestry, and algae companies without chemical or thermal preprocessing. Using these feedstocks for fermentation prevents landfilling or burning them and abates approximately 15.28 tons of carbon dioxide equivalents (CO_2 eq.) per ton of feedstock. Compared to microbial systems that use carbon- and energy-intensive virgin or preprocessed plant materials, Blue Marble's system recycles waste biomass, capturing the carbon it contains.

In 2010, the company scaled up production to a commercial facility in Missoula, MT. This facility is currently undergoing food-grade and kosher certification. It will operate at 100 percent capacity in the first quarter of 2012. Each year, it will use 860 wet tons of feedstock to produce 414,900 kg of carboxylic acids, esters, thiols, and other organosulfur compounds. An on-site water recycling system will reuse 75 percent of the water required for fermentation, saving 574,000 gallons of water per month. Finally, all biogas from the fermentation system will run through an algae remediation system to reduce facility emissions by scrubbing CO_2 and methane. Blue Marble is working with several major manufacturers in the flavoring, food, and personal care industries and with Sigma-Aldrich Fine Chemicals toward global distribution of seven compounds.

Colonial Chemical, Inc.

Suga®Nate: A Safer, Milder, Greener Surfactant

Although lauryl sulfate and its ethoxylated version, lauryl ether sulfate, are the two most common anionic surfactants used in formulating shampoo, body wash, and other personal care products, these ingredients are highly irritating to eyes and skin. Products formulated with ethoxylated lauryl ether sulfate also contain various levels of 1,4-dioxin, a probable human carcinogen. Finally, a large percentage of these surfactants are made from ethylene, a nonrenewable petroleum feedstock.

Colonial Chemical has developed sulfonated alkyl polyglucosides as safer surfactants: they replace lauryl alcohol with alkyl polyglucosides as the hydrophobic component. These unique, patented surfactants represent a breakthrough in mild surfactant technology. They are naturally derived, biodegradable raw materials that are nearly 90 percent renewable and could reach 100 percent renewable as development progresses. These new surfactants do not irritate eyes or skin, allowing formulators of personal care products to use totally irritation-free ingredients. Unlike ethoxylated lauryl ether sulfates, Colonial Chemical's surfactants are completely free of dioxin. An unexpected property is their ability to withstand microbial contamination. Outside testing showed that Suga®Nate 160 has reasonably good antimicrobial activity at the 16 percent active level, which is a normal concentration for a primary surfactant in higher-end shampoos. As a result, Suga®Nate can reduce or even eliminate the antimicrobial additives used in formulations.

The Suga®Nate synthesis has added benefits: it is atom-economical; sodium chloride is the only byproduct; and water is the only solvent. The relatively mild reaction conditions are closer to ambient than those of competing surfactants, and there is no need for separation or purification. The toxicity of these new surfactants is much lower than that of competing products, and the new surfactants are even less toxic than their starting materials. In 2011, Suga®Nate was certified as a biobased product by the U.S. Department of Agriculture (USDA).

Glycerol tert-Butyl Ether (GTBE): A Biofuel Additive for Today

CPS Biofuels, Inc.

Current petroleum-based additives for boosting octane in gasoline improve the miles-per-gallon (mpg) of vehicles, but not significantly. The traditional fuel additive, methyl *tert*-butyl ether (MTBE), has been phased out in many states due to its toxicity and has no obvious replacement.

Glycerol *tert*-butyl ether (GTBE) is a high-value, biobased fuel additive that improves the combustion and efficiency of petroleum and biobased fuels. CPS Biofuels has developed a process to make GTBE from waste glycerol, a low-value, high-volume byproduct of biodiesel production. CPS makes GTBE by acid catalysis of glycerol and isobutylene or other appropriate olefins followed by fractional distillation. Sulfuric acid is the preferred acid catalyst. Although GTBE can have up to three ether linkages, it is preferable to have at least one or two free hydroxyl groups to hydrogen-bond with ethanol and help lower its vapor pressure.

GTBE is a biobased, nontoxic, biodegradable alternative fuel oxygenate and octane booster that helps fuel combust more completely and improves fuel efficiency with cleaner resulting emissions. It both improves gas mileage and reduces greenhouse gas (GHG) emissions; with petroleum diesel fuels, it reduces up to 35 percent of particulates. It is useful as a fuel system icing inhibitor (FSII) in military (JP-8) and commercial (Jet A) kerosene-type jet fuel. GTBE can replace PRIST®, the existing jet fuel FSII, which is severely detrimental to human health.

CPS is focusing on improving the efficiency of the E10 and E15 blends of biofuels for the existing energy infrastructure. GTBE fuel additives are compatible with the U.S. energy infrastructure, providing tremendous advantages over alternatives that require new production facilities or new engines for vehicles. CPS recently completed manufacturing trials, and testing of GTBE showed extremely efficient, essentially emission-free combustion and an octane rating over 120. GTBE has been commercially available as CPS PowerShot™ since January 2011.

Formaldehyde-Free, High-Strength Biocomposites from Sustainable Resources

e2e Materials, Inc.

The formaldehyde and volatile organic compounds (VOCs) used to make conventional coatings, binders, and laminates for the wood composites in furniture contribute significantly to indoor air pollution. e2e Materials is commercializing biocomposite products that contain no formaldehyde or VOCs and are made without hydrocarbons or toxic feedstocks.

e2e's biocomposites are made from lignocellulosic bast fibers, soy protein, and plant polysaccharides; they are biodegradable at the end of their useful lives. The long bast fibers, from sources including kenaf, jute, flax, and hemp, are lightweight and contribute to higher strengths in ways that the short wood fibers used in particleboard and medium-density fiberboard (MDF) cannot. The soy protein and plant polysaccharides are feedstocks for a natural resin system that binds the fibers together into biocomposites.

e2e's biocomposite material is 3–4 times stronger than today's wooden particleboard and MDF. e2e can mold its biocomposites into three-dimensional parts (i.e., net-shape them into whole, structural components) that replace traditional 4 x 8-foot sheets. Net-shaping can create stronger components by molding them as one part rather than assembling them from pieces. The e2e biocomposites also retain screws better than wood composites. These features combine to create stronger furniture while reducing the total amount of material and weight. e2e's biocomposites are inherently fire-resistant because they contain a modified soy protein instead of petrochemical resins. They use only 19 percent of the embodied energy of today's products because the manufacturing process requires less energy and regionally integrated manufacturing minimizes transportation costs.

Products made from today's wood composites have a $100 billion market. e2e is replacing those products with higher performing, safer, more efficient, and more cost-effective biocomposite-based products. These products complement its proprietary biocomposite core with green, cost-effective coatings. Following successful pilot production in 2011 and responding to strong demand for its commercial office furniture products, e2e recently announced a 100,000 square foot manufacturing expansion.

Ecology Coatings

Generally Recognized as Safe (GRAS) Coatings

Using materials that are generally recognized as safe (GRAS) for human consumption, Ecology Coatings has developed coatings that can be applied to food or used in food packaging. These GRAS coatings protect food from outside elements, are safe for human consumption, and use natural ingredients, not plastics or other chemicals derived from fossil fuels. GRAS coatings have barrier properties to air, water, and solvents that will allow them to replace coatings originating from fossil fuels, especially plastic coatings made using acrylates and methacrylates. GRAS coatings have the potential to make food packaging greener and more sustainable by eliminating toxic plastics. Their environmental friendliness could allow increased recycling of food packaging.

The coating includes a polypeptide such as albumin, a denaturing agent, and water as the solvent. It can also include a natural gum, a flavoring agent, a dye, a de-foaming agent, maltodextrin, and an oil. When the mixture is exposed to UV light, it cures and cross-links, but does not coagulate. Used on food, the nominated coating will inhibit oxygen exposure and increase shelf life. GRAS coatings on food packages will also resist grease and can substitute for polyethylene or other petroleum-based coatings. Ecology Coatings' GRAS coating can also be used as a photoinitiator with conventional UV-curable materials that are approved for direct contact with food.

GRAS coating components in powdered form not only promote UV curing but can extend the coverage of pigments. In this use, the nominated technology could replace silica fillers. Finally, the GRAS coating can be used as a matting agent, which cures into the finished film and enhances the UV-curing process. Combined with other biobased additives, the GRAS coating can produce a rough surface that resists water and grease migration. In 2010, Ecology Coatings filed a patent application for this technology.

Electrovaya Inc.

Zero-Emission Production of the Green Lithium Ion SuperPolymer® Battery

The lithium ion cell and battery industry is a multibillion-dollar business that also pollutes the environment. The manufacturing process for lithium ion electrodes includes coating the electrodes with the toxic solvent *N*-methyl pyrrolidone (NMP), then removing NMP by slow evaporation in a furnace up to 100 meters long. Although manufacturers attempt to recover NMP, some escapes. NMP is listed as potentially causing birth defects by environmental agencies in California, Japan, the European Union (EU), and elsewhere. The large quantities of toxic solvents in cell and battery manufacturing also lead to high costs for capital equipment and plant operations as well as uncertain future liabilities.

Electrovaya's SuperPolymer® batteries are based on a nanostructured lithiated manganese oxide material that allows more energy to be stored in a smaller space, making applications smaller, lighter, and more powerful. They also produce approximately 25 percent less carbon dioxide (CO_2) over their lifecycle than do NMP batteries. Electrovaya developed a unique, nontoxic process to manufacture its fuel cells that eliminates all solvents including NMP. Electrovaya has also eliminated some energy-intensive drying and solvent-recovery processes.

Electrovaya's SuperPolymer® batteries address the problem of energy generation and storage. Advanced energy storage for plug-in hybrid electric vehicles and e-bikes can provide an alternative to nonrenewable resources and reduce greenhouse gas emissions. Currently, Electrovaya is testing its battery technology nationwide in a fleet of plug-in hybrid electric versions of Chrysler's RAM pickup trucks and Minivans.

High-capacity energy-storage systems are essential if renewable sources are to supply a significant portion of a grid's energy. Electrovaya's technology is useful for grid energy storage systems to solve the power stability and energy storage problems associated with electricity generated by renewable resources. Electrovaya recently delivered a 1.5 MW energy-storage system to an electric utility in the Southwest United States for use with its photovoltaic operations.

Polymeric, Nonhalogenated Flame Retardants with Broad Applicability in Multiple Industries

FRX POLYMERS® Inc.

Traditional, halogenated, small-molecule flame retardant (FR) additives readily migrate to the surface of plastic formulations, exposing humans to these often toxic chemicals and diminishing their FR protection. Today, over 60 percent of FR plastic formulations are based on halogen-containing additives like brominated and chlorinated hydrocarbons. Electronic device manufacturers have instituted voluntary bans on halogen-containing FR additives; other industries are also replacing them. Consequently, the plastics industry needs alternatives.

FRX POLYMERS® Inc. (FRXP) is the first company to develop polymeric forms of phosphorus for use as nonmigrating, halogen-free FR additives that are also cost-effective. FRXP converts diphenyl methylphosphonate (DPMP) into polymers with over 10 percent phosphorus. These polymers have a limited oxygen index (LOI) of 65 percent, the highest LOI measured for thermoplastic materials, indicating strong FR capability. They can be used alone or can deliver FR performance and additional benefits to polycarbonate blends, polyesters, thermoplastic polyurethane, unsaturated polyesters, epoxies, and polyureas. FRXP polymers can be used in melt-processed fibers and blow-molded articles where previous FR additives could not. Being polymeric, the FRXP materials allow the physical properties of plastics to remain essentially unchanged. FR additives with phosphorus replacing bromine also should allow greater plastic recycling.

The DPMP monomer synthesis has essentially quantitative yields. The polymer synthesis is a solvent-free, melt-based process whose only major byproduct, phenol, can be recycled into starting monomers. FRXP expects less than 5 percent waste from its polymer and copolymer production.

FRXP is scaling up its additives for use in electronic housings, industrial carpeting, textiles, electrical connectors and switches, wires and cables, printed circuit boards, and transparent laminates. Following Premanufacture Review under the Toxic Substances Control Act (TSCA), the FRXP materials are proceeding toward global registration. FRXP plans to expand its current polymer pilot plant from 50 to 100 metric tons per year (TPA) in early 2012 and is building a 2,500 TPA commercial plant for start-up in October 2013.

H-O-H Water Technology, Inc.

Conserving Water and Eliminating Chemical Treatment in Cooling Towers

Commercial HVAC and industrial cooling towers evaporate water to transfer heat to the atmosphere. These systems use roughly 5 trillion gallons of water annually in the United States. The aqueous environment in cooling towers presents four significant challenges to sustained efficient operation: mineral scaling, corrosion, biological activity, and water conservation. Traditional control measures require chemicals specific to each problem, many of which are hazardous.

H-O-H Water Technology's "Green Machine" is generating significant resource savings, eliminating traditional chemical additives, and reducing chemical hazards and pollution. In the Green Machine, carefully engineered electrolytic extraction of calcium carbonate from recirculating cooling water controls deposit formation on heat exchangers and other surfaces. Electrolysis of ion-rich water produces exploitable chemicals in situ so the system requires no external reagents other than electricity.

The Green Machine contains steel tubes that constitute the cathodes of an electrolytic cell, where water is reduced to form molecular hydrogen and hydroxide ion and where calcium carbonate subsequently accumulates. Centered in each tube typically is the anode of the electrolytic cell: a titanium rod coated with ruthenium and iridium oxides called a dimensionally stable anode (DSA). The coating of the anode drives the oxidation of water to produce molecular oxygen, hydrogen ions, and higher oxygen species such as hydroxyl free radicals and ozone. DSA technology allows the efficient splitting of water at a low practical voltage potential. Recently, H-O-H supplemented DSAs with anodes coated with boron-doped, ultrananocrystalline diamond (BD-UNCD), which controls troublesome calcium carbonate deposition, forms chlorine in situ, and degrades organic components more efficiently. Microbiological control in cooling water is significantly more efficient as well.

During 2011, Green Machines installed in 127 cooling water systems totaling 86,660 tons of cooling capacity saved a total of 248 million gallons of make-up water including 44.7 million gallons due to the new BD-UNCD technology.

InfiChem Polymers, LLC

InfiGreen^{TM} Polyols

Polyurethane manufacturers are seeking to pursue sustainability by reducing their carbon footprint, improving their green image, and cutting costs. The growing market for the polyols used to make polyurethane is currently about 11 billion pounds, but has few green options. Biobased polyols (primarily soy-based polyols) reduce polyurethane's carbon footprint, but have significant consequences including higher prices for food and agricultural land. In addition, polyurethane manufacturing generates significant amounts of scrap, and virtually all post-consumer polyurethane scrap goes into landfills.

With InfiGreen^{TM} polyols and recycling technology, InfiChem Polymers is providing sustainable, green, economical raw materials that are not biobased and do not divert land from food production. This technology transforms polyurethane foams into InfiGreen^{TM} polyols with over 60 percent recycled content for reuse in polyurethanes. The process liquefies scrap foam in a reaction with glycol, and then transposes it into various InfiGreen^{TM} polyols by propoxylation or patent-pending chemical steps; it typically generates less than one percent waste. InfiChem Polymers demonstrated its process on a pilot scale with both flexible and rigid foam scrap. Substituting one pound of conventional petroleum-based polyols with InfiGreen^{TM} polyols reduces the carbon footprint by approximately two pounds of carbon dioxide (CO_2).

Polyurethane manufacturers can benefit from closed-loop recycling of their polyurethane production scrap, which can significantly reduce their landfill costs and provide them with

InfiGreen™ polyols at prices typically below those for conventional petroleum-based and biobased polyols.

InfiGreen™ polyols are currently used in automotive seat cushions and in the construction industry. InfiChem Polymers expects to reach its current capacity of one million pounds of InfiGreen™ polyols in late 2011; within 5 years, it expects sales of 50 million pounds in NAFTA countries. With projected worldwide production of 180 million pounds of InfiGreen™ polyols, the company will consume approximately 106 million pounds of polyurethane scrap or approximately 0.03 percent of all polyurethane produced.

Development and Commercialization of Oleic Estolide Esters

LubriGreen Biosynthetics

Each year, 2.4 billion gallons of lubricants are used in the United States, according to industry and EPA estimates. Lubricants comprised of sustainable carbon that perform well in demanding applications are in high demand. Naturally occurring vegetable oils (triglycerides) provide excellent lubricity and have high viscosity indexes; they are also biodegradable, nontoxic, and economically attractive. Their oxidative and hydrolytic instability and their poor performance at low temperatures, however, exclude their use in passenger-car motor oils (PCMOs) and low-temperature environments.

LubriGreen has overcome the inherent disadvantages of vegetable oils and preserved their favorable properties by derivatizing fatty acids from triglycerides into estolides, which are oligomers of fatty acids. Patented oleic estolide esters are central to LubriGreen's technology. Their synthesis proceeds by an acid-catalyzed S_N1 addition of the carboxyl of one fatty acid to the site of unsaturation on another to form an estolide. (The catalyst is a recoverable, reusable organic superacid.) The free acid estolides are then esterified with a branched alcohol. The novel structure of oleic estolides gives them excellent lubricity, high viscosity indexes, and good cold-temperature properties. Like triglycerides, oleic estolides are beneficial in environmentally sensitive settings because they are biodegradable and nontoxic. Because the estolides are fully saturated and their secondary esters create a steric barrier to hydrolysis, they have good oxidative and hydrolytic stability. Estolides are viable for the most severe lubricant and industrial applications, including PCMOs, hydraulic fluids, greases, gear oils, metal working fluids, and dielectric fluids.

Estolides have the potential to displace a significant portion of the lubricant market, reducing emissions and the release of hazardous chemicals into the environment. Test results show that oleic estolide esters may also have advantages in performance and fuel efficiency over petroleum-based PCMOs. LubriGreen is currently working with the world's largest formulators, lubricant distributors, and others to commercialize its products during 2013.

Biobased Chemicals from Low-Cost Lignocellulosic Sugars

Myriant Corporation

Most fermentation routes that produce industrial chemicals require glucose as the main carbon source. These fermentations have significant disadvantages, however, due to the high cost of glucose, the volatility of the sugar markets, and competition with the food and feed industries. The substitution of inexpensive, abundant lignocellulose feedstocks for glucose can create a great advantage for producing organic chemicals.

Lignocellulosic hydrolysates contain a variety of 5- and 6-carbon sugars as well as toxins such as acetic acid, furfural, and 5-hydroxymethylfurfural (HMF). Because these toxins can inhibit bacteria from metabolizing sugars to products, companies usually must remove them by "detoxification" of the hydrolysates in a process that adds unit operations and cost to the fermentation. Efficient fermentation of lignocellulosic hydrolysates requires microorganisms that can metabolize both 5- and 6- carbon sugars as well as tolerate the toxins present in hydrolysates.

Myriant has successfully developed a proprietary process including evolved *E. coli* strains that are able to metabolize multiple sugars simultaneously and can ferment lignocellulosic hydrolysate without any detoxification. These proprietary biocatalysts are capable of fermenting low-cost, non-food, lignocellulosic hydrolysate sugars as well as clean sugars to produce organic acids including lactic acid and succinic acid.

Lifecycle studies comparing Myriant's biosuccinic acid technology to petroleum-derived succinic acid showed a potential reduction in greenhouse gases (GHGs) of more than 50 percent. Myriant's biosuccinic acid and biolactic acid will be used as drop-in and replacement chemicals in current petroleum-based markets. Myriant is developing processes to manufacture biobased butanediol, pyrrolidone, and acrylic acid.

In 2009, Myriant was awarded $50 million from U.S. Department of Energy (DOE), which is supporting the company's commercialization of its lignocellulosic biosuccinic acid and construction of a 30 million pound capacity biosuccinic acid facility in Lake Providence, LA. This facility will use primarily *E. coli* strain KJ122 to produce succinic acid from sorghum flour.

Novomer, Inc.

High-Performance Polyols from CO_2 at Low Cost

The vast majority of polyols currently used in coatings, foams, adhesives, elastomers, and thermoplastic polyurethanes are derived exclusively from petrochemicals. Novomer has developed a proprietary technology platform that transforms waste carbon dioxide (CO_2) into very precise, high-performance polyols at lower cost than polyols from either petroleum or natural oils.

Novomer's polyol technology platform combines several innovations. Novomer has developed a breakthrough cobalt-based CO_2–epoxide catalyst that is over 500-fold more active and far more precise than past zinc-based catalysts. In 2011, Novomer modified its catalyst system with resin bed technology to recover and recycle the catalyst without losing activity or selectivity. Novomer was also the first to develop low-molecular-weight CO_2-based polyols using chain-transfer agents. The manufacturing process for Novomer's CO_2-based polyols is a proven, low-cost, synthetic technology based on chemistry. It can be completed in existing chemical industry infrastructure under mild reaction conditions with conversions of over 90 percent in short timeframes. Using CO_2 cuts raw material costs nearly in half, yielding a significant cost advantage.

The environmental and human health benefits of Novomer's CO_2-based polyol technology platform are considerable. Because these polyols contain 40–50 percent CO_2 by weight, they can potentially sequester 10 billion pounds of CO_2 per year in targeted polyol markets. More important, they enable the chemical industry to eliminate 10 billion pounds per year of petroleum-based raw materials, a source reduction that impacts the entire petrochemical value chain. In addition, because Novomer polycarbonate polyols contain no bisphenol A (BPA), they can potentially eliminate the use of BPA-containing resins in food-contact coatings.

Novomer is commercializing its polyols in several markets. Jointly with the Dutch company, DSM, Novomer will introduce its first large-scale commercial polyol product for coil coating applications in 2012. In partnership with industry-leading polyol producers, formulators, and end users, Novomer is developing additional polyol products for footwear foams, rigid insulating foams, and polyurethane adhesives.

NSR Technologies, Inc.

Electrodialysis and Chromatographic Separation Technology for Chlorine-Free Production of Potassium Hydroxide and Hydrochloric Acid

The United States consumes approximately 2 billion pounds of potassium hydroxide (KOH) per year. The traditional chloralkali process for KOH uses electrolysis of potassium chloride in water and produces chlorine gas (Cl_2), hydrogen gas (H_2), and KOH. Cl_2 is a hazardous air pollutant (HAP) that faces declining demand due to the phase-out of chlorinated chemicals.

NSR has commercialized the first environmentally friendly, cost-effective alternative to the chloralkali process in decades. NSR's new process manufactures 45–50 percent KOH and 7 percent hydrochloric acid (HCl). The process uses NSR's novel electrodialysis IonSel™ stacks, which include bipolar membranes of specialty polystyrenes modified with ion exchange groups. The novel design of IonSel™ stacks allows the cells to operate at high efficiency, consume 40 percent less energy, and generate high-purity products. The process rearranges ions in solution and is particularly suited to recycling salts generated in other applications including those from the pulp and paper industries and from the environmental control systems in coal-fired power plants.

NSR's process yields high-purity, food-grade products without mercury (a health hazard to children) or oxidizing species like chlorate and hypochlorite. The lower energy consumption per unit of KOH made by NSR's process allows smaller plants to produce equivalent amounts of HCl and KOH profitably. Smaller plants cost less, can be built close to end-users, and reduce transportation hazards. NSR supplies food grade 7 percent HCl to Archer Daniels Midland by pipeline. This efficient transfer eliminates the unnecessary transport and accidental release of fuming 35 percent HCl.

NSR's single plant eliminated the production of 2 million pounds of Cl_2 during 2011; at full capacity, it would eliminate the production of 10 million pounds of Cl_2 per year. NSR's technology could potentially eliminate the production of billions of pounds of unnecessary Cl_2 each year.

Producing Industrial Chemicals by Fermenting Renewable Feedstocks at a Lower Cost

OPX Biotechnologies, Inc.

Chemical producers are searching to meet growing worldwide demands for many of today's industrial chemicals with renewable feedstocks and environmentally sustainable methods. The transition to renewable feedstocks has been slow, however, because environmentally sustainable processes must be cost-competitive with traditional petroleum-based chemicals.

OPX Biotechnologies (OPXBIO) has developed a proprietary platform technology called Efficiency Directed Genome Engineering (EDGE™). This technology allows OPXBIO to develop and engineer microorganisms and bioprocesses faster and less expensively than traditional methods. OPXBIO can now develop multiple chemicals cost-effectively from multiple renewable feedstocks.

In 2011, OPXBIO developed a bioprocess for biobased acrylic acid (bioacrylic acid). OPXBIO used its EDGE™ process to engineer both a microorganism to produce 3-hydroxypropionic acid (3-HP) and a process to manufacture bioacrylic acid renewably. A key focus was developing a microbial strain with increased cellular pools of malonyl-CoA, the first committed intermediate in the 3-HP production pathway. Many commercial products may be derived from malonyl-CoA, including fatty acids (and hence long chain alkanes), polyketides, and 3-HP.

An initial lifecycle analysis (LCA) indicates that OPXBIO's process for bioacrylic acid would reduce greenhouse gas emissions by more than 77 percent and crude oil use by 82 percent compared to traditional acrylic acid synthesis from propylene. If the entire global market for acrylic acid (4.5 million tons annually) were replaced with OPXBIO's bioacrylic acid, greenhouse gas emissions would be reduced by more than 5 million tons annually, and industry's use of crude oil would decrease by approximately 2.5 million tons.

In 2011, OPXBIO scaled up its process and demonstrated the fermentation and primary purification of 3-HP at 3,000 liters. If dextrose feedstock costs \$0.14 per pound, metrics predict a commercial cost of bioacrylic acid at approximately \$0.75 per pound. This cost is competitive with the average cost of petroleum-based acrylic acid in 2011, making the process both environmentally and economically sustainable.

Performance Chemicals, LLC

BURN-OUT ™ Durable, Green, Nontoxic Flame Retardant

Each year, an estimated 4 billion pounds of polybrominated diphenyl ethers (PBDEs) are used in flame retardant (FR) applications. There is growing evidence, however, that PBDEs are toxic.

Performance Chemical has developed Burn-Out™ FR, a totally green, nontoxic, durable replacement for PBDEs and other persistent, bioaccumulative, toxic FRs. The Burn-Out™ compound is made of materials that comply with U.S. Food and Drug Administration (FDA) regulations for indirect food contact and are safe for disposal. Phosphorus and nitrogen are its active ingredients; it is formaldehyde-free. In a fire, Burn-Out™ FR forms an intumescent, thermal-insulating carbonaceous char that acts as a barrier between the burning and unburned material. Inert gases, mostly carbon dioxide (CO_2) and water, dilute the combustion gases and cool the surface. Phosphorous-containing compounds react to form phosphoric acid and cause charring. The Burn-Out™ compound releases nitrogen gas and dilutes the flammable gases in synergy with the phosphorus.

Burn-Out™ FR resists water, alcohol, oil, and grease, yet cleans up with soap and water. Burn-Out™ FR contains ingredients that resist the growth of bacteria and fungi. In insulation materials, Burn-Out™ FR resists the formation of airborne *Legionella* bacteria, which can multiply in water systems and are a source of Legionnaires' disease.

In customer formulations, Burn-Out™ FR compounds offer potential cost savings of 20-50 percent compared to current FRs containing halogen and PBDE–antimony. Performance is equal to or exceeds that of other products. Burn-Out™ FR reduces landfill disposal costs associated with hazardous materials.

Burn-Out™ FR may be used in virtually all aqueous systems and many polymer systems. Applications include paper, corrugated packaging, woven and nonwoven textiles, insulation, ceiling tiles, construction materials (e.g., wood, urethane insulation, and steel intumescent coatings), adhesives, paints, and other FR coatings, especially in the automotive, military, and marine markets. Performance Chemicals is planning to test Burn-Out™ FR in bedding and mattresses. Performance Chemicals commercialized Burn-Out™ FR in 2011.

RPS Environmental Solutions, LP

Zero-VOC Cleaning and Remediation Technology

The pollutants in indoor environments can actually reach higher levels than those found outdoors. Although several factors contribute to indoor air quality, fumes and residues from the cleaning chemicals currently used in our homes, offices, and schools have a significant negative effect on the quality of the air we breathe. Many common cleaners contain dangerous and harmful chemicals that are carcinogens, neurotoxins, hormone disruptors, and reproductive toxins.

RPS Environmental Solutions has developed products without volatile organic compounds (VOCs) or harsh chemicals that it is currently using in a wide range of cleaning products from degreasers and odor eliminators to adhesive removers and pet care products. These products are hypoallergenic, rapidly biodegradable, and have undergone rigorous testing to ensure the greatest possible safety and efficacy. RPS carefully manages the entire lifecycle of its products from manufacturing in a zero-discharge facility to using minimal-impact packaging. Independent laboratory testing with the American Society for Testing and Materials International (ASTM) D 4488 protocol for cleaning efficacy shows RPS's products to be 3.5 times more effective than those of the leading "green" competitor, over twice as effective as those of the most-recognizable name-brand competitors, and over 30 percent more effective than those of the most powerful competitor. Although many competitive products compromise safety for effectiveness, RPS cleaning products are both safer and more effective than those of their competitors.

RPS technology has leveraged hydration–dehydration, metal ion reaction, surface charge modification, and the mechanics of conversion to provide cleaning and remediation products that are safer for use near people, pets, and plants. RPS technology not only eliminates the need to produce many dangerous chemicals, but can actually remediate environmental damage caused by many harmful substances and improve human health by improving indoor air quality. RPS expanded and launched several product lines during 2011; RPS products have been recognized by EPA's Design for the Environment partnership program.

Sodium Silicide: A New Alkali Metal Derivative for Safe, Sustainable, and On-Demand Generation of Hydrogen

SiGNa Chemistry, Inc.

Sodium silicide (NaSi) is a stabilized, alkali metal silicide powder that reacts with any water solution to generate hydrogen instantly. SiGNa's patented NaSi powder is modified to delocalize the electrons across the clathrate, forming an air-stable, free-flowing powder.

In a fuel cell, NaSi produces pure hydrogen gas as needed at pressures lower than those in soda cans. NaSi overcomes the most-significant challenges that have prevented low-temperature proton exchange membrane (PEM) fuel cells from commercialization: storing high-pressure hydrogen and building costly infrastructure. NaSi is clean, sustainable, inexpensive, easily transportable, and safe for indoor use. Fuel cells powered by NaSi produce only hydrogen and water vapor; they create no greenhouse gases, toxic byproducts, or harmful emissions. Recyclable fuel cartridges deliver NaSi to any PEM fuel cell; once the NaSi is spent, the nontoxic, environmentally benign residue can be recycled as an industrial feedstock.

SiGNa's NaSi technology offers significant environmental benefits throughout its lifecycle. NaSi is manufactured from renewable, sustainable materials that are independent of oil prices. The manufacturing process requires little energy and has a very small carbon footprint. Replacing lithium batteries and internal combustion (IC) engines with NaSi fuel cells can reduce the release of greenhouse gases (GHG) by nearly 14 percent and significantly reduce the amount of toxic materials entering the waste stream.

SiGNa's novel hydrogen-storage approach can enable cost-effective back-up and portable fuel cells for the medical, military, transportation, disaster relief, and consumer electronics industries. SiGNa's technology is proving that hydrogen fuel cells are not only commercially viable, but even more high-performing and cost-effective than batteries or small IC engines. For example, NaSi can replace the combustion engine/gas back-up in battery-hybrid cars to extend their range by 50 miles. Also, e-bikes powered by NaSi can go 3–4-times farther than bicycles powered by lithium batteries. During 2011, licensee myFC commercialized PowerTrekk, a portable hydrogen charger, in Europe.

Biobased Adipic Acid for Renewable Nylon and Polyurethane Resins

Verdezyne, Inc.

Adipic acid ($C_6H_{10}O_4$) is an important industrial dicarboxylic acid with an estimated global market of $6.5 billion. It is a feedstock for nylon 6,6 and polyurethane resins. It is currently produced from petrochemicals by the nitric acid catalyzed oxidation of cyclohexane. This process generates a waste gas stream including nitrous oxide, non-methane volatile organic compounds (VOCs), carbon monoxide, and nitrogen oxides. The production of adipic acid from renewable resources would result in substantial reductions of environmental pollutants.

Verdezyne has engineered an industrial strain of the yeast *Candida* to produce adipic acid from natural plant-based oils. This yeast normally grows on fatty acids as its sole carbon source by cyclic degradation through its β-oxidation pathway. A *Candida* strain in which this pathway is completely blocked can convert these substrates to the corresponding dicarboxylic acids by selective oxidation of terminal methyl groups through its ω-oxidation pathway to produce diacids with a chain-length distribution that precisely mimics that of its plant-based oil feedstock. By engineering both the β-oxidation and ω-oxidation pathways of yeast, Verdezyne has enabled the highly selective production of adipic acid from any plant-based oil. This engineered strain tolerates saturating concentrations of adipic acid in the fermentation broth, growing at the same rate and to the same density as in its absence.

In addition, Verdezyne has developed fermentation and downstream purification processes to recover polymer-grade bioadipic acid from the fermentation broth and has synthesized nylon 6,6 fibers and pellets from bioadipic acid. The advantages of Verdezyne's biobased technology over petroleum-based manufacturing include lower cost, sustainable feedstock supply, and a smaller environmental footprint. Verdezyne estimates that its production costs will be 30–35 percent lower than the petrochemical process. Verdezyne recently opened a pilot plant in Carlsbad, CA to demonstrate the scalability of its process, validate its cost projections, and generate enough biobased adipic acid for commercial market development.

VH Biotechnology, Inc.

Bacteriocins: A Green, Antimicrobial Pesticide

Pesticides are used worldwide to protect crops and structures, manage pests, and prevent the spread of disease. Pesticides are intended to be toxic, but only to their target organisms. Their intrinsic properties, however, lead these pesticides to pose risks for human health and the environment. There is a continuing need for safer pesticides to replace those that are toxic to nontarget species.

Through evolution, bacteria have acquired the ability to produce molecules such as bacteriocins that inhibit other microorganisms. Bacteriocins are gene-encoded, ribosomally synthesized, antimicrobial peptides that are often small in size (20–60 amino acid residues). Bacteriocins combine with negatively charged surface constituents of target bacteria, creating transmembrane pores that make the target bacterial membrane permeable and thus kill the bacteria. Bacteriocins are not toxic to eukaryotic organisms. They are generally recognized as safe (GRAS) by the U.S. Food and Drug Administration. Moreover, they are currently considered for therapeutic applications such as the development of new vaccines against pathogenic, multidrug-resistant bacteria and as cytotoxic agents against human cancer cells.

VH Biotechnology has developed a novel, green bacteriocin composition for use as a microbicide in commercial applications including pulp and paper mills, fuels, biofuels, cooling water systems, and poultry farms. The bacteriocins are obtained by standard fermentation using lactic acid bacteria. Two paper mills using these bacteriocins showed much lower bacterial counts. In diesel fuel, bacteriocins reduced microbial levels by 99.95 percent over controls; in gasoline, the reduction was 89 percent. When used to sanitize water on poultry farms, bacteriocins at 100 grams per cubic meter of water were able to match the performance of chlorine at 12 grams per cubic meter. VH Biotechnology developed this technology in 2008 and filed a U.S. patent application for it in March 2010.

Entries from Industry and Government

Concrete-Friendly™ Powdered Active Carbon (C-PAC™) to Remove Mercury from Flue Gas Safely

Albemarle Corporation

Coal-fired power plants emit 45 tons of gaseous mercury into the air and produce 65.5 million metric (MM) tons of fly ash annually in the United States. Fly ash has a composition similar to that of volcanic ash and is an excellent replacement for cement in concrete. Currently, about half the concrete produced in the United States contains fly ash. Of the 65.5 MM tons of fly ash generated in 2008, more than 11.5 MM tons were used in concrete and 16.0 MM tons were used in structure fills, soil modification, and other applications. According to EPA's 2008 report to Congress, federal concrete projects used 5.3 MM tons of fly ash in 2004 and 2005 to replace cement, saving about 25 billion megajoules of energy, saving 2.1 billion liters of water, and reducing carbon dioxide (CO_2) emissions by about 3.8 MM tons.

Powdered activated carbon injection (ACI) is a conventional technology that injects mercury sorbents into flue gas in power plants and captures the mercury-laden sorbents in fly ash. Although this reduces mercury emissions, the resulting fly ash is unsuitable for concrete and requires disposal in landfills. If mercury contamination made all fly ash unsuitable for use in concrete, the 11.5 MM tons now used in concrete each year would require more than 33 million cubic feet of new landfill space at a cost of about $196 million.

Albemarle designed, synthesized, developed, and commercialized its novel Concrete Friendly mercury sorbent, Concrete-Friendly™ Powdered Active Carbon (C-PAC™). C-PAC™ is activated carbon with tailored pore structures and surface properties. Albemarle manufactures C-PAC™ from renewable carbon sources using a greener synthesis that includes gas-phase catalytic bromination. C-PAC™ removes large amounts of mercury from air, preserves the quality of fly ash for concrete use, safely sequesters the mercury in the concrete, and eliminates the need for new landfill space. Several power plants across the United States currently use C-PAC™.

Upcycling Waste Plastic Bags into Valuable Carbon Nanotubes and Carbon Spheres

Argonne National Laboratory

Carbon spheres (CSs) and carbon nanotubes (CNTs) find uses in water purification, as additives for lubrication, in energy storage devices such as common lithium-ion batteries, and in other applications. At Argonne National Laboratory, Dr. Vilas Pol has discovered, implemented, and patented an environmentally friendly process to remediate or upcycle waste plastic bags (WPBs) into CSs and CNTs. Argonne's solvent-free, solid-state-controlled pyrolytic process heats WPB of single or mixed types to 700 °C in a sealed chamber to produce pure CSs or CNTs. Systematic characterization of the atomic structure, composition, and morphology of the CSs and CNTs with advanced structural, spectroscopic, and imaging techniques has elucidated the mechanism of CS and CNT formation.

With no catalyst, the process yields smooth CSs of 2–10 microns in diameter that are conductive and paramagnetic. They can be used in toners and printers, as additives for lubricants, and in the tire industry. Industrial collaborators, Superior Graphite and ConocoPhillips, have heat-treated CSs at higher temperatures; this improves their electrochemical performance as anodes for lithium-ion batteries.

With a ferrocene catalyst, the process yields CNTs that Argonne has successfully tested as anodes for energy storage devices and additives for lubrication. This process is the cheapest, most straightforward way to fabricate CNTs in mass quantities. It also avoids the air and water pollution caused by landfilling or incinerating WPBs.

The process uses less energy to manufacture these materials than existing methods; it also replaces a petrochemical feedstock with WPBs. By diverting plastic bags from landfills or toxic incineration factories, this process reduces air and water pollution, ultimately reducing the hazards to public health and environment.

Argonne has designed and built a prototype reactor with 80 cubic centimeter capacity and optimized the reaction conditions. Argonne is working with Grupo Simplex and G2 NanoTechnologies, LLC to commercialize this technology.

Armstrong World Industries, Inc.

BioBased Tile®: A Non-PVC Flooring Made with Rapidly Renewable Resources

Historically, resilient vinyl composition tile (VCT) flooring has been manufactured with binders derived from fossil fuel. Poly(vinyl chloride) (PVC) is the primary binder used to combine plasticizers, processing aids, stabilizers, limestone, and pigments into resilient flooring. Other binders include polyolefins, ethylene acrylic resins, and synthetic rubbers.

In 2008, Armstrong commercialized BioBased Tile® flooring, a revolutionary flooring product that uses natural limestone and a proprietary polyester binder made from rapidly renewable materials. Armstrong developed BioBased Tile® specifically to provide a PVC- and phthalate-free alternative to VCT for K-12 education applications. Armstrong is the first manufacturer in over 100 years to develop a biobased polymer as a binder for a hard-surface flooring product. The new binder created a new category of floor tile that couples improved indoor air quality and environmental benefits with improved performance and affordability.

The polymer binder contains 13 percent biobased content from rapidly renewable corn, which reduces reliance on fossil fuels and lowers the carbon footprint. It was built on technologies that previously won Presidential Green Chemistry Challenge Awards (i.e., biobased polylactic acid and 1,3-propanediol) to replace phthalate-plasticized PVC. The consumer product also contains 10 percent preconsumer recycled limestone. Each year, replacing VCT with BioBased Tile® flooring could save 140 million pounds of virgin limestone, eliminate 336,000 pounds of volatile organic compounds (VOCs) from manufacturing, capture 44 million pounds of carbon dioxide (CO_2) from the atmosphere in biobased components, and reduce energy consumption equivalent to 475 billion Btu (or 56 million pounds of CO_2).

BioBased Tile® flooring is certified by Floor Score with no detectable VOCs. It contains no materials listed in the table of Chronic Reference Exposure Levels (CRELs) established by California's Office of Environmental Health Hazard Assessment (OEHHA). For green building initiatives, BioBased Tile® contributes up to four points toward LEED certification and will be NSF 332 certified in January 2012.

Armstrong World Industries, Inc.

Breakthrough Formaldehyde-Free Coating for Ceiling Tiles

Ceiling tiles can sag if they are not engineered to resist humidity. Armstrong and other ceiling tile manufacturers have historically applied melamine–urea–formaldehyde or other formaldehyde-based resins as back coats to prevent ceiling tiles from sagging. Although formaldehyde is a key ingredient in many building products, there is now great concern for its use. Formaldehyde is a colorless, flammable, odorous gas that is a classified as a "known carcinogen" by the International Agency for Research on Cancer (IARC) and as "reasonably anticipated to be a human carcinogen" by the National Toxicology Program (NTP).

Armstrong World Industries has developed a formaldehyde-free, waterborne coating that can be applied to the surface of any fibrous panel such as a ceiling tile to prevent sagging. Armstrong did extensive research to develop a new coating that expands hydroscopicly at high humidity to resist sag, maintains a high modulus even at high humidity, and is compatible with other coatings and fillers. The new coating system includes a binder based on a combination of dextrose and ammonia-neutralized polyacrylic acid.

Armstrong will use its newly invented coating technology to replace all formaldehyde resin ceiling tile applications. By implementing this new technology globally, Armstrong will eliminate 8.3 million pounds of formaldehyde resins, 416,000 pounds of formaldehyde air emissions, and 134,000 pounds of triethylamine air emissions annually. Eliminating formaldehyde resin (1) avoids employee formaldehyde exposure at four Armstrong manufacturing facilities in the United States and five international facilities; (2) eliminates formaldehyde and triethylamine stack emissions associated with the cross-linking process for the traditional melamine–formaldehyde ceiling tile back coat; (3) eliminates potential formaldehyde emissions from finished products after installation; and (4) reduces lifecycle assessment impacts associated with upstream production of formaldehyde. Armstrong has already successfully converted several key products to the new technology and is converting its remaining products.

Envirez™ Technology: Incorporating Renewable and Recycled Feedstocks into Unsaturated Polyester Resins

Ashland Performance Materials

Unsaturated polyester resins are key components of fiber-reinforced plastic thermoset composites. The annual production of these resins in North America is approximately 1 billion pounds. Historically, these resins have been made almost exclusively from virgin petrochemicals. Expanding on the pioneering work of Professor Richard Wool at the University of Delaware, Ashland developed Envirez™ resins, a novel, versatile family of unsaturated polyester resins made from either renewable or recycled raw materials or both. Ashland uses biobased building blocks including soybean oil, ethanol, 1,3-propanediol, and other proprietary monomers from soybeans, corn, and other renewable raw materials. Additional building blocks for Envirez™ resins are recycled monomers and polymers including postconsumer poly(ethylene terephthalate) (PET).

Ashland recently developed the first Envirez™ resins that employ recycled raw materials and use combinations of both recycled and renewable raw materials. Envirez™ resins now contain more types and higher percentages (up to 40 percent) of renewable raw materials. Ashland has developed formulations for a wide variety of composite fabrication methods including infusion, pultrusion, casting, and gelcoats. These formulations expand the reach of Envirez™ into an assortment of products and markets including green buildings and wind energy devices. They enable composite fabricators to use sustainable components.

Envirez™ technology leads to reduced dependence on petroleum, lower emissions, energy savings, and a smaller carbon footprint. In the last three years, Envirez™ resins have incorporated over 12 million pounds of recycled PET. Using a novel, biobased reactive intermediate, Ashland has developed Envirez™ low styrene resins that lower the traditional styrene content by one-third and reduce both hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). The Envirez™ product line has experienced double-digit growth in the past several years. Envirez™ low styrene resins have completed review under the Toxic Substances Control Act (TSCA) and are undergoing field trials at numerous composite fabricators.

Compostable Multilayer Food Packaging

BASF Corporation

Most conventional food packaging consists of a multilayer film structure comprised of polyolefin or polyamide resins and adhesives. The layers include barriers, colorful print, and adhesives to bond all the layers together. Because conventional packaging is neither recyclable nor compostable, landfills are the only disposal option. When organic material goes into a landfill it degrades over time, releasing landfill gas (LFG), which is a mixture of the environmental pollutants methane gas and carbon dioxide (CO_2). Because less than 30 percent of the landfills in the United States collect LFG, the majority of organic material placed into landfills eventually releases LFG.

In 2011, BASF's Biodegradable Polymers Group successfully made a completely compostable multilayer food packaging structure with high barrier properties. The structure consists of six layers: an Ecoflex® and Ecovio® outer layer, Joncryl SLX (printing ink layer), Epotal P 100 ECO (adhesive coating), a metallization layer, Versamid® (pre-met primer), and an Ecoflex® and Ecovio® inner layer. Ecoflex® is a bioplastic copolyester and Ecovio® is a compound of Ecoflex® with polylactic acid (PLA). This packaging structure meets the barrier requirements for a large number of packaged consumer goods.

For the first time, food packaging wastes can be diverted to industrial composting facilities that create end-of-life value far beyond putting the packaging in landfills. Composting and the subsequent use of the finished compost produce beneficial factors for the environment and resource management. BASF compostable multilayer packaging will allow landfill diversion for programs throughout the United States that are working toward Zero Waste. One of the benefits of diverting organic waste from landfills is increasing landfill lifespans. This reduces the need to build new landfills or expand existing ones, which will save energy, reduce emissions to water, and reduce air pollutants from building new landfills. BASF is partnering with the Seattle Mariners in their zero waste initiative through the Green Sports Alliance to replace trash cans with recycle and compost bins.

Bayer MaterialScience and Bayer AG

One-Component, UV-Curable, Waterborne Polyurethane Coatings

In the 1980's, Bayer MaterialScience (BMS) developed water-based unsaturated polyesters that were UV- or peroxide-curable and reduced volatile organic compounds (VOCs) and very hazardous air pollutants (VHAPs). Unfortunately, this technology did not displace the acid-catalyzed nitrocellulose lacquer systems. In 1992, Bayer's two-component (2K) water-based polyurethane coatings entered the wood coatings market. This technology displaced high-VOC and high-VHAP coating systems and won the 2000 Presidential Green Chemistry Award, but it was limited in its user-friendliness and slow drying speeds, especially on automated wood coating lines.

In 1999, BMS developed a one-component (1K), UV-curable, waterborne polyurethane with reduced VOCs and VHAPs for wood coatings. In this nominated process, BMS reacts a polyisocyanate and a polyol in a BMS production facility to create a polyisocyanate prepolymer. They then react this with a UV-curable polyol through an isocyanate–alcohol reaction to form 1K, UV-curable waterborne polyurethanes. The process develops high-molecular-weight polymers (over 200,000 g/mol) in water without residual isocyanate monomer or polyisocyanate prepolymer. The product contains ultra-low VOCs because BMS's proprietary process removes the acetone carrier after manufacturing.

Renowned manufacturers of office furniture now advertise products made with BMS coating systems as having low emissions and being environmentally compatible. Large furniture companies are increasingly specifying coating systems with low or no solvent. BMS coatings cure in just seconds under UV light and meet low- or no-solvent specifications very cost-effectively.

Between 2007 and 2011, commercial use of this coating system to replace acid-catalyzed varnishes or nitrocellulose lacquers resulted in reductions of 50–90 percent for VOCs and 50–99 percent for VHAPs, which is equivalent to removing 2.6 million pounds of organic solvents and 49,000 pounds of formaldehyde from the U.S. environment. Emerging markets for BMS's 1K UV-curable waterborne polyurethane include aerospace and defense, site-applied UV-cured flooring, sunshine-cured wood decking, special effects coatings, and wet-strength papers.

FIREBLOCK™ Intumescent Resin

CCP Composites

Composites used to manufacture interior and exterior parts for applications in trains, tramways, subways, and other rolling stock must meet fire retardant specifications. Traditional chemicals used in fire retardant composites are decabromodiphenyl ethers and antimony trioxide, which are carcinogens, mutagens, and reproductive toxins. The manufacturing of these fire retardant composites requires handling highly toxic substances. In case of accidental combustion, polybrominated aromatic compounds release free radicals that act in synergy with antimony trioxide to produce bromide radicals and toxic fumes.

Intumescent coatings swell with heat, offering passive fire protection. Intumescent coatings have been known for years, but these products were very difficult to formulate and apply. In 2008, CCP Composites developed a breakthrough product, FIREBLOCK™ intumescent unsaturated polyester resins (UPRs), which can be molded with glass fiber to manufacture fire retardant parts. In the intumescence mechanism, high temperatures cause ammonium polyphosphate to release an acid that simultaneously reacts with melamine in the resin to liberate a gas. The gas diffuses into small bubbles and carbonizes the carbon-rich polyalcohol. These actions form foam that solidifies into a char and shields the underlying material to stop the combustion cycle.

FIREBLOCK™ resin is a commercially viable alternative to bromine-containing fire retardant UPRs used in a wide variety of composites. It is completely free of halogens, mutagens, carcinogens, and reproductive toxins. In addition to meeting the same standards on materials fire behavior as do traditional fire retardants, FIREBLOCK™ intumescent resin also has a lower density than standard unsaturated polyester resins. It is environmentally friendly, with a 13 percent reduction in carbon dioxide (CO_2) emissions compared to standard fire retardants in the railway industry. A significant portion of today's estimated 10 million pounds annual use of brominated UPRs could be converted into FIREBLOCK™ technology in the next five years in the United States.

Vegetable Oil Insulating Fluid for Improved High Voltage Transformer Capability

Cooper Power Systems

Polychlorinated biphenyls (PCBs) form the basis for traditional dielectric coolant fluids, but they present environmental problems and liabilities for the electric power industry. Cooper Power Systems has developed a replacement insulating fluid, Envirotemp™ FR3™ fluid, to provide the electric power industry with a sustainable dielectric coolant that has an innocuous environmental and health profile. Envirotemp™ FR3™ fluid contains approximately 97 percent food-grade soy oil blended with small amounts of additives for long-term performance.

The National Institute of Standards and Technology (NIST) directly compared FR3™ fluid to mineral oil in its total lifecycle assessment called BEES® 4.0, Building for Environmental and Economic Sustainability. Using the carbon dioxide equivalent (CO_2 eq.) amount of greenhouse gas (GHG) generated from raw materials through end of life, FR3™ fluid has reduced GHG emissions by over 98 percent (or over 102,000 tons of CO_2 eq.) to date compared to mineral oil. This essentially carbon-neutral result assumes that FR3™ fluid or mineral oil would be placed in equivalent transformers. Roughly 450,000 transformers now contain over 25 million gallons of Envirotemp™ FR3™ fluid instead of petroleum-based mineral oil.

In 2011, Cooper combined the chemistries of FR3™ fluid and solid insulating paper with advanced high voltage transformer design to produce a new generation of even greener biotransformers. The chemical interactions between FR3™ fluid and the solid insulating structure create greater thermal capacity that allows an optimized biotransformer design. With this increased capacity, Cooper removed 3–15 percent of the fluid volume and 3 percent of the construction materials from the biotransformers. Using the BEES analysis on 25 million gallons of FR3™ fluid, the new generation of biotransformers could save an additional 2,000 tons of GHG emissions. Other advantages include improved fire safety, remediation of accidental spills, and sustainable supply benefitting U.S. farmers. New transformer designs with FR3™ fluid will be available in 2012.

Cytec Industries Inc.

Saturated Polyester–Phenolic Resin Systems for Bisphenol A-Free Interior Can Coatings for Food Packaging

Bisphenol A (BPA) is a key raw material for the binders in interior coatings of food cans, but recent animal studies have found that BPA exhibits potential endocrine-disrupting effects. Because these coatings are a significant source of consumer exposure to BPA, the food industry is demanding coatings without BPA. Although U.S. regulatory agencies have not promulgated regulations, the elimination of BPA from interior can coating systems is a matter of public and scientific interest.

Cytec has developed a new generation of BPA-free, saturated polyester resins for the main binder. These polyester resins, together with phenolic resins, can be used in interior can coatings. Coating systems based on these resins exhibit performance comparable 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 daltons. All the monomers in its synthesis comply with food contact laws. It does not contain any significant levels of free solvent if properly cured, and it complies fully with the U.S. Food and Drug Administration's (FDA's) regulation 21 CFR §175.300 for polyesters. Computer modeling indicates that DUROFTAL PE 6607/60BGMP does not have the estrogenic properties of BPA. 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 interior can coatings so the system can eliminate BPA completely and perform comparably to existing systems. Commercial sales began in 2008. In 2010, Cytec began its first full-scale production of the phenolic part of the system. In 2011, Cytec's first commercial sales of DUROFTAL PE 6607/60BGMP eliminated about 10 tons of BPA.

The Dow Chemical Company

EVOQUE™ Pre-Composite Polymers

Titanium dioxide (TiO_2) is the primary white pigment in paint; it provides opacity by scattering visible light. The process that derives TiO_2 from titanium ore requires large quantities of energy, complete digestion with excess chlorine or sulfuric acid, and a multistep purification.

Dow has developed EVOQUE™ Pre-Composite Polymer Technology for making paint with 10–20 percent less TiO_2. Dow controls the interaction between individual pre-composite polymers and TiO_2 pigment particles to achieve a TiO_2-centered structure surrounded by polymer molecules. As the pigment–polymer composites in paint dry to a film, the pre-composite polymers keep the individual TiO_2 particles separated so they are evenly distributed. Performance benefits resulting from improved film formation and reduced photodegradation (due to reduced TiO_2, which promotes photodegradation) are expected to improve exterior durability by 20 percent.

Third-party validated lifecycle assessment (LCA) shows that TiO_2 reductions facilitated by EVOQUE™ Pre-Composite Polymer Technology in exterior house paint reduce the associated carbon footprint by 22.5 percent, water consumption by 30 percent, NO_X and SO_X emissions by 24 percent, potential water eutrophication (algal bloom) by 27 percent, potential chemical oxygen demand (COD) by 30 percent, and non-methane volatile compounds (NMVOC) by 35 percent. These last two factors impede water quality and air quality, respectively.

EVOQUE™ Pre-Composite Polymer Technology is currently compatible with white and pastel acrylics, which account for approximately 165 million gallons of U.S. paint produced annually. Based on TiO_2 removal alone, using EVOQUE™ Pre-Composite Polymer Technology in half of this paint could reduce associated greenhouse gas (GHG) emissions by approximately 54,000 metric tons of carbon dioxide equivalents (CO_2 eq.). The enhanced performance and durability expected from paints with EVOQUE™ Pre-Composite Polymer Technology could increase this reduction to 123,000 metric tons of CO_2 eq., which is comparable to the annual CO_2 emissions generated from the gasoline used by approximately 14,000 cars.

INFUSE™ Olefin Block Copolymers

The Dow Chemical Company

INFUSE™ Olefin Block Copolymers (OBCs) are produced with a patent-pending shuttling process that represents an innovation in catalyst technology and that delivers breakthrough performance using new combinations of properties. These block copolymers have alternating blocks of "hard" (highly rigid) and "soft" (highly elastomeric) segments as the result of reversible chain transfers between two different catalysts. Dow's catalytic shuttling technology generates a variable, yet controllable, distribution of block lengths that can generate tailor-made olefins for specific uses. OBCs have highly differentiated material properties that break the traditional relationship between flexibility and heat resistance. They also provide significantly improved compression set and elastic recovery properties compared to other polyolefin plastomers and elastomers. OBCs possess the ease of formulation and processing that are typical of polyolefins.

The unique block architecture of OBCs enables Dow's customers to expand into a wide range of innovative market applications currently served by high-performance thermoplastic elastomers, thereby adding value to fabricators and end-users alike. The sustainable chemistry benefits of OBCs include (1) atom efficiency due to improved selectivity; (2) reduced toxicity and risk compared to other polymers; (3) minimized auxiliary substances because the complex chain-shuttling, dual-catalyst system is highly efficient; (4) reduced energy requirements for both polymer synthesis and fabrication; and (5) better recycling and end-of-life management because OBCs are compatible with disparate plastic waste streams and can even enhance the quality of waste streams. The OBC manufacturing process fits into existing facilities with only limited changes to equipment, leading to significant resource savings. OBCs are suitable for a very large number of applications; their economic benefits are great, thereby enhancing market selection.

Dow created INFUSE™ OBCs using its INSITE™ Technology. From 2008 to 2011, Dow OBCs replaced a number of existing polymers including styrene–ethylene–butylene–styrene (SEBS), thermoplastic vulcanizates (TPV), and flexible poly(vinyl chlorine) (f-PVC) for 85 customers worldwide.

Chlorantraniliprole: Increased Food Production, Reduced Risks, More Sustainable Agriculture

DuPont Company

The caterpillar larvae of many lepidopteran species are major agricultural pests, defoliating plants and attacking fruit and root systems. Lepidopteran pests are likely responsible for 30–40 percent of insect damage to crops; they consume 50 percent of all crops in many developing countries. Although insecticides are available to control these pests, many present significant risks to humans or the environment.

DuPont redesigned its discovery process for new pesticides by integrating chemistry and biology with toxicological, environmental, and site-of-action studies to optimize safety and product performance simultaneously. The resulting product, chlorantraniliprole, has excellent safety and environmental profiles yet is one of the most potent, efficacious chemical insecticides ever discovered.

Chlorantraniliprole selectively interferes with muscle contraction in insects by activating a site in ryanodine receptor channels that is highly divergent between insects and mammals. Because it selectively targets insects, chlorantraniliprole is inherently safer to people and other nontarget organisms. EPA classifies chlorantraniliprole as a reduced risk pesticide. It may be the safest of all lepidopteran insecticides, including those derived from natural sources. Chlorantraniliprole is usually one to two orders of magnitude more potent against target pests than are pyrethroids, carbamates, and organophosphates. Its lower use rates mean less pesticide gets into the environment with a corresponding reduction in the exposure of workers and the public. Chlorantraniliprole's proven safety to bees and other beneficial arthropods allows its use in integrated pest management (IPM) programs. In addition, its mode of action provides an important new tool for managing insecticide resistance.

DuPont manufactures chlorantraniliprole in a convergent commercial process that minimizes organic solvents, recovers and recycles the solvents it does use, minimizes waste, eliminates regulated waste products, and establishes inherently safer reaction conditions. Chlorantraniliprole is rapidly displacing less desirable products from many key markets. In 2011 alone, more than 20 million farmers and 400 crops benefitted from insect control by chlorantraniliprole.

DuPont Company

Development of a Commercially Viable, Integrated, Cellulosic Ethanol Production Process

Traditional production of ethanol from starches, such as corn grain, diverts resources from food production. DuPont has developed a biochemical technology that produces ethanol from non-food lignocellulosic biomass such as corn stover. DuPont's process is an integrated pathway with sufficiently high yields and titers of ethanol to be commercially viable.

It integrates three components: First, dilute ammonia pretreatment decouples the carbohydrate polymers from the lignin matrix with minimal formation of compounds that inhibit subsequent fermentation. This pretreatment runs at up to 70 percent biomass with less than 10 percent ammonia by weight. Second, genetically engineered cellulase and hemicellulase enzymes from *Hypocrea jecorina* (a filamentous fungus) produce high yields and titers of fermentable 6-carbon and 5-carbon sugars. Third, the optimized metabolic pathways of a recombinant ethanologen (*Zymomonas mobilis*) produce ethanol efficiently by simultaneously metabolizing both the 6-carbon and 5-carbon sugars. Integrating and optimizing these three components enables a very efficient process, a green footprint, and lower costs, including less capital investment than other known cellulosic ethanol processes. If corncob feedstocks cost $50 per dry ton, the ethanol from DuPont's process could cost less than $2 per gallon.

Removing the yield, titer, and cost barriers to commercializing cellulosic ethanol is a significant step toward large-scale production of cleaner, more sustainable liquid transportation fuels. Comprehensive well-to-wheel lifecycle assessments (WTW LCA) show that DuPont's process could potentially reduce greenhouse gas (GHG) emissions by over 100 percent compared to gasoline, which is substantially larger than GHG reductions from other grain-based ethanol processes.

A flexible-feedstock, 250,000 gallon-per-year demonstration facility in Vonore, TN is currently yielding over 70 gallons per U.S. ton of biomass and ethanol titers in excess of 70 grams per liter. In 2014, the first commercial-size facility to convert corn stover to over 25 million gallons of ethanol annually is expected to start up in Nevada, IA.

Production of Isobutanol from the Synergy between Metabolic and Process Engineering

DuPont Company and Butamax™ Advanced BioFuels LLC

Isobutanol, an advanced biofuel, offers significant technical and commercial advantages over fossil fuels and ethanol. Isobutanol has a high octane number, good distillation qualities, low vapor pressure, high compliance value in fuels, materials compatibility, low toxicity, and the ability to reach targeted production economics.

DuPont was the first to create and develop integrated biological and process technologies that use microbes to produce isobutanol from renewable resources. DuPont's strategy for low-cost commercialization includes retrofitting existing ethanol plants to produce isobutanol from current ethanol-industry feedstocks (i.e., corn grain and sugarcane), lignocellulosic biomass, and macroalgae (seaweed). A proprietary yeast strain engineered with a novel biosynthetic pathway ferments sugars from these feedstocks to isobutanol. DuPont selected key enzymes based on their isobutanol specificity and cofactor requirements, then maintained flux through to isobutanol by eliminating byproduct reactions that could compete with the chosen pathway. This yeast-based isobutanologen is a drop-in biocatalyst suitable for retrofitted ethanol plants.

A major challenge in commercial isobutanol production by microbes is the intolerance of the microbes to commercially relevant aqueous titers of isobutanol. DuPont met this challenge by reducing the aqueous concentration of isobutanol in fermentations, thereby avoiding enzyme inhibition by its product while minimizing production cost and environmental footprint.

The fermentation rate, titer, and yield are significantly superior to those of traditional acetone–butanol–ethanol (ABE) fermentations. This performance demonstrates cost-effective biological production of isobutanol for chemicals and fuels. DuPont's technology can displace petroleum-based syntheses for isobutanol and directly replace refined gasoline from crude oil with a greener, biobased product. Further, its advantages over incumbent technologies include reducing greenhouse gas (GHG) emissions by 40–70 percent, local and national economic benefits, and increased national security through domestic fuel supplies. During 2011, DuPont began operating a large-scale demonstration plant for isobutanol in the United Kingdom in a joint venture with Butamax™ Advanced BioFuels.

Grignard Reactions Go Greener with Continuous Processing

Eli Lilly and Company

The synthetic pathways of numerous intermediates for food additives, industrial chemicals, and pharmaceuticals have included the Grignard reaction since the start of the 20th century. Despite these successes, the acute hazards of the Grignard reaction make it one of the more challenging reactions to bring to commercial scale. These hazards include: (1) strongly exothermic activation and reaction steps; (2) heterogeneous reactions with potential problems suspending and mixing the reaction mixture; and (3) extreme operational hazards posed by ethereal solvents such as diethyl ether.

Eli Lilly and Company has developed inherently safer Grignard chemistry using a continuous stirred tank reactor (CSTR) that allows continuous formation of Grignard reagents with continuous coupling and quenching operations. This strategy minimizes hazards by operating at a small reaction volume, performing metal activation only once for each campaign, and using 2-methyltetrahydrofuran (2-MeTHF) as a Grignard reagent and reaction solvent that may be derived from renewable resources. Grignard reactions using 2-MeTHF also result in products with enhanced chemo- and stereoselectivity. Relative to batch processing, the continuous approach allows rapid, steady-state control and overall reductions up to 43 percent in magnesium, 10 percent in Grignard reagent stoichiometry, and 30 percent in process mass intensity (PMI). The continuous approach reduces reaction impurities substantially. In addition, small-scale operation at end-of-reaction dilution allows all ambient processing conditions.

Lilly is using its CSTR Grignard approach to produce three pharmaceutical intermediates. One of these is the penultimate intermediate of LY2216684.HCl, a norepinephrine reuptake inhibitor that is under phase 3 clinical investigation for treatment of depression. Lilly uses a similar approach to synthesize an intermediate for LY500307, an investigational new drug candidate under clinical evaluation to treat benign prostatic hyperplasia. Lilly anticipates commercial production on 22 liter scales that will replace the 2,000 liter reactors used in batch processes.

IBM Corporation

Catalytic Treatment of Hydrogen Peroxide in IBM Semiconductor Wastewater

Semiconductor manufacturing produces a large ammonia and hydrogen peroxide wastewater stream that requires treatment. Through 2009, the industry standard for treating this wastewater stream was to reduce the hydrogen peroxide with sodium bisulfate then to neutralize it with sodium hydroxide. The next step was separating ammonia by distilling the wastewater to remove ammonium hydroxide. The added sodium bisulfite and sodium hydroxide contributed high levels of total dissolved solids (TDS) to IBM's wastewaters and final effluent discharge, and both were also becoming increasingly expensive.

In 2003, IBM's East Fishkill plant (EFK) began an initiative with the New York State Department of Environmental Conservation to reduce the TDS in the site's effluent discharge to a small receiving stream. Over the next six years, IBM EFK investigated alternative technologies to remove sources of TDS from its manufacturing wastewaters and wastewater treatment processes. In early 2009, IBM qualified a catalytic enzyme process to replace the existing sodium bisulfate process for removing hydrogen peroxide from the ammonia wastewater. This process uses a small quantity of a catalase derived from *Aspergillus niger* fermentation to decompose peroxide into water and oxygen. It does not contribute TDS to the site's effluent discharge and costs a fraction of the previous treatment. The new process incorporates existing building equipment as much as possible and integrates flawlessly into the existing treatment system.

IBM started and completed design and construction of the full-scale peroxide treatment system in 2009, with startup continuing through March 2010. Annually, this new process eliminates the use of 510,000 gallons of 38 percent sodium bisulfite and 135,000 gallons of 50 percent sodium hydroxide for acid neutralization. It reduces chemical costs by $675,000 per year. The catalytic reduction of hydrogen peroxide process has been online continuously since the beginning of 2010 and is currently patent-pending.

IBM Corporation

Elimination of PFOS and PFOA in IBM Semiconductor Manufacturing Processes and Development of Photoacid Generators Free of Perfluoroalkyl Sulfonates

In 2002, EPA restricted new applications of perfluorooctane sulfonate (PFOS) compounds because scientific evidence showed that PFOS persists and bioaccumulates in the environment. Because semiconductor manufacturers demonstrated limited release and exposure for PFOS, however, EPA allowed PFOS compounds "as a component of a photoresist substance, including a photoacid generator or surfactant, or as a component of anti-reflective coating, used in a photolithography process to produce semiconductors or similar components of electronic or other miniaturized devices."

Voluntarily, IBM began searching for alternatives to PFOS and perfluorooctanoate (PFOA). In 2006, IBM issued a Corporate Directive to eliminate PFOS and PFOA from all manufacturing processes by 2010. IBM worked with chemical suppliers to identify and qualify a non-PFOS replacement for the PFOS surfactant in buffered oxide etch (BOE) chemicals. In 2008, after a multiyear investigation and extensive qualifications, both IBM fabrication plants finished replacing the PFOS surfactant in all BOE chemicals with perfluorobutane sulfonate (PFBS), for which EPA has fewer environmental concerns.

IBM also sought replacements for specific photoresists and antireflective coatings (ARCs) that contained PFOS or PFOA as a surfactant or photoacid generator (PAG). In January 2010, after significant investment and qualification of replacement chemistries across many wet etch and photolithography processes, IBM completed its conversion to non-PFOS, non-PFOA lithographic chemicals. This change eliminates approximately 140 kilograms of PFOS and PFOA annually. Total annual PFOS consumption by the semiconductor industry worldwide is estimated at 8,000 kilograms. IBM believes it is the only company in the world to eliminate PFOS and PFOA compounds completely from semiconductor manufacturing. IBM has also developed PAGs free of perfluoroalkyl sulfonates (PFAS) for both dry and immersion 193-nm semiconductor photolithography processes, with equivalent performance in 45-nm and 32-nm semiconductor technology. IBM is pursuing technology transfer opportunities to commercialize its PFAS-free PAGs for a wider range of applications.

NATRASURF™ PS-111 Polymeric Surfactant: Achieving Next Generation Mildness in Personal Care Products with a Reduced Environmental Footprint

Johnson & Johnson Consumer Companies, Inc. and AkzoNobel Surface Chemistry LLC

The production of personal cleansing products, such as shampoos, body washes, and facial cleansers, consumes sizable, ever-increasing volumes of surfactants. Traditionally, the industry used largely nonrenewable, petroleum-derived synthetic detergents to achieve mildness in personal cleansers. Although these well-established surfactants are safe and cost-effective, they could be improved in their mildness, renewability, manufacturing processes, and biodegradability.

Johnson & Johnson and AkzoNobel have collaborated to develop NATRASURF™ PS-111, an innovative, starch-based polymeric surfactant (PS) for formulating mild personal care products. PS-111 is based on the patented discovery that PSs overcome the problem of surfactant-induced irritation because they cannot penetrate living tissue. NATRASURF™ PS-111, the first personal care ingredient of its kind, delivers the cleaning and foaming performance of traditional surfactants and has virtually no irritation potential.

NATRASURF™ PS-111 minimizes environmental impacts throughout its lifecycle. PS-111 is sodium hydrolyzed potato starch dodecenylsuccinate, a 90 percent renewable material derived by reacting hydrolyzed potato starch with an alkenylsuccinic anhydride. This low-temperature, aqueous esterification offers many advantages over traditional esterifications, including energy efficiency and atom economy. The starch ester used for PS-111 is nonirritating to skin and eyes, nonallergenic, nontoxic to humans and aquatic organisms, nonbioaccumulative, and readily biodegradable. PS-111 is supplied to manufacturers as a self-preserving, spray-dried powder; this eliminates the need for chemical preservatives and reduces the energy used to store and ship conventional aqueous surfactant solutions.

PS-111 has the potential to replace millions of pounds per year of nonrenewable, poorly biodegradable surfactants and emulsifiers. Further, this technology can be readily leveraged for use in agricultural, household, and industrial applications. NATRASURF™ PS-111 exemplifies how green chemistry can enable cost-effective, sustainable materials that benefit both consumers and the environment without sacrificing performance or efficacy. In December 2011, Johnson & Johnson launched the AVEENO® Pure Renewal line of shampoos, the first products containing NATRASURF™ PS-111.

Kop-Coat, Inc.

Tru-Core® Protection System for Wood

Wood is the most widely used residential building material in the United States. Its environmentally positive characteristics include excellence as a carbon sink, low embodied energy, and high sustainability. Among its few shortcomings, however, is its relative lack of durability due to its susceptibility to decay and insect attack. Preservatives and insecticides can improve the durability of wood significantly, but methods to deliver these protectants into wood are largely based on old, environmentally damaging technologies.

Kop-Coat developed Tru-Core® Protection System to treat wood in an environmentally positive manner. The Tru-Core® system incorporates the principles of green chemistry in several ways. For example, most conventional treatments for wooden window frames and doors use petroleum-based solvent carriers, such as mineral spirits, that emit volatile organic compounds (VOCs). The Tru-Core® process uses water as the carrier, resulting in a significant reduction in organic solvent use. Because the Tru-Core® process uses only a small amount of water to carry the preservatives, it also eliminates the energy-intensive step of re-drying wood after treatment.

The Tru-Core® system employs a unique chemical infusion process that includes nonvolatile, highly polar bonding carriers (amine oxides in water) that penetrate the cellular structure of wood to deposit and bind wood protection chemicals (preservatives and insecticides) within the substrate. Buffers such as borates maintain a basic pH that inhibits the natural acids present in wood, allowing the amine oxides and preservatives to penetrate rapidly. Tru-Core® extends the service life of wood at a cost that is less than one quarter the cost of the closest competing treatment technology.

In 2010, EPA registered the patented Tru-Core® technology as a wood preservative. In 2011, Tru-Core® technology was used in the dual treatment process for approximately two million railroad ties. Tru-Core® Type 1 is currently undergoing evaluation by ICC-ES (International Code Council Evaluation Service) for acceptance into the 2012 International Building Code.

Masterchem Brands

KILZ MAX™ PRIMER-SEALER-STAINBLOCKER: Oil-Based Performance in a Water-Based Formula with Less Environmental Impact

Solvent- and shellac-based stain-blocking primers typically include resins that require petroleum-based solvents such as mineral spirits or ethanol. These solvents are not only combustible (and in some cases flammable); they also release significant amounts of volatile organic compounds (VOCs) during application and drying. Water-based primers made with a variety of acrylic and styrene–acrylic resins are available, but they have extended dry times and cannot approach the stain-blocking properties of solvent-based primers.

Masterchem Brands has developed KILZ MAX™ primer, using specialized epoxy-based resin technology to provide heavy stain-blocking and odor blocking in a more eco-friendly, water-based formula. This product has the benefits of solvent- or shellac-based primers including the ability to block severe stains and odors, resist tannin stains, and more. It does not have the associated drawbacks of high odor, high VOCs, or clean up that requires mineral spirits. Independent testing confirms that KILZ MAX™ performs as well or better than oil- and shellac-based primers on virtually all problem stains, odors, and other surface imperfections. It also meets or exceeds the performance of many products marketed as having similar technology.

KILZ MAX™ primer has a VOC level near 75 grams per liter; this is over seven-fold lower than competitive shellac-based primers and six-fold lower than typical competitive specialty primers.

Replacing the solvent with water in KILZ MAX™ primer eliminates approximately 3 pounds of VOCs per gallon compared to KILZ® Original solvent-based primer. In 2007, Masterchem Brands sold over 3.3 million gallons of KILZ® Original primer. Replacing the higher-VOC version with KILZ MAX™ primer would reduce airborne VOCs by as much as 9 million pounds annually. Another benefit is the ability to sell high-performance stain-blockers in areas regulated by the South Coast Air Quality Management District (SCAQMD), the California Air Resources Board (CARB), and others. KILZ MAX™ primer was first produced and launched in retail markets in 2011.

Revolutionizing Insect Control: Bt Technology

Monsanto Company

Crop insect pests have limited food production for centuries. Although chemical insecticides were the most advanced tools for insect control until the 1990s, they had undesirable environmental effects, were toxic to some nontarget organisms, and required repeated applications to crops.

Unlike traditional pesticides, Monsanto's recently patented technology uses insect control present in nature. *Bacillus thuringiensis* (*Bt*, a ubiquitous soil microbe) produces Cry (crystal) proteins, which are insecticidal toxins. Using biotechnology, Monsanto combined its knowledge of Cry proteins with pioneering plant molecular genetics to create crop plants that express synthetic *Bt* Cry proteins engineered to be highly specific toxins against insect pests. In addition to reducing the use of pesticides, the specificity of Cry proteins ensures only target organisms are affected and not humans, animals, or nontarget, beneficial insects. Monsanto's application of biotechnology to controlling pests makes both pesticide manufacturing and chemical pesticide applications less necessary.

Farmers planting insect-resistant crops experience improved safety and health because of reduced handling and use of pesticides. They spend less time applying insecticides. Reduced applications mean fewer containers, less fuel, and less aerial spraying: all factors that benefit the environment while increasing yields and enhancing farmers' lives.

Bt technology continues to be applied across many plant varieties, increasing yields and reducing the need for chemical pesticides. All *Bt* traits in commercial use have been created with Monsanto's patented synthetic *Bt* gene technology; traits Monsanto developed have been licensed to and sold by numerous seed companies, as well as by Monsanto itself. Some companies have developed their own insect resistance traits, but all of these traits have used Monsanto's synthetic gene technology covered by a recently issued patent (U.S. patent 7,741,118 B1). In 2010, 65 percent of all corn grown in the United States and 75 percent of all cotton grown in the United States included one or more *Bt* traits.

NALCO's APEX™ Program: Sustainable Technology for Paint Detackification

NALCO

For decades, manufacturers have used hazardous melamine–formaldehyde–acid colloids to detackify paint overspray in spray booths. Melamine is an irritant, however, and chronic exposure may cause cancer or reproductive damage. Formaldehyde is a known carcinogen according to the Occupational Safety and Health Administration (OSHA). Further, the colloid is derived from feedstocks based on nonrenewable petroleum or natural gas. In searching for an alternative, U.S.-based manufacturing companies established an initiative to create a green method for paint detackification using innovative chemistry.

NALCO developed the APEX™ program to support this initiative. The APEX™ program consists of an etherified, cationically modified corn starch mixed with a small amount of a proprietary amphoteric polymer and a polybasic aluminum salt. It is formulated from over 99 percent sustainable resources. When added to a paint system at a pH above 7.0, APEX™

generates a highly cross-linked "sweep floc" that rapidly coagulates and completely detackifies paint solids, creating an easily dewaterable sludge. The APEX^{TM} program completely eliminates formaldehyde and other harmful, nonrenewable raw materials in these applications.

The APEX^{TM} program benefits every manufacturing company that adopts it by: (1) reducing total costs of operation (typically over 30 percent); (2) reducing chemical use (typically over 80 percent); (3) reducing the generation and transportation of wastes (typically over 50 percent); (4) reducing water use; and (5) reducing emissions of volatile organic compounds (VOCs).

A large automotive plant in Alabama first implemented APEX^{TM}, where it reduced solid waste generation by 267,000 pounds and saved $90,000 in disposal costs. It reduced VOC generation by over 3,000 pounds (an 80% reduction). It also reduced the frequency of booth cleaning from weekly to once per quarter, saving an additional $160,000 in operating costs and significantly reducing use of cleaning chemicals. NALCO's APEX^{TM} program is currently used in 85 assembly plants.

Pacific Northwest National Laboratory and Archer Daniels Midland Company

Propylene Glycol from Renewable Sources

Propylene glycol (PG) is a commodity chemical used in everyday consumer products such as liquid detergents, hand sanitizers, pharmaceuticals, and cosmetics, as well as in industrial products such as plastics, paint, antifreeze, and aircraft deicer. The largest use of PG is as a monomer in plastics, especially fiberglass resins. Until recently, PG has been produced almost entirely from petroleum resources. Each year, worldwide PG production consumes more than two billion pounds of petroleum.

To eliminate this use of petroleum and to replace the toxic feedstocks involved, Battelle scientists at Pacific Northwest National Laboratory (PNNL) developed a catalytic process for producing PG from renewable sources. The propylene glycol from renewable sources (PGRS) process relies on a carbon-supported bifunctional metal catalyst in combination with a soluble base co-catalyst. The multistep process proceeds in a single reactor to produce PG in high selectivity and at high conversion. This safe, sustainable, cost-competitive, and commercially viable alternative converts plant-based, seed-oil-derived glycerol or plant sugar alcohols into PG, which can then be purified to meet a variety of market specifications. The glycerol can come from a variety of sources, including the crude glycerol byproduct of biodiesel production. The PGRS process currently produces propylene glycol for the first time on a commercial scale entirely from renewable resources. A lifecycle analysis shows that the PGRS process eliminates up to 61 percent of the greenhouse gas (GHG) produced by the traditional propylene oxide route to PG.

Archer Daniels Midland (ADM) commissioned and is now operating a new 100,000 metric ton per year PG facility using Battelle's technology. This represents the first of its kind in the world: an operational, commercial-scale facility producing PG that meets U.S. Pharmacopeia (USP) specifications entirely from renewable resources. Other competing technologies have been unable to produce PG from renewable materials of this high-quality material at full scale.

Pfizer

New Green Commercial Biocatalytic Route to Atorvastatin Calcium, the Lipitor API

Atorvastatin is the active pharmaceutical ingredient (API) in Lipitor. Since its launch in 1997, Lipitor has been the most-prescribed branded cholesterol-lowering medication in the world. This success, together with Pfizer's commitment to continuous improvement, made the production of atorvastatin an obvious target for improvement. Pfizer challenged itself to make dramatic improvements in both the efficiency and environmental performance of the manufacturing route to atorvastatin.

The original manufacturing process required a chiral starting material. Because optimizing this process would not achieve the transformational changes that Pfizer sought, the company developed a completely new, more efficient, commercial route to atorvastatin calcium using a biocatalytic process.

The new green process incorporates a water-based 2-deoxyribose-5-phosphate aldolase (DERA) enzyme at the beginning of the route to make a lactol from an amino aldehyde (i.e., 3-phthalimidopropionaldehyde; PPA) and acetaldehyde. The synthesis eliminates the use of cyanide or azide moieties to introduce nitrogen because it is already present in the lactol. In contrast to the original synthesis, the DERA enzyme sets both stereocenters with high selectivity in water at room temperature. Converting the resulting lactol into isopropyl acetonide atorvastatin (IAA) is extremely efficient: it involves four high-yield chemical steps (oxidation, esterification, deprotection, Paal Knorr) with only the IAA product being isolated as a solid. Finally, IAA is converted to atorvastatin calcium, the API product.

Pfizer's green process substantially reduces the environmental impact by eliminating hazardous steps and reducing or eliminating required chemicals. For example, the new synthesis eliminates the previous high-pressure hydrogenation step with its associated metal catalysts. It also avoids pyrophoric *n*-butyl lithium and its associated butane waste gas. The need for significant other reagents and solvents has either been eliminated or dramatically reduced. The U.S. Food and Drug Administration (FDA) approved the new manufacturing process in April 2010. Pfizer manufactured commercial scale validation batches in 2011 and is currently transitioning to full-scale commercial manufacture.

Ethos™ Modular Commercial Floor Coverings

Tandus Flooring

Polymeric poly(vinyl butyral) (PVB) is a thermoplastic terpolymer of vinyl acetate, vinyl alcohol, and vinyl butyral that provides shatterproof properties to windshields and other safety glass. Although recyclers have recovered the glass from safety glass and sold it into other markets for years, most of the PVB film has been sent to landfills or burned for energy.

Tandus Flooring is the first manufacturer to use the abundant PVB waste stream and recycle it into high-performance carpet backing. Ethos™ secondary backing, made from PVB film reclaimed from windshields and other safety glass, can replace other structured carpet backings such as poly(vinyl chloride) (PVC), ethylene–vinyl acetate (EVA), polyurethane, polyolefin, and bitumen. Producing ethos™ backing from recycled material reduces the energy and environmental impacts associated with extracting, harvesting, and transporting virgin raw materials.

Tandus evaluated PVB against 10 other polymer-based materials using stringent performance and environmental criteria. In these tests, PVB was superior to the other polymers in material availability, recyclability, reduction of virgin resources, avoidance of hazardous emissions (e.g., dioxin), and elimination of chemicals of concern such as chlorine, fly ash, and phthalate plasticizers. In addition, ethos™ backing has extremely low environmental lifecycle impacts compared to other products. Tandus's patented, closed-loop process can also recycle postconsumer carpet with ethos™ backing and other manufacturing waste into new floor coverings.

Initially, Tandus successfully introduced a six-foot-wide ethos™ cushion backing, Powerbond, to meet the needs of Kaiser Permanente for high-performance, PVC-free, soft-surface flooring. In November 2009, the company introduced ethos™ modular. Its production has increased 18-fold in the last two years. Every square yard of ethos™ modular replaces approximately 5.25 pounds of PVC in carpet backing. To date, Tandus has recycled more than 10 million pounds of PVB into flooring products, keeping PVB from landfills, and potentially replacing 52 million pounds of PVC.

Verenium Corporation

Pyrolase® Cellulase Enzyme Breaker as a Biodegradable Replacement for Corrosive Acids and Oxidizers in Hydraulic Fracturing Operations

Hydraulic fracturing (fracking) is an advanced drilling technique used to unlock vast stores of oil and shale gas across the country. It involves pumping pressurized water, sand, and chemicals underground to open fissures in oil- and gas-containing formations such as shale and improve the flow to the surface. Fracturing uses a host of corrosive acids and oxidizers to degrade and remove fracturing fluid residues from formation pores. The fracturing process has drawn harsh criticism from environmentalists claiming that potential contamination of underground water by fracturing poses a significant environmental risk. In December 2011, EPA first stated publicly that fracturing might be to blame for groundwater pollution in Wyoming.

Verenium has developed Pyrolase® cellulase to replace the corrosive acids and hazardous oxidizers used in fracturing. Verenium discovered and isolated the gene for Pyrolase® cellulase, a thermostable enzyme from the eubacterium *Thermotoga maritime*, found in geothermally heated sediment on the ocean floor. Pyrolase® cellulase is a broad-spectrum β-glycosidase with both endo- and exo-glucanase activities that provides a complete viscosity break on fracturing fluids across a broader range of temperatures, wider pH ranges, and higher salinity than other commercial enzymes. Pyrolase® cellulase is also useful in a wider variety of down-hole conditions. It excels in hydrolyzing linear and cross-linked fluids, such as guar gum, derivatized guar, and carboxymethyl cellulose, at speeds easily controlled by varying the enzyme loading. It offers superior performance with zero environmental impact.

Pyrolase® cellulase is an easy-to-use liquid. One pound of biodegradable Pyrolase® cellulase can replace more than 20 pounds of hazardous chemicals, some of which are implicated in soil and water contamination. Pyrolase® cellulase is a significant step toward addressing the environmental and health concerns over hydraulic fracturing both for workers and for those living near fracturing operations. Verenium launched a campaign in 2011 to commercialize Pyrolase® cellulase to the oil and gas services industry.

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Award winners are indicated with asterisks.

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