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Presidential Green Chemistry Challenge Awards Program:

Summary of 2011 Award Entries and Recipients

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Presidential Green Chemistry Challenge Awards Program: Summary of 2011 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 16 years of the awards program, EPA has received more than 1,400 nominations and presented awards to 82 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 together our 82 winning technologies are responsible for reducing the use or generation of more than 199 million pounds of hazardous chemicals, saving 21 billion gallons of water, and eliminating 57 million pounds of carbon dioxide releases to air. Adding the rest of the nominated technologies makes the benefits far greater.

This booklet summarizes entries submitted for the 2011 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 2011 awards. Judging criteria included health and environmental benefits, scientific innovation, and industrial applicability. Five of the nominated technologies were selected as winners and were nationally recognized on June 20, 2011, 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 2011 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

Towards Ending Our Dependence on Organic Solvents

Professor Bruce H. Lipshutz, Department of Chemistry and Biochemistry, University of California, Santa Barbara

Innovation and Benefits

Most chemical manufacturing processes rely on organic solvents, which tend to be volatile, toxic, and flammable. Chemical manufacturers use billions of pounds of organic solvents each year, much of which becomes waste. Water itself cannot replace organic solvents as the medium for chemical reactions because many chemicals do not dissolve and do not react in water. Professor Lipshutz has designed a safe surfactant that forms tiny droplets in water. Organic chemicals dissolve in these droplets and react efficiently, allowing water to replace organic solvents.

Organic solvents are routinely used as the medium for organic reactions and constitute a large percentage of the world's chemical production waste. Most organic solvents are derived from petroleum and are volatile, flammable, and toxic. Typically, organic reactions cannot be done in water because the reactants themselves are insoluble. Surfactants can be used to increase the solubility of organic reactants in water, but they often disperse the reactants, slowing the reactions.

Professor Lipshutz has designed a novel, second-generation surfactant called TPGS-750-M. It is a "designer" surfactant composed of safe, inexpensive ingredients: tocopherol (vitamin E), succinic acid (an intermediate in cellular respiration), and methoxy poly(ethylene glycol) (a common, degradable hydrophilic group also called MPEG-750). TPGS-750-M forms "nanomicelles" in water that are lipophilic on the inside and hydrophilic on the outside. A small amount of TPGS-750-M is all that is required to spontaneously form 50–100 nm diameter micelles in water to serve as nanoreactors. TPGS-750-M is engineered to be the right size to facilitate broadly used organic reactions, such as cross-couplings. Reactants and catalysts dissolve in the micelles, resulting in high concentrations that lead to dramatically increased reaction rates at ambient temperature. No additional energy is required.

Several very common organic reactions that are catalyzed by transition metals can take place within TPGS-750-M micelles in water at room temperature and in high isolated yields. These reactions include ruthenium-catalyzed olefin metatheses (Grubbs), palladium-catalyzed cross-couplings (Suzuki, Heck, and Sonogashira), unsymmetrical aminations, allylic aminations and silylations, and aryl borylations. Even palladium-catalyzed aromatic carbon–hydrogen bond activation to make new carbon–carbon bonds can be done at room temperature, an extraordinary achievement. Product isolation is straightforward; complications such as frothing and foaming associated with other surfactants are not observed. Recycling the surfactant after use is also very efficient: the insoluble product can be recovered by extraction, and the aqueous surfactant is simply reused with negligible loss of activity. Future generations of surfactants may include a catalyst tethered to a surfactant to provide both the "reaction vessel" (the inside of the micelle) and the catalyst to enable the reaction. Tethering catalysts in this way may reduce one-time use of rare-earth minerals as catalysts.

In all, this technology offers opportunities for industrial processes to replace large amounts of organic solvents with very small amounts of a benign surfactant nanodispersed in water only. High-quality water is not needed: these reactions can even be run in seawater. Sigma-Aldrich is currently selling TPGS-750-M, making it broadly available to research laboratories.

Small Business Award

BioAmber, Inc.

Integrated Production and Downstream Applications of Biobased Succinic Acid

Innovation and Benefits

Succinic acid is a true "platform molecule," that is, a starting material for other important chemicals, but the high cost of producing succinic acid from fossil fuels has restricted its use. Now, however, BioAmber is producing succinic acid that is both renewable and lower cost by combining an *E. coli* biocatalyst licensed from the Department of Energy with a novel purification process. BioAmber's process uses 60 percent less energy than succinic acid made from fossil fuels, offers a smaller carbon footprint, and costs 40 percent less.

Succinic acid has traditionally been produced from petroleum-based feedstocks. In addition to its current use in food, drug, and cosmetic applications, succinic acid is a platform molecule that can be used to make a wide range of chemicals and polymers.

BioAmber has developed an integrated technology that produces large, commercial quantities of succinic acid by fermentation rather than from petroleum feedstocks. Since early 2010, BioAmber has been producing succinic acid by bacterial fermentation of glucose in the world's only large-scale, dedicated, biobased succinic acid plant. This $30 million plant includes an integrated, continuous downstream process. BioAmber believes its renewable succinic acid is the first direct substitution of a fermentation-derived chemical for a petroleum-derived chemical.

BioAmber has successfully scaled up an *E. coli* biocatalyst licensed from the Department of Energy and integrated a novel, water-based downstream purification process. The fermentation process, although pH neutral, produces no significant byproducts. BioAmber's technology produces succinic acid at a cost that is 40 percent below that of petroleum-based succinic acid. Even at oil prices below $40 per barrel, BioAmber's product boasts cost advantages over succinic acid derived from fossil fuels.

BioAmber's economic advantage has given a number of chemical markets the confidence both to use succinic acid as a substitute for existing petrochemicals and to develop new applications for succinic acid. Succinic acid can replace some chemicals directly, including adipic acid for polyurethane applications and highly corrosive acetate salts for deicing applications. BioAmber has also made it economically feasible to (1) transform biobased succinic acid into renewable 1,4 butanediol and other four-carbon chemicals; (2) produce succinate esters for use as nontoxic solvents and substitutes for phthalate-based plasticizers in PVC (poly(vinyl chloride)) and other polymers; and (3) produce biodegradable, renewable performance plastics. BioAmber is leading the development of modified polybutylene succinate (mPBS), a polyester that is over 50 percent biobased and offers good heat-resistance (above 100 °C) and biodegradability (ASTM D6400 compliant). BioAmber's process reduces energy consumption by 60 percent compared to its petrochemical equivalent and actually consumes carbon dioxide (CO_2), rather than generating it.

In 2011, BioAmber plans to begin constructing a 20,000 metric ton facility in North America that will sequester over 8,000 tons of CO_2 per year, an amount equal to the emissions of 8,000 cross-country airplane flights or 2,300 compact cars annually. BioAmber has also signed partnership agreements with several major companies, including Cargill, DuPont, Mitsubishi Chemical, and Mitsui & Co. The scale up of biobased succinic acid to commercial quantities will expand markets, reducing pollution at the source and increasing health benefits at numerous points in the lifecycles of a variety of chemicals made from succinic acid.

Greener Synthetic Pathways Award

Genomatica

Production of High-Volume Chemicals from Renewable Feedstocks at Lower Cost

Innovation and Benefits

1,4-Butanediol (BDO) is a high-volume chemical building block used to make many common polymers, such as spandex. Using sophisticated genetic engineering, Genomatica has developed a microbe that makes BDO by fermenting sugars. When produced at commercial scale, Genomatica's Bio-BDO will be less expensive, require about 60 percent less energy, and produce 70 percent less carbon dioxide emissions than BDO made from natural gas. Genomatica is partnering with major companies to bring Bio-BDO to the market.

Most high-volume commodity chemicals, including monomers, are made from natural gas or petroleum. Genomatica is developing and commercializing sustainable basic and intermediate chemicals made from renewable feedstocks including readily available sugars, biomass, and syngas. The company aims to transform the chemical industry through the cost-advantaged, smaller-footprint production of biobased chemicals as direct replacements for major industrial chemicals that are currently petroleum-based in a trillion-dollar global market. By greening basic and intermediate chemicals at the source, Genomatica's technology enables others to make thousands of downstream products more sustainably without changing their manufacturing processes. By producing the building-block chemicals directly, Genomatica also reduces unwanted byproducts.

The first target molecule for Genomatica is 1,4-butanediol (BDO). BDO is used to make spandex, automotive plastics, running shoes, and many other products. It has an approximately 2.8 billion pound, $3 billion worldwide market. Genomatica has been producing Bio-BDO at pilot scale in 3,000 liter fermentations since the first half of 2010 and is moving to production at demonstration scale in 2011. Multiple large chemical companies have successfully tested Genomatica's Bio-BDO as a feedstock for polymers. The performance of Bio-BDO has met the standards set for petroleum-based BDO. Initial lifecycle analyses show that Genomatica's Bio-BDO will require about 60 percent less energy than acetylene-based BDO. Also, the biobased BDO pathway consumes carbon dioxide (CO_2), resulting in a reduction of 70 percent in CO_2 emissions. Fermentation requires no organic solvent, and the water used is recycled. Furthermore, the Bio-BDO fermentation process operates near ambient pressure and temperature, thus providing a safer working environment. These advantages lead to reduced costs: production facilities should cost significantly less, and production expenses for Bio-BDO should be 15–30 percent less than petroleum-based BDO. Genomatica expects Bio-BDO to be competitive at oil prices of $45 per barrel or at natural gas prices of $3.50 per million Btu.

Genomatica's unique, integrated bioprocess engineering and extensive intellectual property allow it to develop organisms and processes rapidly for many other basic chemicals. Because the chemical industry uses approximately 8 percent of the world's fossil fuels, Genomatica's technology has the potential to reduce carbon emissions by hundreds of millions of tons annually.

Genomatica has entered into partnerships with several major companies including Tate & Lyle, M&G (a major European chemicals producer), Waste Management, and Mitsubishi Chemical to implement their technology at a commercial scale. Genomatica expects to begin commercial production of Bio-BDO in 2012. They plan to roll out plants in the United States, Europe, and Asia over time.

Kraton Performance Polymers, Inc.

NEXAR™ Polymer Membrane Technology

Innovation and Benefits

Purification of salt water by reverse osmosis is one of the highest-volume uses of membrane filtration. Kraton has developed a family of halogen-free, high-flow, polymer membranes made using less solvent. The biggest benefits are during use: A reverse osmosis plant using NEXAR™ membranes can purify hundreds of times more water than one using traditional membranes, save 70 percent in membrane costs, and save 50 percent in energy costs.

Polymer membranes are used in a variety of purification processes. Membranes selectively allow some molecules to pass while preventing others from crossing the barrier. Membrane purifications include water desalination by reverse osmosis, water ultra-purification, salt recovery, and waste acid recovery. Membrane efficiency is limited by the rate at which water (or another molecule) crosses the membrane, a property called the flux. Increasing the pressure of the "dirty" side of the membrane can increase the flux, but a higher pressure requires a stronger membrane.

Kraton Performance Polymers has developed NEXAR™ polymer membrane technology for applications requiring high water or ion flux. Kraton's NEXAR™ polymers are block copolymers with separate regions that provide strength (poly(*t*-butyl styrene)), toughness and flexibility (poly(ethylene–propylene)), and water or ion transport (styrene–sulfonated styrene). These A-B-C-B-A pentablock copolymers exhibit strength and toughness in dry and wet conditions. Kraton's production process for NEXAR™ polymers uses up to 50 percent less hydrocarbon solvent and completely eliminates halogenated cosolvents.

The biggest benefits are during use. NEXAR™ polymers have an exceptionally high water flux of up to 400 times higher than current reverse osmosis membranes. This could translate into significant reductions in energy and materials use. Modeling shows that a medium-sized reverse osmosis (RO) plant could save, conservatively, over 70 percent of its membrane costs and approximately 50 percent of its energy costs. For applications in electrodialysis reversal (EDR), the higher mechanical strength of NEXAR™ polymers makes it possible to use thinner membranes, which reduces material use by up to 50 percent and reduces energy loss due to membrane resistance. More important, NEXAR™ polymers eliminate the current use of PVC (poly(vinyl chloride)) in electrodialysis membranes. The outstanding water transport rate of NEXAR™ membranes also significantly improves energy recovery ventilation (ERV), by which exhausted indoor air conditions incoming fresh air. For other humidity regulation applications, including high-performance textiles and clothing, NEXAR™ polymers offer environmental benefits by completely eliminating halogenated products such as Nafion® polymers and PTFE (poly(tetrafluoroethylene)) that may require hazardous halogenated processing aids.

Kraton introduced NEXAR™ polymers in the United States, China, and Germany during 2010. In the third quarter of 2010, Kraton completed its first successful large-scale production of NEXAR™ of about 10 metric tons.

Designing Greener Chemicals Award

Water-based Acrylic Alkyd Technology

The Sherwin-Williams Company

Innovation and Benefits

Oil-based "alkyd" paints have high levels of volatile organic compounds (VOCs) that become air pollutants as the paint dries. Previous acrylic paints contained lower VOCs, but could not match the performance of alkyds. Sherwin-Williams developed water-based acrylic alkyd paints with low VOCs that can be made from recycled soda bottle plastic (PET), acrylics, and soybean oil. These paints combine the performance benefits of alkyds and low VOC content of acrylics. In 2010, Sherwin-Williams manufactured enough of these new paints to eliminate over 800,000 pounds of VOCs.

The high cost and uncertain availability of petroleum-based raw materials makes dependence on these materials unsustainable. Furthermore, the tightening of volatile organic compound (VOC) regulations by the Ozone Transport Commission (OTC) and the South Coast Air Quality Management District (SCAQMD) necessitates VOC-compliant waterborne coatings in place of solventborne coatings. Today, acrylic latex emulsions dominate the low-VOC waterborne coatings and alkyds dominate the solventborne coatings, but latex-based coatings have difficulty meeting all the performance and application properties of solventborne coatings.

To address this challenge, The Sherwin-Williams Company developed a novel, low-VOC, water-based acrylic alkyd technology based on sustainability principles. At the heart of this water-based acrylic alkyd technology is a low-VOC, alkyd–acrylic dispersion (LAAD). This polymer dispersion has PET (poly(ethylene terephthalate)) segments for rigidity, hardness, and hydrolytic resistance; it has acrylic functionality for improved dry times and durability; and it has soya functionality (from soybean oil) to promote film formation, gloss, flexibility, and cure. Sherwin-Williams designed this water-based acrylic alkyd technology to meet key performance attributes of solvent-based alkyds for architectural and industrial maintenance coatings applications, but with lower VOCs, without surfactants, and with excellent hydrolytic stability similar to that of latex paints. Sherwin-Williams water-based acrylic alkyd coatings bring together the best performance benefits of alkyd and acrylic paints, offering the application and finish of alkyds, including high gloss and excellent adhesion and moisture resistance, with the low VOC content, low odor, and non-yellowing properties of acrylics.

Since the launch of their LAAD products, ProClassic Waterbased Acrylic Alkyd, ProMar 200 Waterbased Acrylic Alkyd, and ProIndustrial Waterborne Enamel, in 2010, Sherwin-Williams has eliminated the use of over 800,000 pounds of VOC solvents and other petroleum-based feedstocks.

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

Imines are essential intermediates in many reactions of pharmaceutical interest. For example, diaryl aldimines are used to synthesize blockbuster drugs such as Taxol® (used in chemotherapy) and Zetia® (used in cholesterol reduction). Diaryl aldimines are also used as additives to polyethylene to increase its rate of photodegradation in the environment. Unfortunately, traditional syntheses of diaryl aldimines are typically inefficient and environmentally unfriendly. They often use hazardous solvents such as benzene, toluene, and methylene chloride and require energy-intensive, multihour reflux steps. Although some recent imine syntheses have successfully used more benign solvents or conditions, these still require long reaction times and recrystallization or other purifications that negate some of the benefits of the otherwise greener syntheses.

Recently, Professor Bennett found that ethyl L-lactate, an FDA-approved food additive, can replace the hazardous solvents traditionally used to synthesize imines. Since then, she and her undergraduate students have used this method to synthesize over 140 diaryl aldimines. The method is extremely efficient under ambient conditions; it has a median yield of over 95 percent and a median reaction time of less than 10 minutes. The method also requires less solvent than published methods. The resulting imines are usually of such purity that recrystallization is unnecessary, thus avoiding additional waste. The key to the process is "tuning" the polarity of the ethyl lactate by adding water. The starting materials remain dissolved, but the imine crystallizes out of solution as it forms. Traditional methods often remove water to drive the reaction forward. In contrast, Professor Bennett's method drives the reaction forward by removing the product by direct crystallization. In summary, her ethyl 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 previous methods. During 2010, Professor Bennett filed a provisional patent for this technology.

Metal Adhesive Polymers from Cu^I-Catalyzed Azide–Alkyne Cycloaddition: A New Approach to Solder Replacements

Professor M.G. Finn, The Scripps Research Institute

Lead–tin solder is typically used to assemble printed circuit boards for personal microelectronic devices such as cell phones. The global proliferation of these devices results in unacceptable exposures of workers to lead, tin, and other toxic chemicals during device fabrication and, eventually, disassembly for recycling. International and state laws are beginning to limit these toxic substances in electronics, expanding the market for lead-free solder replacements.

In his research on finding lead-free solder, Professor Finn at The Scripps Research Institute has pioneered the discovery and application of Cu^I-catalyzed azide–alkyne cycloaddition (CuAAC) reactions. The Sharpless and Finn labs were first to use this reaction to produce metal-adhesive materials from multivalent azide and alkyne monomers. Metallic copper at surfaces of metal substrates exposed to air provides enough Cu^I ions to catalyze the formation of triazole cross-links, which bind the metal tightly. Triazole cross-links are also nontoxic and resistant to oxidation, reduction, irradiation, and heat. The highly efficient CuAAC process provides high conversions of azide and alkyne groups to triazoles. This process maximizes the cross-link density of the adhesive and thereby its strength, but at the expense of increasing the brittleness of the material. The incorporation of flexibility-inducing components and additional amine ligands in the adhesive mixtures enhances strength as determined by measuring maximum load before failure in a modified peel test on a custom-built, high-throughput instrument.

Current research is examining the conductivity, surface composition, and thickness of mixtures of the adhesive with conjugated molecular wires, silver nanoparticles, and carbon black using conductive probe atomic force microscopy (CP-AFM), X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy, and ellipsometry. This work provides exciting prospects for replacing resource-intensive solder composites with low-cost, nontoxic, conductive organic mixtures. In 2008, Professors Finn and Sharpless submitted a patent application for this technology and had a second patent published.

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

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

The worldwide transition from petroleum-based technologies to alternatives creates an extraordinary need for 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 the glycan into monosaccharides, then derive useful products efficiently and inexpensively. The most successful schemes will be those that produce the highest yields, minimize capital and operating expenses, and allow the greatest feedstock flexibility.

In 2008, Professor Mascal and his group described a method to convert cellulose into a mixture of 5-(chloromethyl)furfural (CMF) and three minor furfural-derived products in a remarkable 85 percent overall yield. This method involves acidic digestion of cellulose in a biphasic aqueous–organic solvent reactor. Once formed, the organic products separate from the acid before they decompose. Subsequently, Professor Mascal discovered that his method works equally well on raw biomass. The Mascal method produces not only CMF in high yield from the cellulose fraction of biomass, but also furfural itself from the C5-sugar (hemicellulose) fraction. Thus, it exploits all of the carbohydrate in the biomass.

More recently, Professor Mascal upgraded his process such that cellulose produces only CMF (84 percent) and levulinic acid (LA, an important chemical building block; 5 percent) in an overall 89 percent yield. The same method processes sucrose into CMF and LA in a remarkable 95 percent yield. The method also works well on biodiesel feedstocks; from safflower seeds, for example, the method leads to a 25 percent increase in biofuel production. The product is a hybrid lipidic–cellulosic biodiesel. No other known process gives simple organic products from cellulose in comparable yield. Professor Mascal has now expanded the derivative manifold to include renewable polymers, agrochemicals, and pharmaceuticals. He is forging development partnerships with Dow Chemical, Clorox, Aerojet, the U.S. Navy, and Micromidas.

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

Highly Efficient, Practical Monohydrolysis of Symmetric Diesters

Water is among the most environmentally friendly solvents and is the least expensive of all 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 made easily on a large scale from inexpensive precursors. Water-mediated desymmetrization of symmetric organic compounds is, therefore, of tremendous synthetic value and can make a significant contribution to green chemistry.

Professor Niwayama pioneered water-mediated desymmetrization and has been developing the monohydrolysis of symmetric diesters to half-esters with remarkable success. Half-esters have considerable commercial value. They are highly versatile building blocks for organic synthesis and are used frequently to synthesize polymers, dendrimers, and hyperbranched polymers with applications to 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. In contrast, alternate ring-opening reactions of cyclic acid anhydrides to half-esters usually require hazardous organic solvents.

Professor Niwayama discovered a highly efficient, practical ester monohydrolysis of symmetric diesters. In this reaction, aqueous sodium hydroxide or potassium hydroxide is added to a symmetric diester suspended in water that may or may not contain a small amount of an aprotic cosolvent such as tetrahydrofuran at 0 °C. Monohydrolysis occurs at the interface between the aqueous phase and the organic phase containing the diester. This reaction produces pure half-esters in high to near-quantitative yields without hazardous organic solvents or dirty waste products. This reaction is anticipated to contribute significantly to green chemistry in both industry and academia. Two companies have licensed the technology and 10 resulting half-esters are now available commercially.

Ethylene: A Superior Reagent for Enantioselective Functionalization of Alkenes

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

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. To qualify as green, 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 up to 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, Professor RajanBabu published three papers on this work.

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

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

Acetic acid is the traditional solvent used to synthesize terephthalic acid commercially, but it has several drawbacks. First, acetic acid is flammable. Second, the commercial terephthalate process requires an expensive, energy-intensive distillation to separate acetic acid from water, which is a byproduct of terephthalic acid synthesis, and allow acetic acid recycling. Third, acetic acid oxidizes during the reaction. At current terephthalate production levels, replacement of oxidized acetic acid requires approximately 4 billion pounds of makeup acetic acid worldwide every year. Manufacturing this makeup acetic acid not only requires substantial raw materials and energy but also creates pollutant emissions. Finally, acetic acid reacts with the bromide catalyst to produce high levels of methyl bromide emissions. According to EPA's Toxics Release Inventory, a single terephthalic acid plant releases about 45,000 pounds of methyl bromide annually.

Professor Savage has discovered reaction conditions and a reactor strategy for the catalyzed partial oxidation of *p*-xylene at high concentrations in high-temperature liquid water to synthesize terephthalic acid in high yields at nearly 100 percent selectivity. As a replacement solvent, water eliminates the formation and emission of methyl bromide as well as oxidative solvent losses. As a result, this process eliminates the raw materials, energy, and pollutant emissions associated with producing 4 billion pounds of make-up acetic acid annually. Because the byproduct and solvent are both water, the distillation is eliminated, along with its associated costs and energy use.

Professor Savage and his group have developed and analyzed conceptual chemical process designs for this new reaction medium to show quantitatively that it is competitive in its economics, energy consumption, and environmental impacts. They have also developed processing strategies so that these greener reaction conditions can be used at the high concentrations required for commercial processes. In 2008, University of Michigan filed a provisional patent application for this technology.

Professor David Schiraldi, Department of Macromolecular Science and Engineering, Case Western Reserve University and Aeroclay, Inc.

AeroClay®: A Green Aerogel for Industry

Expanded polystyrene (EPS) is made from polystyrene (PS), a petroleum product. It is used as a packaging material, thermal insulator, and acoustical insulator. PS is foamed into EPS beads using pentane, a volatile organic compound (VOC), as the blowing agent. The EPS beads are expanded and molded into blocks, which are then cut into specific shapes as required for various applications. Of the 2.62 million tons of polystyrene generated in 2008, only 0.8 percent were recycled and less than 1 percent were incinerated for energy.

AeroClay® is a sustainable, tough, lightweight material that has the potential to replace EPS. AeroClay® is made by mixing clay and biodegradable polymers such as casein or poly(vinyl alcohol) with water, pouring the mixture into molds, and then freezing and freeze-drying it. Water is both the only byproduct and the only processing aid in AeroClay® manufacture, so byproduct water can be incorporated back into the manufacturing process. AeroClay® can be formed into a variety of molded shapes to meet many demanding applications, eliminating the need for cutting or shaping to fit any one application. It is water-soluble and is expected to be biodegradable.

AeroClay® eliminates worker exposure to styrene, a suspected carcinogen, and does not require any blowing agents. Instead, AeroClay® uses poly(vinyl alcohol) and clay, which are essentially nontoxic, nonhazardous materials that would not harm workers who are currently exposed to chemicals during EPS manufacture. AeroClay® would also reduce the amount of waste in landfills. Because it is biodegradable, AeroClay® does not take up space in landfills or cause pollution during production or incineration. AeroClay® is also less flammable than EPS, while providing similar mechanical properties in packaging and insulating applications. During 2010, Aeroclay, Inc. established a pilot facility in Cleveland, Ohio, to produce and test prototypes and to produce small batches.

An Efficient, Biocatalytic Process for the Semisynthesis of Simvastatin

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

Statins are important drugs for treating cardiovascular diseases. Lovastatin, a secondary metabolite produced by the fungus, *Aspergillus terreus*, was the first FDA-approved statin. Simvastatin, a semisynthetic derivative of lovastatin, has two methyl groups instead of one at the C2′ position of the side chain. Simvastatin has become the second-highest-selling generic drug in the world since 2007 when it went off-patent as Merck's Zocor®.

Converting lovastatin into simvastatin by adding a methyl group currently requires protecting and then deprotecting other functionalities in the lovastatin molecule in a multistep synthesis. There are two main commercial routes. In the first route, lovastatin is hydrolyzed to the triol, monacolin J, followed by protection with selective silylation, esterification with dimethyl butyryl chloride, and deprotection. The second route involves protecting the carboxylic acid and alcohol functionalities, methylating the C2′ carbon with methyl iodide, and deprotecting the product. These routes are inefficient at less than 70 percent overall yield and are mass-intensive due to protection and deprotection.

Professor Tang and his group have developed an efficient route that circumvents protection and deprotection and results in greater atom economy, reduced waste, and overall less hazardous reaction conditions. First, they cloned LovD, a natural acyltransferase produced by *Aspergillus terreus* that is involved in synthesizing lovastatin and can accept low-cost, non-natural acyl donors. They recognized that LovD might be a type of simvastatin synthase and a starting point for creating a new biocatalytic process. They then evolved this enzyme toward commercial utility.

Codexis licensed Professor Tang's technology, engineered the enzyme further, and optimized the process for pilot-scale simvastatin manufacture. During 2010, Codexis scaled up enzyme manufacture to the 150 kilogram batch scale and manufactured simvastatin ammonium salt in 400 kilogram batches for sampling with customers. Approvals of regulatory agencies in the United States and European Union are expected in 2011.

Pre-Pulping Extraction of Hardwood Chips to Recover Hemicelluloses as a High-Value Renewable Chemical Feedstock that Reduces Waste and Saves Fossil Fuel

Professors Adriaan van Heiningen, Joseph Genco, Peter van Walsum, and Hemant Pendse, Forest Bioproducts Research Institute, University of Maine

Commercial pulp mills do not generally recover hemicelluloses because traditional hot-water extraction also extracts lignin, which can stick to and clog the mill piping and digesters. As a result, hemicelluloses are usually degraded and burned.

A novel pre-pulping extraction technology discovered by researchers at the University of Maine uses green liquor, an existing wood extract stream at Kraft pulp mills, to recover hemicelluloses from hardwood chips prior to conventional pulping. The near-neutral green liquor (NNGL) is rich in oligomeric hemicelluloses that can be a valuable, renewable feedstock for biorefineries. Acetic acid is a major coproduct.

The NNGL extraction prevents pollution by recovering hemicelluloses that would otherwise be wasted, improving energy efficiency by reducing fossil fuel used by lime kilns, and using existing pulp mill facilities to create a new feedstock. Using forest products instead of corn, the current dominant renewable feedstock, could further reduce greenhouse gases and toxic chemicals.

This new technology does not change the yield or physical properties of the pulp. In a demonstration of the NNGL extraction process for over 800 hours at full commercial scale, the Old Town mill in Maine produced several million gallons of extract while maintaining quality pulp output. University of Maine researchers have successfully demonstrated both the fermentation of NNGL wood extracts into ethanol and lactic acid and the separation of acetic acid from the extract. The Old Town mill is currently designing a commercial satellite biorefinery to convert pre-pulping wood extract into biobutanol and acetic acid. Peer-reviewed analysis shows that a 1,000 ton-per-day pulp mill could produce ethanol from NNGL wood extracts at \$1.63–\$2.07 per gallon and acetic acid at \$1.98–\$2.75 per gallon. With this technology, the bleached hardwood Kraft pulp mills in the United States could recover over 1 million tons of hemicelluloses per year for biofuel and bioplastics.

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

Bacteriophage-based Test for MRSA/MSSA Infections Acquired in Hospitals

Staphylococcus aureus causes most staphylococcal infections. The overuse of antibiotics may have caused the emergence of methicillin-resistant *Staphylococcus aureus* (MRSA), which is now a major, worldwide nosocomial pathogen. Over the past 15 years, hospitals have seen double-digit growth in the number of observed MRSA cases. By 2005, there were nearly 95,000 reported MRSA infections in the United States, resulting in 18,650 deaths.

Professor Voorhees has developed a greener, more efficient method for detecting *S. aureus* at the point of care. His method uses phage (bacteriophage) amplification to identify *S. aureus* rapidly and distinguish between MRSA and methicillin-susceptible *S. aureus* (MSSA) infections without time-consuming bacterial cultures.

Phages are highly species-specific viruses that infect bacteria. The rapid infection process can amplify phage numbers up to 10^5-fold. This reduces incubation times for phage amplification assays, resulting in complete phage-based assays in 1–5 hours instead of 24–48 hours for traditional bacterial culture assays. Professor Voorhees and MicroPhage have miniaturized the process and incorporated modern approaches, such as lateral flow immunochromatography, to detect the species-specific progeny phage. The test looks and functions much like a typical immunoassay, but requires neither expensive instruments nor highly trained personnel. This phage amplification platform is the first and only rapid, direct, in vitro diagnostic tool to identify bacteria and determine their antibiotic resistance or susceptibility.

The phage-based MRSA/MSSA hospital acquired infection test specifically incorporates green chemistry into its design, resulting in benefits to human health and the environment relative to existing methods. The test eliminates culturing, reduces the generation of waste, eliminates a hazardous synthesis, minimizes the use of auxiliaries and energy, uses renewable feedstocks, and is safer to use. The U.S. Food and Drug Administration is currently reviewing a 2010 application for this test. In 2009, MicroPhage received approval and began marketing the test in Europe.

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

Organic Catalysis: A Broadly Useful Strategy for Green Polymer Chemistry

Catalysis is a foundation for sustainable chemical processes, but conventional routes for synthesizing polyester plastics require metal oxide or metal alkoxide catalysts that have negative environmental impacts. In addition, although plastics are ubiquitous, useful materials, their lack of biodegradability and indiscriminate disposal have left an adverse, enduring environmental legacy.

Motivated by their desire to generate new classes of metal-free polymeric materials for microelectronic applications, the team of Professor Waymouth and Dr. Hedrick has pioneered the design and application of organic catalysts for polymer chemistry. Together, they have developed highly active, environmentally benign, metal-free catalytic processes for polyesters that contribute to meeting a central goal of green chemistry. Several new families of organic catalysts that they discovered rival or exceed metal-based alternatives for polyester synthesis, both in activity and selectivity. Their work includes developing a broad class of organic catalysts to synthesize biodegradable and biocompatible plastics.

These new synthetic strategies provide an environmentally attractive, atom-economical, low-energy alternative to traditional, metal-catalyzed processes. This technology includes organocatalytic approaches to ring-opening, as well as anionic, zwitterionic, group transfer, and condensation polymerization techniques. Their monomer feedstocks are primarily renewable compounds such as lactides from biomass, but also include some petrochemicals.

The team has designed and implemented organic catalysts to depolymerize such petrochemically derived polymers as poly(ethylene terephthalate) (PET) quantitatively. This allows a bottle-to-bottle recycling strategy to reduce the millions of pounds of PET that are disposed of in landfills. These catalysts also tolerate a wide variety of functional groups, enabling the synthesis of well-defined biocompatible polymers for biomedical applications. As these catalysts do not remain bound to the polymer chain, they are effective at low concentrations. These results, coupled with cytotoxicity measurements in biomedical applications, have highlighted the environmental and human health benefits of this approach. The team holds eight patents on this work.

Entries from Small Businesses

AeroClay®: A Green Aerogel for Industry

Aeroclay, Inc. and Professor David Schiraldi, Department of Macromolecular Science and Engineering, Case Western Reserve University

NOTE: This project is the result of a partnership between Professor David Schiraldi of Case Western University and Aeroclay, Inc. The project was judged in both the academic and small business categories. The abstract appears in the Academic section on page 12.

Source Reduction through Software Technology

Chemical Safety Software

Source reduction is the core of Chemical Safety's EMS (Environmental Management Systems) software. The most recent version, EMS 2010, introduced Chemical Safety's greener chemical alternatives search tool in its material safety data sheet (MSDS) and chemical inventory modules. EMS software is the only technology that incorporates greener chemical alternatives as a key feature for inventory search, procurement, and use. EMS software offers the ability to search for and select greener chemical alternatives in a database of chemical alternatives identified by EPA as well as leading universities and institutions. Users range from chemists and researchers to manufacturing and facilities managers. With EMS software, users reduce their acquisition, use, and release of toxic and hazardous chemicals and materials used for research, manufacturing, maintenance, repair, and operations; they also maximize their acquisition and use of environmentally preferable products.

EMS software provides steps essential to efficient chemical procurement, storage, distribution, reuse, recycling, and disposal. These steps reduce unnecessary chemical purchasing, reduce the footprints of hazardous chemicals at facilities, and decrease the generation and disposal of chemical waste. Chemical Safety has incorporated EPA's Design for the Environment (DfE) program into its EMS software. The DfE program evaluates the human health and environmental effects, performance, and cost of traditional and alternative technologies, materials, and processes. It helps reduce the use and disposal of chemicals of concern.

EMS software supports easy tracking of chemical containers and important data from the point materials are purchased or received through delivery, use, and storage to disposal and ultimate destruction. When users request a chemical from their company's inventory that is maintained in EMS 2010, the system prompts them to substitute a safer chemical. Clients as diverse as the Department of Energy's Stanford Linear Accelerator, Novartis Vaccines and Diagnostics, E&J Gallo, the L'Oreal Group, Baxter Healthcare, and EPA Region 9 laboratories are currently using this EMS software.

Suga®Nate: A Safer, Milder, Greener Surfactant

Colonial Chemical, Inc.

Currently, the two most common anionic surfactants used in shampoo, body wash, and other personal care products are based on lauryl sulfate and lauryl ether sulfate. A large percentage of these surfactants are made from ethylene, a petroleum feedstock. Products with these ingredients are highly irritating to eyes and skin. Products containing ethoxylated lauryl ether sulfate also contain various levels of 1,4-dioxin, a known carcinogen. Some manufacturers and retailers no longer make or carry products with these ingredients.

Colonial Chemical developed sulfonated alkyl polyglucosides to replace lauryl alcohol as the hydrophobic component of surfactants. These unique, patented products represent a breakthrough in mild surfactant technology. They are produced from renewable resources, using naturally derived, biodegradable raw materials. They do not irritate eyes or skin, giving formulators of personal care products an opportunity to start with totally irritation-free ingredients. They are also completely free of dioxin.

These products are synthesized using raw materials that are nearly 90 percent renewable and could reach 100 percent renewable as development progresses. The synthetic pathway is very atom-economical and the only byproduct is sodium chloride. Water is the only solvent used to make these products. The relatively mild reaction conditions are closer to ambient than those of competing technologies, and there is no need for separation or purification.

The toxicity of these products is quite low compared to the toxicity of competing technologies; surprisingly, these products are even less toxic than their raw starting materials. The products are also readily biodegradable and are not irritating to humans in tests of both eye and skin irritation. These products have been used in commercial shampoo in the United States since 2007. In 2010, Colonial Chemical submitted data for approval by the REACH program (Registration, Evaluation, Authorization, and Restriction of Chemicals) in the European Union.

Commercial Fluid Power LLC

Elimination of Hexavalent Chromium Used in Hydraulic and Pneumatic Tubing

Chrome-plated rods and tubes are the backbones of the hydraulic and pneumatic cylinders used in the fluid power market. These cylinders are used in applications from oil and gas production to food processing. Chrome plating is used widely because it has an excellent wear surface, great lubricity, and good corrosion resistance; it is also economical, time-tested, and readily available. The plating process is problematic, however, because plating produces a mist containing hexavalent chromium ions (i.e., Cr(VI), Cr^{6+}) that are carcinogenic. Most large chrome-plating facilities currently meet or exceed EPA, OSHA, and other government standards for air quality, disposal, and containment of waste. There is a trend toward tighter regulatory controls, however, and more stringent regulations will increase the cost of chrome plating.

Commercial Fluid Power is taking steps to reduce the use of industrial hard chrome or engineered chrome in the fluid power market. The company is developing and marketing Nitro-tuff tubes as safe, environmentally friendly replacements for chrome-plated tubes. Nitro-tuff tubes are ferritic nitro-carburized steel. During their manufacture, the surface of the steel is converted to a nonmetallic epsilon iron nitride (ε-Fe_3N) in an atmosphere of ammonia and carrier gas. Following nitriding, an oxidizing atmosphere is introduced to produce a thin, corrosion-resistant, black surface film of Fe_3NO_{3-4}. The iron nitride layer is the basis for the steel's extraordinary wear and corrosion resistance. Advances in mechanical properties, size, and finish control now allow Nitro-tuff tubes to substitute for chrome-plated tubes without losing quality or strength. These efforts are reducing the use of hexavalent chromium.

Recent research, development, and testing have overcome earlier challenges and opened new markets for Nitro-tuff tubes and bars. In conjunction with NitroSteel and Nitrex, Commercial Fluid Power continues to strive to bring an eco-friendly, cost-effective solution to the fluid power market.

Desilube Technology and United Soybean Board

High-Performance, Soy-Based Metalworking Fluids

Metalworking fluids used in operations requiring high lubricity are typically formulated with petroleum oil and chlorinated paraffins, which are neither environmentally friendly nor readily biodegradable. In fact, EPA has placed chlorinated paraffins under regulatory scrutiny because they exhibit aquatic toxicity and certain chain lengths are considered to be carcinogens. Current annual sales of chlorinated paraffins for metalworking fluids are approximately 75 million pounds.

Desilube Technology has developed an environmentally friendly metalworking fluid that contains the methyl ester of soybean oil plus the organic amine salt of a phosphoric acid and a fatty acid. This fluid does not contain any chlorinated or sulfurized compounds and is not prepared with petroleum oil. It has been used successfully in commercial applications that require high lubricity. Desilube's soybean oil based metalworking fluid outperforms conventional petroleum oil formulated with 35 percent chlorinated paraffin in two heavy-duty machining operations: deep drawing and fine blanking. The performance of Desilube's metalworking fluid is due to synergism between the methyl ester of soybean oil and the amine salt of phosphoric acid with a fatty acid. This synergism also applies to water-dilutable metalworking fluid designed for metal removal applications.

Most, if not all, metalworking fluids currently used in these and other heavy-duty applications contain chlorinated paraffins. Desilube's soy-based metalworking fluid has the potential to help replace chlorinated paraffins. In addition, the soybean oil base stock also has the potential to replace petroleum oil, reduce the dependency of the United States on crude oil, and take advantage of the large domestic supply of soybean oil provided in good part by farmers supporting the United Soybean Board.

The most recent patents for these soy-based technologies were published in 2010 and assigned to the United Soybean Board. Commercial sales of the environmentally friendly metalworking fluid over the past two years have averaged $45,000 per year.

A Safer, Less Toxic, Reliable, and Green Water Treatment by Smart Release® Technology

Dober Chemical Corporation

Smart Release® Technology is a controlled-release technology designed to prevent scale, corrosion, and microbial proliferation in water systems through the revolutionary delivery and application of existing chemical treatments. Initially, the technology focused on controlling corrosion and scale in cooling towers using tablets coated with a patented polymer that releases the treatment chemicals over a specified time period. In 2010, Dober expanded its Smart Release® product line to include biocides in solid granular form by creating a patent-pending canister membrane that also releases the chemicals over a specified time period, often 30 or 60 days.

Treating cooling towers with Smart Release® technology has many advantages over traditional liquid water treatments. Unlike traditional treatments, Smart Release® technology does not require toxic additives. Smart Release® treatments contain 95 percent active ingredients compared to 10–20 percent active ingredients in liquid treatments. The technology uses no pumps and so requires no electricity. Reduced packaging and shipping weight lowers its carbon footprint by 74 percent compared to that of conventional liquids. This technology may also help facilities gain up to eight LEED (Leadership in Energy and Environmental Design) credit points.

Benefits to humans include safe handling because the coating prevents contact with active ingredients. Because the concentration of active ingredients is so high, 100 pounds of Smart Release® chemicals equate to 600 pounds of standard liquid chemicals. The simplicity and reliability of Smart Release® technology means that less service time is required.

Smart Release® technology has been endorsed by two of the leading water treatment companies in the United States and a leading global supplier of cooling towers, fluid coolers, and evaporative condensers. During 2010, Dober created an enhanced corrosion and scale-inhibitor tablet that contains no phosphate. Due to increased regulations limiting phosphate products, Dober expects this product to have large sales in the future.

Earth Friendly Products

Earth Conscious Chemistry: Eliminating 1,4 Dioxane in Cleaning Products

1,4-Dioxane is an unwanted contaminant in many common personal care products sold in the United States. It occurs as a byproduct of common ethoxylated surfactants (e.g., sodium lauryl ether sulfate). 1,4-Dioxane is a cyclic ether that is highly miscible in water and migrates rapidly in soil. EPA has listed the compound as a probable human carcinogen based on the results of animal studies. 1,4-Dioxane is also listed with a group of pollutants in state and federal guidance for air pollution control.

Earth Friendly Products has worked diligently to remove 1,4-dioxane from all of its products. Testing for 1,4-dioxane by gas chromatography/mass spectrometry conducted by the Organic Consumers Association (OCA) included new results from 20 laundry detergents: 13 conventional, mainstream brands and 7 brands self-identified as "natural." The conventional brands had significantly higher levels of 1,4-dioxane. The highest were Tide® with 55 ppm, Ivory Snow® with 31 ppm, and Tide® Free with 29 ppm. OCA has confirmed in their latest report for 2010 that ECOS® Laundry detergent by Earth Friendly Products was free of 1,4-dioxane.

Since June 2008, Earth Friendly Products has successfully scaled up its formulas to produce natural products that do not contain any harmful chemicals, including 1,4-dioxane. The company uses a blend of coconut oil with anionic fatty acid chains that make excellent surfactants due to their dual hydrophilic and lipophilic properties. There is no sodium chloride salt added or used in any step of manufacturing or production of the company's laundry products. Each product is made with sustainable, plant-based ingredients that are studied to ensure minimal environmental impact before and after production. This ensures that all of the company's products are not only biodegradable, but also free of phosphate, caustic, formaldehyde, petrochemicals, chlorine, synthetic perfume, and ammonia.

FRX Polymers Inc.

Polymeric, Non-Halogenated Flame Retardants with Broad Applicability in Multiple Industries

Traditional, halogenated, small-molecule flame retardant (FR) additives readily migrate out of their applications, exposing humans to these often toxic chemicals and diminishing the application's flame retardant function. Electronic device manufacturers have instituted voluntary bans on plastic formulations with halogen-containing FR additives. Consequently, the plastics industry is searching for cost-effective, non-migrating, halogen-free alternatives.

FRX Polymers is the first company to develop polymeric forms of phosphorus for use as non-migrating FR additives that are also cost-effective and halogen-free. FRX makes diphenyl methylphosphonate (DPMP) into polymers with over 10 percent phosphorus. These unique polymers have the highest limited oxygen index (LOI) measured for thermoplastic materials, highlighting their FR functionality. The polymers can be used as standalone, inherently FR materials; they can also deliver FR performance and often additional beneficial properties to polycarbonate blends, polyesters, thermoplastic polyurethane (TPU), unsaturated polyethylene terephthalate (UPET), epoxies, and polyureas. Being polymeric, the FRX materials will hardly deteriorate the physical properties of these plastics. Replacing bromine with phosphorus in FR additives should allow greater recycling of plastics after use.

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 the starting monomers. Less than 5 percent waste is expected from FRX polymer and copolymer production. Because they can be processed by melting, FRX polymers can be used in applications such as fibers and blow-molded articles that were impossible with other FR additives.

FRX is scaling up its additives for applications including electronic housings, industrial carpeting, textiles, electrical connectors and switches, wire and cable, printed circuit boards, and transparent laminates. The FRX materials have completed Premanufacture Review under the Toxic Substances Control Act (TSCA) and are proceeding toward global registration. FRX plans to expand its current pilot plant from 50 to 100 metric tons per year during 2011.

Surachi Fuel Technology

Fuel Energy Service Corporation

Surachi fuel technology oxygenates petroleum fuels and other alternative hydrocarbon fuels. The technology modifies the fuel with a reaction in water in the presence of a recyclable, organic, semisolid catalyst. The reaction adds a hydroxy group and hydrogen atom at the former alkene bond in the fuel. The catalyst does not stay in the fuel, but is removed after the chemical reaction for reuse. This technology works for all internal combustion fuels including diesel, gasoline, jet fuel, Bunker C, and other heavy fuel oils.

Fuel Energy Service Corporation developed the Surachi technology in collaboration with the inventor. The technology allows internal combustion engines to run cleaner, quieter, and with more power, but with lower levels of soot, unburned hydrocarbons, and other harmful exhaust emissions. It expands the actual volume of the fuel and increases the Btu. The process removes most of the sulfur from fuel: the sulfur precipitates and is deposited on the semisolid catalyst, from which it can be removed. The Surachi technology does not adversely affect critical fuel characteristics, such as viscosity, low corrosivity, or other parameters that are common problems for fuel additives such as ethanol and other oxygenated species. The modified fuels are essentially identical to the original fuel in storage, holding, and handling capabilities.

The Surachi process has not yet been scaled up to production volume, either as a batch or a continuous process. In 2009, a patent was issued for this technology.

Polyelectrolytes: Reduce Your Carbon Footprint Using an Eco-Friendly Technology to Disperse Wax in Water without Heat

JEEN International Corporation

Emulsions containing waxes are common ingredients in wood or tile polishes, personal care products, coatings, and sealants. The traditional process of making oil–wax–water emulsions generally requires heating two mixing vessels: one for the aqueous phase and another for the oil phase. The temperature of each vessel needs to be higher than the melting point of the wax in the oil phase. Typically, steam, hot water, or cold water pumped through jackets around the vessels control the temperature. Once formed, emulsions must be cooled very carefully because the rate of cooling affects the aesthetics of traditional emulsions.

Previous cold process technologies solved the problems of multiple mixing vessels and the necessity of heating and cooling. Because existing cold process emulsions do not contain wax, however, they tend to feel more like gels than like conventional emulsions.

JEEN's Jeesperse Cold Process Wax (CPW) revolutionizes the science of making emulsions with wax. The combination of waxes and polyelectrolytes in Jeesperse products allows formation of complete emulsions without either heating or cooling. It uses only one mixing vessel and reduces manufacturing time by 50–75 percent over conventional processes. Sodium polyacrylate is the first polyelectrolyte used in Jeesperse CPW products, but many other polyelectrolytes can be used. In the future, natural gums in combination with natural waxes will lead to natural CPW products. Natural gums that can be used to create CPW products include sodium polyaspartate, sodium alginate, carrageenan, guar, and xanthan.

Jeesperse CPWs do contain wax and will make emulsions that feel like conventional, heat process ones. The ability to use waxes in cold process emulsions will expand the use of cold process manufacturing. During 2010, JEEN applied for U.S. patents. The nominated technology is available commercially as Jeesperse CPW.

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

Bacteriophage-based Test for MRSA/MSSA Infections Acquired in Hospitals

NOTE: This project is the result of a partnership between Professor Kent Voorhees of Colorado School of Mines and MicroPhage, Inc. The project was judged in both the academic and small business categories. The abstract appears in the Academic section on page 14.

Nanotech Industries, Inc.

Green Polyurethane™

The manufacture and use of isocyanate-based polyurethanes (PU) require very strict safety measures. Isocyanate monomers are hazardous and are considered potential human carcinogens. Acute exposures to isocyanates can cause irritation of skin and mucous membranes, chest tightness, and difficult breathing. Prolonged exposure can to cause severe asthma and even death. Isocyanates are also very sensitive to moisture. These problems lead to a highly regulated, costly environment for PU manufacturing.

Green Polyurethane™ from Nanotech Industries (NTI) is the first modified hybrid PU to be manufactured without isocyanates. The main raw materials for Green Polyurethane™ are polyoxypropylene triols and epoxidized vegetable oils. NTI also uses primary aliphatic diamines prepared by biomimetic synthesis in its production of Green Polyurethane™.

Green Polyurethane™ is a potential replacement for current, isocyanate-based polyurethanes, especially those polyurethanes in foams and coatings that contain free isocyanates in aerosol form after polymerization. Green Polyurethane's™ unique formulation combines the best mechanical properties of polyurethane with the chemical resistance properties of epoxy binders. Green Polyurethane™ coatings contain no volatile organic compounds (VOCs). They are solventless, 100 percent solids-based, 30–50 percent more resistant to chemical degradation, 10–30 percent more adhesive with some substrates, and 20 percent more wear-resistant. These coatings can also be applied on wet surfaces and will cure in cold conditions.

Insulating foam made from Green Polyurethane™ provides energy savings of more than 30 percent, has one of the highest R values per inch of all insulation materials, does not require a primer, and has greater adhesiveness.

In 2010 EPA added Cycloate A, a key binder ingredient in Green Polyurethane™, to the Toxic Substances Control Act (TSCA) Inventory following Premanufacture Review. NTI submitted a Premanufacture Notice under TSCA for its proprietary hydroxyalkyl urethane modifier (HUM). Also in 2010, Nanotech Industries began commercializing its hybrid non-isocyanate polyurethane UV-resistant coating technology.

Natural State Research, Inc.

Conversion of Waste Plastics into Fuel

EPA estimates that the United States recycles less than 6 percent of the 30 million tons of waste plastic it produces each year. In landfills, waste plastics produce methane gas, a greenhouse gas that is 23-times more harmful than carbon dioxide (CO_2). The worldwide fishing industry dumps an estimated 150,000 tons of plastic into the ocean each year, which constitutes almost 90 percent of all rubbish floating in the oceans.

Natural State Research, Inc. (NSR) has developed a patent-pending, award-winning technology that converts municipal solid waste plastics (PETE-1, HDPE-2, PVC-3, LDPE-4, PP-5, and PS-6) into liquid fuels. The typical NSR process involves heating small pieces of waste plastic to 280–420 °C to form a liquid slurry. After it cools, the slurry is distilled in the presence of cracking without catalyst to recover light gas and liquid hydrocarbons. Fractionation of the liquid hydrocarbons produces fuels similar to gasoline, naphtha, diesel, jet fuel, fuel oil, and home heating fuel that can be used in the majority of combustion engines.

NSR's technology is a new alternative to fossil fuels: it creates fuel sustainably without depleting natural resources. The raw material required to make NSR fuel, waste plastic, is abundant; until now, its disposal has posed significant environmental problems. Unlike other technologies, the NSR thermal technology does not use any pyrolysis, catalyst, vacuum, or chemicals during its process, and the overall yield is higher than for other methods.

When developed to commercial scale, the NSR technology can convert one ton of waste plastics into about 335 gallons of liquid fuel at a cost of about $0.50–$0.75 per gallon. NSR will license its technology to others, creating locally owned franchises employing up to 50 workers each. NSR has produced about 200 gallons of fuels to date.

Catalytic Transformation of Waste Carbon Dioxide into Valuable Materials

Novomer, Inc.

Novomer has developed a technology based on an innovative, proprietary catalyst system that transforms waste carbon dioxide (CO_2) into valuable plastics and resins. The resulting polypropylene carbonate (PPC) and polyethylene carbonate (PEC) contain up to half CO_2 by weight and thus, not only sequester CO_2 but also displace one-half the petroleum feedstock required for competing materials. Novomer technology has the potential to sequester and avoid approximately180 million metric tons of annual CO_2 emissions. Novomer products have three other advantages relative to competing materials: (1) inexpensive CO_2 enables competitive pricing, (2) the highly selective catalyst enables unique performance characteristics, and (3) Novomer products are free of bisphenol A (BPA). This combination of environmental responsibility, high performance, and low cost make Novomer polymers commercially attractive in a broad range of applications, including interior can coatings, packaging films, foams, and composite resins.

Novomer technology uses a greener synthetic pathway based on a novel catalyst system developed at Cornell University. The catalyst is a highly selective, cobalt-based complex that is over 25-times more active than current, zinc-based catalysts. It enables the creation of polymers with a precise CO_2-epoxide molecular structure. It does what earlier catalysts could not: it enables a waste greenhouse gas to replace petroleum-based raw materials in commercially viable polymers. The process is also solvent-free. Novomer's energy-efficient manufacturing process makes its reaction conditions greener than those of existing products.

Novomer materials are well-positioned to have a broad, significant impact on the polymer industries and transform the broader polymer landscape. During 2009–2010, Novomer successfully produced pilot-scale quantities of products for a wide range of applications. Now it is partnering with major polymer producers and brand owners to refine, qualify, and commercialize these products. The company expects to introduce its initial commercial products to the specialty coatings industry in 2011.

NSR Technologies, Inc.

A Novel, Energy-Efficient, Emission-Free Route to Produce Potassium Hydroxide

Potassium hydroxide (KOH) is a strong alkali with many industrial applications. The current U.S. consumption of KOH is approximately 1.3 billion pounds annually. During KOH production alone, the traditional, electrolytic chlor-alkali process makes about 800 million pounds of chlorine gas (Cl_2) annually in the United States and an estimated 1.8 billion pounds worldwide. Cl_2 is a hazardous air pollutant (HAP); chlorine acts as free-radical catalyst that contributes to destroying the ozone layer. Although chlor-alkali producers recover and sell Cl_2, the demand for Cl_2 is decreasing as ozone-depleting, chlorinated chemicals are phased out.

NSR has developed and commercialized an electrodialysis process that manufactures 45–50 percent KOH and 7 percent hydrochloric acid (HCl). The process hinges on NSR's IonSel™ technology, which uses layers of ion- and bipolar-selective membranes to separate and rearrange potassium and chlorine ions from the potassium chloride (KCl) feedstock. NSR's technology is the first environmentally friendly, cost-effective alternative to the chlor-alkali process in decades. It yields high-purity products free of mercury and oxidizing species such as chlorate and hypochlorite. NSR's process operates under safer conditions and does not produce Cl_2.

NSR's manufacturing process uses about 40 percent less energy per unit of product and has a compact design that allows smaller plants to produce equivalent amounts of acid and alkali profitably. Lower capital investments and smaller plants make manufacturing safer by enabling NSR to build plants close to end users, reducing shipping costs and hazards.

Both the chlor-alkali process and NSR's process can also produce sodium hydroxide (NaOH). As of July 2008, more than 500 companies worldwide used chor-alkali processes and recovered 140 billion pounds of Cl_2 as a byproduct of NaOH production. Global implementation of NSR's technology could eliminate billions of pounds of Cl_2 production. NSR has been operating a commercial plant and selling products to customers since 2009.

Orono Spectral Solutions

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

The 1974 Clean Water Act lists oil and grease together as one of five conventional pollutants. All National Pollution Discharge Elimination Systems (NPDES) permits, all pretreatment permits, and all Industrial Effluent Guidelines require measurements of oil and grease. Millions of analyses for oil and grease are done annually in the United States.

Following the Montreal Protocol in 1989, EPA replaced a Freon extraction method for oil and grease testing with an *n*-hexane extraction method (EPA 1664; EPA 1664a). This created several problems: (1) *n*-hexane is a hazardous, flammable liquid; (2) *n*-hexane is a known neurotoxin; and (3) testing generates millions of liters per year of *n*-hexane waste that require disposal. Thus, the current methodology is inconsistent with the intent of the Clean Air Act and Clean Water Act, both of which identify *n*-hexane as a hazardous pollutant.

Orono Spectral Solutions (OSS) developed a solid-phase, infrared-amenable extractor technology that both eliminates solvents from oil and grease analysis and provides more economical, accurate analyses. OSS's extractor unit is small, robust, and disposable (or partially recyclable), and it contains no toxic substances. The extractor unit includes a Teflon™-based polymeric membrane to capture and concentrate oil and grease from water, a metal-membrane support, and a polypropylene housing designed for pressurized water samples. The membrane does not absorb IR light in the spectral regions of interest; after drying, the device can be put into an IR spectrophotometer to determine the amount of oil and grease.

This patent-pending technology has successfully completed ASTM (American Society for Testing and Materials International) multi-laboratory validation and received ASTM method number D7575. EPA is currently considering replacing method 1664 with this one. This replacement would save one million liters of hexane annually and produce estimated benefits to the U.S. economy of $50–$60 million. OSS is actively commercializing this technology worldwide.

Enzymatic Catalysis for Biodiesel Production

Piedmont Biofuels Industrial, LLC

Biodiesel is comprised of monoalkyl esters of long-chain fatty acids derived by transesterification or acid esterification of vegetable oils or animal fats. High-quality feedstocks for biodiesel are primarily triglycerides (e.g., vegetable oils), which are easy to process by alkaline transesterification. Low-quality feedstocks (e.g., yellow and brown greases) have higher levels of free fatty acids (FFAs). They are difficult to process and thus largely underused. The decomposition of fats and oils also creates FFAs. Alkaline transesterification catalysts (e.g., potassium and sodium hydroxide) react with FFAs to produce soaps that complicate downstream processing and reduce the yield of biodiesel. Using a strong acid to catalyze esterification reduces soap formation and improves yields but generates an acidic methanol waste.

Enzymes can easily convert both triglycerides and free fatty acids into fuel-grade esters. In collaboration with Novozymes A/S, Piedmont developed three techniques for enzymatic biodiesel production: (1) lipase transesterification to replace alkaline transesterification for high-quality feedstocks; (2) bulk lipase esterification to replace acid esterification for feedstocks with high levels of FFAs; and (3) an acid-value reduction process for low amounts of FFAs. Piedmont's enzymatic process accommodates low-quality and high-quality feedstocks without loss of biodiesel yield. Enzymatic catalysis operates near room temperature and does not form soaps, require vacuum or pressure, or produce unintended side-reactions. The process eliminates water use, requires little excess methanol feedstock, and significantly improves glycerin quality to low-ash, technical grade with over 97 percent purity. The soap-free, enzymatic biodiesel process improves separation between biodiesel and glycerin phases because the emulsifier (soap) is not present. The new process also uses less energy than the current process or other second-generation processes (e.g., metal oxides). Piedmont's biodiesel meets ASTM (American Society for Testing and Materials International) standards and is economically viable for existing biodiesel processors. During 2011, Piedmont Biofuels and Novozymes A/S will commercialize this process.

Zero-VOC, BioBased HiOmega® Linseed Oil Epoxies, Adhesives, and Alkyd Resins as Replacements for Epichlorohydrin–Epoxy Resins and Other VOC-Containing Coatings, Paints, Adhesives, and Epoxies

Polar Industries, Inc.

Of the 2 billion pounds of epichlorohydrin manufactured worldwide each year, 76 percent is used in epoxy resins. Epichlorohydrin is both a probable human carcinogen and a deadly poison at high levels.

Polar Industries is commercializing products from HiOmega® linseed, a flax plant developed by conventional breeding that is an annual, renewable crop grown in the United States and Canada. HiOmega® linseed oil is highly suitable for epoxidation because it has 20–40 percent more α-linolenic acid than does conventional linseed oil. Environmentally friendly epoxidation methods at moderate temperatures yield epoxidized HiOmega® linseed oil with high oxirane values (11.0–13.0) that exceed the highest values of epoxidized conventional linseed oil (9.0–10.0). Epoxy and alkyd resins made from HiOmega® linseed oil contain no volatile organic compounds

(VOCs). They are biodegradable and require no special handling or disposal. The entire lifecycle of HiOmega® linseed oil epoxy resins, from crop growth and harvest to oil extraction, epoxidation, industrial use, and final disposal, is nonhazardous and follows environmentally sound practices.

In initial testing, the performance of HiOmega® epoxy resins and alkyd resins met or exceeded the performance of other linseed oil epoxy resins in bonding strength, moisture resistance, and resistance to fatigue. HiOmega® linseed oil epoxy resins are suitable replacements for epoxy resins made from epichlorohydrin. HiOmega® epoxy resins can be used in conventional two-part epoxy systems (i.e., resin and amine hardener) or one-part, UV-photoinitiated systems. Biobased, environmentally friendly, nontoxic epoxy resins and adhesives synthesized with epoxidized HiOmega® linseed oil could potentially reduce epichlorohydrin production by approximately 1.5 billion pounds per year.

Polar Industries has successfully commercialized nontoxic epoxy coatings, epoxy adhesives, and alkyd resins made from HiOmega® components. The California Department of Transportation is currently using Green Graffiti Coat, an antigraffiti clear coating based on HiOmega® epoxidized linseed oil, to protect road signs.

SiGNa Chemistry, Inc.

Sodium Silicide: On-Demand Hydrogen Generation for Back-Up Power and Portable Fuel Cells

Sodium silicide (NaSi) is a stabilized alkali metal silicide powder developed by SiGNa that reacts with water to generate hydrogen. In a fuel cell, NaSi produces pure hydrogen gas in real time, as needed, and at pressures less than those found in a soda can. NaSi eliminates the most significant challenges that have prevented low-temperature proton exchange membrane (PEM) fuel cells from becoming commercial products: storing high-pressure hydrogen and building costly infrastructure for hydrogen refilling.

By generating hydrogen on demand, NaSi will enable high-performance, portable, commercially viable fuel cell systems. This clean, sustainable material is inexpensive, easily transportable, and safe for indoor and outdoor use. Fuel cells powered by NaSi produce only hydrogen and water vapor; they create no greenhouse gases, toxic byproducts, or harmful emissions. Recyclable fuel canisters can easily deliver NaSi to any PEM fuel cell. Once the NaSi in a canister is spent, the nontoxic residue, sodium silicate, can be recycled as an industrial feedstock for many products.

SiGNa's NaSi technology offers significant environmental benefits throughout its lifecycle. SiGNa manufactures NaSi using 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 will significantly reduce both greenhouse gases released into the atmosphere and toxic materials entering the waste stream.

In the marketplace, SiGNa's new technology is proving that hydrogen fuel cells are not only commercially viable, but are even more cost-effective than batteries or low-power IC engines (under 3 kilowatts). For example, an electric bicycle powered by a NaSi fuel system can go 3–4-times farther than a bicycle powered by traditional lithium-powered batteries. SiGNa's hydrogen-generation approach can enable cost-effective back-up and portable fuel cells for the medical, military, transportation, disaster relief, and consumer electronics industries.

Solvair LLC

Solvair Cleaning System

Eighty percent of the 30,000 commercial drycleaning facilities in the United States use perchloroethylene. Unfortunately, perchloroethylene is a hazardous air pollutant under the Clean Air Act (CAA) and waste streams generated by perchloroethylene drycleaning are hazardous under the Resource Conservation and Recovery Act (RCRA). In California, health and environmental concerns are leading to the phase-out of perchloroethylene drycleaning; other states are proposing similar actions. Alternative solvents are available for use in conventional drycleaning systems, but all rely on evaporative hot-air-convection drying to remove the solvent from the textiles after cleaning. As a result, these alternatives have similar problems with environmental release, operator exposure, and hazardous waste streams.

Solvair initially developed its technology to replace traditional drycleaning with a safer, more environmentally friendly, more-effective cleaning technology. The Solvair system replaces evaporative hot-air-convection drying with a counter-current process including multiple liquid carbon dioxide (CO_2) rinses that remove the solvent from textiles after cleaning. It allows the practical use of safer, more effective drycleaning solvents including dipropylene glycol *n*-butyl ether (DPnB). DPnB is miscible in liquid CO_2 and is readily rinsed from textiles. It is commonly used in household cleaners, has extremely low volatility, and is biodegradable. Compared to conventional perchloroethylene systems, the Solvair system with DPnB eliminates hazardous waste streams, reduces the amount of waste by approximately 60 percent (including eliminating contact waste water), and maximizes the recovery and reuse of fluids in the system. The CO_2 in the Solvair process is a byproduct of other industrial processes and not a new source of CO_2 release.

Because the Solvair cleaning technology can use a wide range of solvents, it has potential applications in many industrial and commercial cleaning applications beyond drycleaning. In December 2010, commercial facilities using the Solvair cleaning technology processed over 3 million pounds of garments.

Development and Commercial Application of SAMMS®: A Novel Compound that Adsorbs and Removes Mercury and Other Toxic Heavy Metals

Steward Advanced Materials

Mercury contamination poses a serious threat to the environment and human health, but many common adsorbents are themselves problematic. Self-assembled monolayers on mesoporous supports (SAMMS®) successfully adsorb and remove toxic metals (e.g., mercury, cadmium, lead) and replace less-effective adsorbents (e.g., activated carbon, ion exchange resins). SAMMS® is a mesoporous ceramic substrate with a single layer of functional sorbent molecules bonded to the surface. The functional molecules have high affinity for specific ions. SAMMS® has superior adsorption capacity for targeted heavy metals, is cost-effective, and significantly reduces the volume of hazardous waste. The original SAMMS® synthesis required toluene and other flammable organic solvents. The resulting waste stream contained water, methanol, toluene, and traces of mercaptan. It required disposal as hazardous waste.

Steward Advanced Materials dramatically improved the SAMMS® synthesis with nonflammable, nontoxic supercritical carbon dioxide (SC CO_2). With this patented, commercially viable, green chemical process, SAMMS® manufacturing is faster and more efficient; it also yields a higher-quality product. The only byproducts are carbon dioxide (CO_2) and the alcohol resulting from the hydrolysis of the alkoxysilane. The CO_2 and alcohol are readily separated, allowing the CO_2 to be captured and recycled. The pure alcohol can be recycled as a feedstock, rather than becoming waste as in the original synthesis. The SAMMS® materials emerge from the reactor clean, dry, and ready for use. The benefits of the green manufacturing process for SAMMS® materials coupled with the superior adsorption characteristics of SAMMS® materials currently deployed in the chemical industry result in substantially reduced releases of toxic metals to the environment.

Commercial uses of thiol-SAMMS® include removal of: (1) multiple toxic heavy metals from contaminated mining impoundments, (2) heavy metal catalysts from pharmaceutical reaction mixtures, and (3) mercury from contaminated ground water and industrial process water with a discharge limit of 1.3 parts per trillion.

Terrabon, Inc.

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

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

Feedstocks for the MixAlco® process include a number of wastes that typically end up in landfills: municipal solid waste (MSW), sewage sludge, forest product residues (e.g., wood chips and wood molasses), and non-edible energy crops (e.g., sweet sorghum). The process can also use liquid wastes such as leachate from landfills and raw sewage. Terrabon's process will increase landfill life and replace nonrenewable petroleum. A life cycle analysis (LCA) using the GREET model (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) shows that the MixAlco® process will reduce greenhouse gas emissions by over 174 percent compared to conventional gasoline. With high-water effluents as the water source along with MSW, this process does not compete with local water resources.

Terrabon currently operates a demonstration plant in Bryan, Texas to confirm the commercial scalability of this process. This plant can potentially ferment the equivalent of about 5 dry tons of biomass per day to produce 100,000 gallons of biogasoline per year. The on-site conversion to biogasoline includes dewatering the fermentation salt product by evaporation and drying, thermally converting it into ketones, and catalytically converting the ketones into alcohols and hydrocarbons. Terrabon has successfully produced good-quality gasoline at this plant. In 2011, the company will begin constructing a 220 dry ton-per-day biorefinery at the Waste Management landfill in Alvin, Texas. This plant will convert MSW into 5 million gallons of gasoline per year.

Timber Treatment Technologies, LLC

TimberSIL®

Toxic, waterborne chemical infusion processes are typically used to pressure-treat lumber and industrial wood products. The new TimberSIL® glass wood chemistry uses environmentally friendly, nontoxic, sustainable chemicals and processes to protect wood.

To produce TimberSIL® glass wood, Timber Treatment Technologies converts sodium silicate, a common industrial chemical, into amorphous glass in situ with a suitable substrate such as wood or another natural fiber. Amorphous glass forms as millions of microscopic ribbons become intimately attached to the wood fiber to make TimberSIL® lumber. Production of the proprietary TimberSIL® formulation uses no petroleum products. Most of the wood used comes from renewable, sustainable, southern yellow pine trees. In addition, the processing of recycled rice hulls to make sodium silicate, a primary component of the glass wood chemistry, requires no energy, has no greenhouse gas emissions, and produces two times more energy than the combustion of coal.

TimberSIL® glass wood can take any shape that can be milled by existing wood mills. It is stronger, more stable, and more resistant to fire, rot, and decay than pressure-treated wood. It can readily be used wherever long-lasting wood materials are the proper design and economic choice. The strength of TimberSIL® lumber means that less lumber is needed to achieve the same building integrity.

TimberSIL® technology can eliminate many toxic materials that are widely used in wood treatments. For example, every mile of TimberSIL® rail ties that replaces creosote rail ties eliminates 108,000 pounds of crude oil. Over its lifetime, one mile of TimberSIL® railroad ties displaces over 9,300,000 pounds of carbon dioxide (CO_2). With no toxic mode of action and increased strength, TimberSIL® glass wood is an environmentally superior choice for residential, commercial, and industrial applications. Since 2005, installations of TimberSIL® glass wood have totaled approximately 2.7 million board-feet in the United States.

Saf-T-Vanish®: A Zero-VOC, Green Replacement for Petroleum Solvent Vanish Oils

Tower Oil & Technology Co.

Tens of thousands of U.S. manufacturers who make metal parts by stamping or drawing use evaporative lubricants known as vanish oils. These oils typically contain over 90 percent highly evaporative, combustible, or flammable petroleum hydrocarbon solvents plus small amounts of lubricants. The human health and environmental impact of the solvents is of major significance. In the United States alone, vanish oils release over 120 million pounds of volatile organic compounds (VOCs) each year and expose tens of thousands of metalworking plant employees to noxious and potentially hazardous fumes. On January 1, 2010, South Coast Air Quality Management District (SCAQMD) Rule 1144 went into effect in Southern California, banning the use of high-VOC vanish oils from the local marketplace. Until recently, however, U.S. manufacturing had no proven, successful, environmentally friendly alternative to high-VOC vanish oils.

In July 2009, Tower Oil & Technology introduced Saf-T-Vanish®, the first truly green technology to prove itself as a successful replacement for high-VOC vanish oils. It is derived from renewable feedstock and is both fully recyclable and biodegradable. Saf-T-Vanish® is VOC-free and nonhazardous to manufacturing workers and the environment. Saf-T-Vanish® contains no mineral oils or hazardous air pollutant (HAP) ingredients; it is totally nonflammable and emits no noxious fumes.

To date, Saf-T-Vanish® has enabled the total elimination of vanish oil VOCs in hundreds of manufacturing applications throughout the United States. It has vastly improved plant and worker safety while making huge contributions to corporate environmental goals. In addition, Saf-T-Vanish® is the only commercially available, truly green technology that enables Southern California manufacturers to comply totally with SCAQMD Rule 1144. As the manufacturing industry continues to replace conventional vanish oils, Saf-T-Vanish® could eliminate over 120 million pounds of VOCs per year from the environment.

Entries from Industry and Government

GLDA: The Greener Chelate; Sustainable, Safe, and Strong

AkzoNobel Functional Chemicals, LLC

Because chelating agents solubilize metal ions, they have many applications, including cleaners, water treatment, and agriculture. Many traditional chelates such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are based on aminocarboxylic acids; others such as sodium tripolyphosphate (STPP) are based on phosphorous in the form of phosphates or phosphonates. However, these chelates and several similar structures are not environmentally friendly and safe. The degradation of phosphorous-containing materials in the environment can lead to the eutrophication of waterways, and common phosphorous-free alternatives have their own problems with biodegradation and safety.

To address concerns surrounding traditional chelates, AkzoNobel has developed a strong, nontoxic, nonpolluting, readily biodegradable chelate, GLDA (tetrasodium L-glutamic acid, *N,N*-diacetic acid). The principle raw material for GLDA is the monosodium salt of glutamic acid (MSG), which is both a natural amino acid and a fermentation product of readily available corn or beet sugars. MSG is renewable, making GLDA the only chelating agent manufactured from such a renewable feedstock. The GLDA manufacturing process is also waste-free.

As a chelate for calcium, GLDA is more than twice as effective as Baypure® (i.e., sodium iminodisuccinate, IDS), a previous Presidential Green Chemistry Challenge-winning technology. GLDA is also stronger than many other common, readily biodegradable counterparts. GLDA offers an impressive human and ecological safety profile that is comparable to IDS, but IDS and other green chelates are made almost exclusively from petroleum feedstocks. GLDA has a smaller environmental impact than EDTA, NTA, and STPP because it uses a renewable feedstock, biodegrades rapidly, and lacks phosphorous.

These attributes make GLDA ideal for applications including household and industrial cleaners and detergents, gas sweetening, metal and oil industries, personal care products, polymer production, printing ink, textile processing, and pulp and paper processing. Since late 2009, AkzoNobel has expanded its Lima, Ohio, plant and commercialized GLDA as Dissolvine® GL.

Concrete-Friendly™ Powdered Active Carbon (C-PAC™) for Safely Removing Mercury from Air

Albemarle Corporation

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

Activated Carbon Injection (ACI) technology injects mercury sorbents into flue gas in power plants and captures the mercury-laden sorbents in fly ash. Although this technology reduces mercury emissions, conventional mercury sorbents render fly ash unsuitable for concrete and thus, generate huge amounts of landfill waste. Disposal of 11.5 million tons of sorbent-contaminated fly ash would require more than 322 million cubic feet of landfill space and cost about $196 million.

Albemarle, with partial funding from the National Science Foundation (NSF), designed, synthesized, developed, and commercialized the novel 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, and eliminates the need for large amounts of landfill space. Several power plants across the United States currently use C-PAC™.

Argonne National Laboratory

Upcycling Plastic Bags into More Valuable Products

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 researched, demonstrated, implemented, and patented an environmentally friendly process to remediate or upcycle waste plastic bags (WPB) into CSs and CNTs. Argonne's original, solvent-free, solid-state-controlled, pyrolytic process upcycles WPB of single or mixed types by heating them to 700 °C to produce pure CSs and 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 catalysis, the process yields smooth, micrometer-sized carbon spheres that are conductive and paramagnetic. They can be used in toners and printers, as additives for lubricants, and in the tire industry. An industrial collaborator, Superior Graphite, has heat-treated CSs at higher temperature; this improves their performance significantly as anodes for lithium-ion batteries.

With a cobalt acetate catalyst, the process yields CNTs that have been successfully tested at Argonne 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 WPB.

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

Argonne designed a prototype reactor with an 80 cubic centimeter capacity and optimized the reaction conditions. Argonne is working with G2 NanoTechnologies, LLC to scale up and develop high-volume reactors to commercialize this technology.

Ashland Performance Materials

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

Envirez™ resins are a versatile family of unsaturated polyester resins synthesized with both renewable and recycled raw materials. The renewable raw materials are obtained from corn, soybeans, and other biomass. The biobased building blocks include soybean oil, ethanol, 1,3-propanediol, and proprietary monomers derived from biomass. Other building blocks are monomers and polymers recycled from postconsumer poly(ethylene terephthalate) (PET) and airplane deicer. Envirez™ resins meet the same performance and processing requirements of 100 percent petroleum-based unsaturated polyester resin products. They are used to fabricate an ever-expanding portfolio of thermoset composite products for the building, construction, infrastructure, transportation, and marine industries.

The first Envirez™ resin was targeted at compression-molded parts for agricultural equipment. With its growing interest in sustainable materials, Ashland recently strengthened and expanded the Envirez™ family of resins in several significant ways: First, Envirez™ resins now exist for a wide variety of composite fabrication methods. Ashland has developed formulations for infusion, pultrusion, casting, and gelcoats, expanding the reach of Envirez™ into a much wider assortment of products and markets including green buildings and wind energy. Second, Envirez™ resins now contain a higher percentage and wider assortment of renewable raw materials. Ashland accomplished this by intensive, on-going research and development to identify and use new biobased building blocks. Third, Ashland synthesized and developed the first Envirez™ resins that incorporate recycled raw materials and combine both recycled and renewable raw materials. Fourth, Envirez™ resins have become an enabling technology for composite fabricators interested in using sustainable components. This product line has experienced double-digit growth in the past several years.

A significant, recent milestone that illustrates the growing, widespread acceptance of Envirez™ was the launch of CompositeBuild.com at the 2010 GreenBuild Expo. This showcase and its accompanying website featured a portfolio of interior and exterior building products based on Envirez™ resin technology commercialized since 2008.

Green Sense℠ Concrete

BASF Corporation

Concrete is the most widely used, versatile building material in the world. It uses raw materials such as Portland cement and water (cement paste) as glue to hold fine and coarse aggregates together, creating a solid material for constructing buildings, houses, and roadways. Portland cement manufacturing requires so much energy that it produces a reported 5 percent of the world's carbon dioxide (CO_2) emissions according to the Portland Cement Association. Although the CO_2-equivalent emissions, or carbon footprint, of products like concrete are often used as the only measure of environmental impacts, this information alone may produce misleading conclusions because the mining of aggregates also depletes natural resources. Considering several environmental impacts and rigorously measuring the comprehensive environmental impact and lifecycle costs of products allow more informed and science-based decisions on the most sustainable solutions.

BASF has developed a series of Glenium® chemical admixtures for use in concrete for multiple applications. The Glenium® chemical admixtures are engineered and carefully formulated products containing an aqueous solution of dispersants based on polycarboxylate ether chemistry. The aqueous Glenium® admixtures are nontoxic, nonhazardous, and nonflammable. These admixtures, when combined with alternative raw materials in concrete mixes, make up Green Sense℠ Concrete. Glenium® admixtures allow BASF to replace CO_2-intensive Portland cement with traditional waste materials such as fly ash, slag, and cement kiln dust.

BASF also developed its Eco-Efficiency Analysis (EEA) tool for concrete. EEA is a third-party-validated, award-winning holistic and strategic environmental lifecycle assessment methodology that focuses on multiple environmental parameters, not only CO_2 emissions. With this tool, BASF can analyze each concrete mix to achieve new levels of economy and sustainability.

In 2009, BASF introduced Glenium® admixtures, Green Sense℠ concrete, and its EEA tool. In 2010, BASF Construction Chemicals worked with hundreds of concrete producers in the United States to optimize their concrete mixes with Glenium® admixtures and Green Sense℠ concrete.

Champion Technologies, Inc.

Lysine-Based Phosphonate Scale Inhibitor with Improved Biodegradation and Maintained Performance

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

Organic phosphonates inhibit scale formation as low-dose additives (sometimes at levels below parts-per-million, far below the dosage required for comparable carboxylate chelants). They have high efficacy, low toxicity, and a low tendency to bioaccumulate. They typically exhibit low rates of biodegradation, however, and legislation in the United States and North Sea countries has driven research into biodegradable scale inhibitors. Although polymeric scale inhibitors can substitute for phosphonates because they have greater biodegradation rates and a low tendency to bioaccumulate, they cost more and require higher dosages to be effective.

Champion Technologies has developed new phosphonate scale inhibitors that biodegrade more readily and offer a competitive price yet preserve the inherently high performance, low toxicity, and low bioaccumulation of phosphonates. Champion replaced diethylenetriamine (DETA) and other synthetic polyamine starting materials for traditional phosphonates with lysine, a naturally occurring amino acid that is also a renewable polyamine. Champion optimized the extent of phosphonomethylation to maximize both performance and biodegradation. Lysine phosphonate exhibits the desired scale inhibition and is inherently biodegradable, demonstrating 20–60-percent biodegradation in 28 days by OECD 306 (the seawater biodegradation test of the Organisation for Economic Co-operation and Development). By comparison, traditional phosphonates are nonbiodegradable, with less than 20 percent biodegradation in 28 days by OECD 306. In 2009, Champion submitted a patent application for this technology.

Cooper Power Systems

Green Chemistry for High-Voltage Equipment: The Research, Development, and Application of Soy-Based Dielectric Coolant

Polychlorinated biphenyls (PCBs) formed the basis for traditional dielectric coolant fluids, but they presented 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 the best possible environmental and health profile.

Envirotemp™ FR3™ fluid contains approximately 97 percent soy oil blended with nontoxic cold-flow modifiers and food-grade oxidation stabilizers. The inherent properties of soy oil result in improved fire safety, hydrolytic interaction, biodegradability, high gas absorption, and compatibility with common transformer materials. Envirotemp™ FR3™ fluid was 99.9 percent biodegradable in EPA's Office of Chemical Safety and Pollution Prevention (OCSPP) Biodegradation Test. In EPA's Acute Aquatic Toxicity Test, Envirotemp™ FR3™ fluid was nontoxic with zero mortality. Envirotemp™ FR3™ fluid has the most favorable Biobased for Environmental and Economic Sustainability (BEES) score among dielectric coolants, including an outstanding score for being essentially carbon-neutral from planting the soy seeds through filling a transformer.

The degradation of the insulating paper in power transformers is a major factor in their operating life expectancy. Cooper researchers discovered that their fluid decreases the aging rate of transformer insulating paper compared to other common fluids; the soy oil hydrolyzes with water to dehydrate both the fluid and the paper. Transformers filled with soy-based fluid have a lower lifecycle cost than do transformers filled with mineral oil.

Envirotemp™ FR3™ fluid has the highest flash and fire points of all common dielectric fluids. Its fire point is twice that of mineral oil, which leads to increased safety. Currently, transformers filled with soy-based fluid have operated over one million unit-years in the field without any reported fire incidents.

Cooper holds nine U.S. patents for this technology. Envirotemp™ FR3™ fluid is listed in the Federal BioPreferred™ product catalog.

iSUSTAIN® Green Chemistry Index Tool for Sustainable Development

Cytec Industries Inc.

Cytec Industries Inc., in collaboration with Dr. John Warner, has developed the iSUSTAIN® Green Chemistry Index scoring tool. This is the first such tool to be based on the 12 Principles of Green Chemistry. The tool includes a metric for each of the twelve principles, which range from atom economy to reduced energy use and process hazard. The tool makes assessments using a novel algorithm and a database of safety, health, environmental impact, and regulatory status scores for the raw materials used to prepare the products being assessed. Information for assessments comes from several sources including EPA's Sustainable Futures™ modeling, qualitative structure-activity analysis (QSAR), literature searches, and testing.

iSUSTAIN® measures the sustainability of Cytec's products and processes, allowing the company to develop both initial sustainability baselines and improvements. The index allows Cytec's technical community to identify those factors within their control that can affect the overall sustainability of their processes. Cytec has been using the tool internally since 2009 to score both new product ideas and existing commercial products. Cytec has also incorporated the tool as part of its Stage-Gate New Product Introduction (NPI) system.

Starting in March 2010, Cytec, in partnership with Sopheon Corporation and Beyond Benign Foundation, made the iSUSTAIN® Green Chemistry Index available to the public without charge. An enhanced version is available for a fee, but Cytec provides it free to academic users. iSUSTAIN® will foster learning and change the mindset of university scientists so future researchers will have the principles of sustainability ingrained in their thinking. By the end of 2010, over 771 users including industry, government, and academia had logged onto the tool. Users signed up from 114 unique domains and 30 different domain types, creating over 1,000 scenarios using 442 substances from the materials database of 5,494 substances.

MAX HT® Bayer Sodalite Scale Inhibitor

Cytec Industries Inc.

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

Cytec developed its MAX HT® Bayer sodalite scale inhibitor products for the Bayer process. No other scale inhibitors are on the market for this application. The active polymeric ingredient contains silane functional groups that inhibit crystal growth by incorporation into crystals or adsorption onto their surfaces. Dosages range from 20 to 40 ppm. Assessments of these polymers under EPA's Sustainable Futures™ program indicated an overall low 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 becomes more efficient. Increased evaporation makes the countercurrent washing circuit more efficient and reduces caustic losses. Using less steam reduces emissions from burning carbon-based fuels. Finally, reducing the sulfuric acid used to clean heaters reduces both worker exposure and waste.

There are about 70 operating Bayer process plants worldwide with annual capacities of 0.2 million–6 million tons of alumina; most plants are in the 1.5 million–3 million ton range. Thirteen Bayer process plants worldwide have adopted MAX HT® technology, and 13 more plants are testing it. Each plant using MAX HT® saves $2 million–$20 million annually. Fewer cleaning cycles and less acid per cycle result in a realized annual hazardous waste reduction of 50 million–150 million pounds. The annual realized reduction of 50 percent caustic is 50,000 tons–125,000 tons. The realized annual energy savings are 6 trillion–31 trillion Btu, which equals about 0.7 billion–5 billion pounds of carbon dioxide (CO_2) that are not released into the atmosphere.

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 used 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 made final regulatory decisions, the elimination of BPA from interior can coating systems has become a matter of public and scientific interest.

Cytec has developed a new generation of BPA-free, saturated polyester resins for the main binder. Together with phenolic resins, the polyester resins can be used in interior can coatings for the metal packaging goods industry. 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 monomers used 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 21 CFR §175.300. 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 be completely free of BPA and have performance comparable to existing systems. Commercial sales began in 2008. In 2010, Cytec began its first full-scale production of the phenolic part of the system. Currently, Cytec is negotiating the U.S. production of the polyester part.

Cytec Industries Inc.

Waterborne, Ambient-Cure, Stain-Blocking Primer

When red cedar and other tannin-rich woods are painted, their tannins can bleed into topcoat paints, producing undesirable discolorations. Solventborne, universal-stain-blocking primers reduce tannin bleed and discoloration. Typical solventborne primers are based on alkyd resins and contain volatile organic compounds (VOCs) at 350–450 grams per liter. During painting, these solvents are released directly into the air. Eco-friendly systems, such as waterborne systems, are needed to reduce VOCs, but existing commercially available waterborne primers, many of which are based on anionic alkyd resins, are generally less effective in blocking tannin bleed than are their solventborne counterparts.

Cytec Industries has developed a family of cationic, waterborne, epoxy ester resins. The new cationic polymer emulsions are synthesized by reactions of epoxy resins, fatty acids, and amines. The polymers are neutralized with organic acids such as acetic or lactic acid and then dispersed in water. To achieve the best film-forming properties, the emulsion is reacted with additional epoxy resin to increase its molecular weight. These low-VOC esters show excellent tannin-blocking performance. Their manufacturing uses a solvent-free process in which exothermic reactions heat the reaction mixture to processing temperature. They also provide better drying performance because they do not require oxidative cross-linking reactions, but only solvent evaporation for complete drying. The primers cure at ambient or even low temperatures.

Cytec's new waterborne primers require very little cosolvent. Conventional stain-blocking primers can contain up to 40 percent solvent, whereas the new products need only 1–2 percent cosolvent. The VOC content of Cytec's cationic, waterborne, stain-blocking primers is 20–45 grams per liter.

In 2010, Cytec produced its first technical-scale batch of primer and made its first commercial sales to U.S. paint manufacturers. These small, initial sales reduced VOC emissions by approximately 20 tons. Potential VOC reductions from low-VOC waterborne primers of equal performance are 35,000–49,000 tons annually.

ReNew Air Scrubber Technology

Diversey Inc.

Rendering facilities process the inedible parts of food stock into value-added materials such as tallow, high-protein components for animal feed, and materials for the cosmetics and pharmaceutical industries. The rendering process uses high-temperature cookers to convert livestock waste into these finished products, but it also generates significant levels of malodorous volatile organic compounds (VOCs). Rendering plants trap VOCs with several devices including air scrubbers. Conventional air scrubbers rely on oxidizers, such as sodium hypochlorite, chlorine dioxide, chlorine gas, and ozone, to convert insoluble VOCs in exhaust air into water-soluble organic salts. Sodium chlorite, sodium bromide, sodium hydroxide, and mineral acids are often used during scrubber operation or cleaning.

ReNew Air Scrubber technology is a pollution control program that reduces emissions of unwanted VOCs from rendering plants. The program includes novel chemistry, a dosing system indexed to the intensity of the incoming VOC-containing gases, several air-handling system modifications, and air scrubber performance monitoring. ReNew Air Scrubber technology uses enzymes, surfactants, and 50 percent citric acid (a relatively mild organic acid) to replace conventional harsh chemicals. This technology removes odorous VOCs with efficiency that is quantifiably equal to or better than the VOC-removal efficiency of conventional technology.

The ReNew Air Scrubber technology reduces total operating costs, uses chemicals that are safer for workers and the environment, requires less water and energy to operate, and delivers air quality results equal or superior to conventional systems. It does not produce any EPA-regulated pollutants in the effluent water.

Since 2007, when Diversey started tests at customer sites, several dozen customer sites have fully installed the ReNew Air Scrubber technology. Since its initial commercialization, this technology has saved over 54.5 million gallons of water at U.S. rendering facilities and prevented the use of over 5 million pounds of oxidizers and mineral acids.

The Dow Chemical Company

INFUSE™ Olefin Block Copolymers

INFUSE™ Olefin Block Copolymers (OBCs) are produced with a patent-pending shuttling process that represents an innovation in catalyst technology and delivers breakthrough performance through 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. 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 2010, 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.

Ecolab Inc.

DryExx Conveyor Lubricant Program

In commercial food and beverage container filling operations, conveying systems typically move at very high speeds. Copious amounts of dilute, aqueous lubricant solutions are applied to the conveyors or containers with spraying or pumping equipment. Traditionally, these solutions lubricate the conveyor chain, run off the conveyor, and eventually enter the facility's effluent stream. Concentrated lubricant solutions often consist of fatty acid or fatty amine surfactants.

Traditional lubricant solutions and their associated technology have several disadvantages. First, dilute aqueous lubricants typically require large amounts of water on the conveyor line. The area near the conveyor line becomes very wet and the excess water must then be disposed of or recycled. Second, some aqueous lubricants can promote microbial growth. Third, diluting the concentrated lubricant before use can produce variable concentrations of dilute solution and thus, variable performance. Finally, variations in water quality can alter the performance of the dilute lubrication solution. For example, alkaline water can lead to environmental stress cracks in poly(ethylene terephthalate) (PET) bottles.

The DryExx Conveyor Lubricant Program lubricates conveyor chains without added water. The DryExx Program consists of the DryExx chemical formulation and a dispensing concept. The DryExx formulation contains a mixture of water-miscible silicone material and a water-miscible lubricant. It contains no hazardous ingredients in quantities requiring reporting. The product is targeted for food and beverage bottlers who package products in PET containers using conveyors with plastic or polyacetyl chains. Currently, Ecolab estimates this program is saving U.S. bottling facilities 240 million gallons of water annually and is preventing an additional 1 million gallons of conventional lubricant concentrate from entering the effluent stream.

Low-Temperature Cleaning In Place

Ecolab Inc.

Most industrial processes for cleaning in place (CIP) combine chemistry, temperature, time, and mechanical energy. Traditional CIP systems require high-strength chlorinated caustic soda and temperatures of 150 °F. In an average fluid milk plant, these CIP processes account for approximately half of the plant's total fossil fuel use and carbon dioxide (CO_2) emissions.

Ecolab has developed the Advantis LT two-product program for CIP in the dairy and food industries. The first product is an alkaline detergent including water conditioners and a transition metal catalyst ($MnSO_4$ or $Fe_2(SO_4)_3$). The second product is a detergent containing hydrogen peroxide (H_2O_2). Injecting the two products sequentially into the CIP balance or supply tank during circulation generates microbubbles of oxygen on soiled structures, enabling fluid in the system to flush away the loosened soil. The Advantis LT program results in successful cleaning at lower temperatures: steam heat exchangers bring the temperature up to 110 °F instead of 150 °F, saving 50 percent in energy. A typical cheese plant could save steam equal to 5,000 decatherms of natural gas annually; the 350 large dairy plants in North America could save a total of 2.0 million decatherms.

Lower-temperature cleaning cycles reduce the length of heat-up steps by as much as 10–15 minutes per object being cleaned. In many plants, this can translate to increased output. Reduced cleaning temperatures also extend equipment life by avoiding temperature stress on stainless steel structures and elastomeric gaskets and seals. Finally, Ecolab's technology reduces caustic soda consumption by 35 percent without using any chlorine bleach, resulting in less wastewater.

Calculations for the International Dairy Foods Association estimate that the Advantis LT program can reduce the overall carbon footprint of a fluid milk plant by up to 10 percent. Following further refinements, Ecolab plans to commercialize this technology during the latter half of 2011.

Chlorantraniliprole: Greener Chemistry for Sustainable Agriculture

E.I. du Pont de Nemours and Company

DuPont redesigned its discovery process for new active ingredients by integrating chemistry and biology with toxicological, environmental, and site-of-action studies to optimize safety and product performance simultaneously. This approach focused on those candidates combining high levels of crop protection with the greatest safety. 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. On key safety measures, it may be the safest of all lepidopteran insecticides, including those derived from natural sources. Its unique mode of action selectively targets insects, making it inherently safer to people and other nontarget organisms. Chlorantraniliprole is classified by EPA as a reduced risk pesticide. Chlorantraniliprole is usually one to two orders of magnitude more potent against target pests than commercial standards such as pyrethroids, carbamates, and organophosphates. Its resulting lower use rates translate into less pesticide going into the environment and 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. It is sold under multiple trade names including Coragen®, Altacor®, and Acelepryn®. In the United States during 2010, over 900,000 acres of vegetables were treated with Coragen® and over 600,000 acres of tree fruit, nuts, and vines were treated with Altacor®.

E. I. du Pont de Nemours and Company

Development of a Commercially Viable, Integrated Cellulosic Ethanol Technology

DuPont and Genencor have developed and scaled up an improved biochemical technology for producing ethanol from lignocellulosic biomass. This process integrates three components. First, dilute ammonia pretreatment prepares the biomass for hydrolysis 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 of fermentable sugars at high titers. Third, optimized metabolic pathways of a recombinant ethanologen (*Zymomonas mobilis*) produce ethanol efficiently by metabolizing both 6-carbon and 5-carbon sugars from the sugars produced by pretreatment and enzymatic hydrolysis. Integrating and optimizing these three components enables a very efficient process and a green footprint with lower cost and less capital investment than other known cellulosic ethanol processes. At the 200 liter semiworks scale, this technology achieves consistent ethanol yields of over 80 gallons per U.S. ton of biomass and ethanol titers of over 80 grams per liter.

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 this combined process could potentially reduce greenhouse gas (GHG) emissions by over 100 percent compared to gasoline. The combined process could potentially have significantly lower GHG emissions than current grain-based ethanol processes. If suitable feedstocks cost $50 per ton, the ethanol from this process could cost $2 per gallon.

In 2010, a flexible-feedstock, 250,000 gallon-per-year facility began operating in Vonore, Tennessee, to scale up this technology and develop basic data for commercial-scale facilities. The first commercial plant, a facility to convert corn stover feedstock to over 25 million gallons per year of ethanol, is expected to start up in 2013 in the U.S. Midwest.

E. I. du Pont de Nemours and Company

Pioneering Industrial Biotechnology to Meet Global Needs for a Cost-effective, Drop-in, Renewable Fuel and Chemical

As an advanced biofuel, isobutanol can offer significant 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 has developed an economical, green-chemistry-based process that uses microorganisms to manufacture isobutanol from renewable biomass. DuPont's strategy for low-cost commercialization includes retrofitting existing ethanol plants to produce biobutanol. One key is using current ethanol-industry feedstocks (i.e., corn grain, wheat grain, and sugar cane), low-cost lignocellulosic biomass, and macroalgae. A second key is developing a yeast-based isobutanologen as a drop-in biocatalyst for the retrofitted ethanol plants.

Initially, DuPont focused on developing an efficient biocatalyst that functions on saccharified feedstocks. DuPont engineered yeast strains with a novel pathway of several engineered enzymes that convert pyruvate to isobutanol in the yeast cytosol. 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 their chosen pathway. To establish a redox-balanced pathway and achieve the desired yield, DuPont changed the nucleotide cofactor preference of the ketol-acid reductoisomerase (KARI) enzyme from NADPH to NADH. Finally, they integrated novel process technologies to reduce the aqueous concentration of isobutanol in fermentations, thereby avoiding enzyme inhibition by its product and eliminating energy-intensive purification. This second-generation biocatalyst has achieved the milestones of yield, rate, and titer that demonstrate cost-effective production of isobutanol.

DuPont's accomplishment is a significant step towards commercializing a green process to produce isobutanol. This biobutanol technology reduces greenhouse gases (GHG) by 40–70 percent compared to gasoline or traditional acetone–butanol–ethanol (ABE) fermentations. During 2010, DuPont began operating a large-scale demonstration plant for biobutanol in the United Kingdom in a joint venture with Butamax Advanced BioFuels, LLC.

*Continuous Processing Enables a Convergent Route to a New Drug Candidate: LY2624803*H_3PO_4*

Eli Lilly and Company

The commercial production of LY2624803*H_3PO_4, an investigational new drug candidate currently in phase II clinical trials, illustrates the importance and impact of designing green processes. Lilly acquired this drug with its purchase of Hypnion, Inc. The original synthesis enabled early development, but was not amenable to large-scale manufacture. Lilly identified several major environmental and safety issues with the original chemistry. Among them were: (1) dimethylformamide/sodium hydride (DMF/NaH) in step 1, (2) methylene in various steps, (3) a molten step with observed self-heating, (4) an aldehyde purification that would be unsafe at increased scale, (5) phosphoryl chloride ($POCl_3$) in large excess, (6) chromatographic purification.

After brief explorations, Lilly discovered a convergent variant of the original route. Flow processing proved critical to this new route's success. First, an extremely efficient carbonylation replaced an inefficient oxidation catalyzed by TEMPO (tetramethyl pentahydropyridine oxide). Subsequently, hydrogen replaced sodium triacetoxyborohydride (STAB) in a reductive amination. Although both operations require high pressure (1,000 psi) that is unsafe in traditional batch tanks, both proved amenable to flow processing, resulting in safe, efficient syntheses.

Lilly uses process mass intensity (PMI) in its process development. PMI is the total mass of raw materials (including water) put into a process for every kilogram of drug produced. The original route had a PMI of over 1,000 before chromatography. Lilly's new route has a net PMI of 59, representing a 94 percent reduction (96 percent reduction including chromatography). This PMI is extraordinary given the complexity of the drug and its nine-step synthesis. Lilly implemented its new route for LY2624803*H_3PO_4 on a pilot-plant scale in Indianapolis, Indiana, during 2009 and on a commercial scale in Kinsale, Ireland, during 2010. Lilly's application of green chemistry, as well as its development and use of flow chemistry, led to an efficient, convergent synthetic route and a significantly improved manufacturing process.

Eli Lilly and Company

Grignard Reactions Go Greener with Continuous Processing

Since the start of the 20th century, the Grignard reaction has been applied to the synthesis of numerous intermediates for food additives, industrial chemicals, and pharmaceuticals. 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 developed inherently safer Grignard chemistry using a novel, continuous stirred tank reactor (CSTR) that allows continuous formation of Grignard reagents with continuous coupling and quenching. This strategy minimizes hazards by operating at a small reaction volume, performing metal activation only once during each campaign, and using 2-methyltetrahydrofuran (2-MeTHF) as a superior Grignard reagent and reaction solvent that may be derived from renewable resources. Grignard reactions using 2-MeTHF also result in products with chemo- and stereoselectivity superior to Grignard products using other ethereal solvents. Relative to batch processes, the continuous approach allows rapid, steady-state control and reductions of 43 percent in metal use, 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, something impossible with batch processing.

Lilly is using its CSTR Grignard approach to produce two key materials including the penultimate intermediate of LY2216684·HCl, a norepinephrine reuptake inhibitor currently under clinical investigation for treatment of depression and ADHD. Lilly uses a similar approach to synthesize a key intermediate for an investigational new drug candidate under clinical evaluation to treat benign prostatic hyperplasia. Lilly anticipates commercial production on a 22 liter scale that will replace the 2,000 liter reactors used in batch processes.

FMC Corporation

VigorOx® Biocide: Advancing Environmentally Responsible Energy Production

Recent advances in horizontal drilling and hydraulic fracturing have unlocked significant reserves of natural gas in the United States, providing opportunities to increase the nation's energy independence. Because microbes present in well treatment fluids can fowl wells, the oil and gas industries must use biocides. Some of these biocides could contaminate ground water and drinking water wells, however, so the industry has been seeking biocides with minimal environmental impact. Glutaraldehyde, the most commonly used biocide in the oilfield industry, is an effective biocide but is also toxic to aquatic organisms and requires high rates of application. Historically, oxidizing biocides have not been practical because they may interact negatively with other chemicals in well treatment fluids.

FMC Corporation has met this challenge with VigorOx® biocide. FMC's research team took peracetic acid (PAA), a safe chemical that was already established in the healthcare and food processing industries, and reformulated it for energy-production applications. VigorOx® biocide is a mixture of high-purity hydrogen peroxide and acetic acid treated with a proprietary purification process and a small amount of chemical stabilizer.

PAA is an oxidizing biocide that rapidly destroys aerobic and sulfate reducing bacteria (SRB) while decomposing into environmentally benign oxygen, water, and acetic acid, thus minimizing risk to the environment and human health. VigorOx® peracetic acid formulations contain lower levels of hydrogen peroxide than standard PAA blends, so they do not inhibit the polyacrylamide friction reducers commonly used in “slick water” fracturing. Field trials confirm that PAA does not persist in the environment or pose chronic toxicity risks. Moreover, the oxidizing power of peracetic acid can be used to clarify produced water, allowing greater water reuse in hydraulic fracturing operations. The low rates of use can also provide an economic advantage.

In 2010, FMC’s patent-pending formulation received EPA pesticide registration #65402-3 for oil and gas applications.

Ecomate®: Environmentally Benign Blowing Agent for Polyurethane Foams

Foam Supplies, Inc.

Traditionally, chlorofluorocarbons (CFCs) were the preferred blowing agents for polyurethane foams. Foams blown with CFCs had good insulating and structural properties for use in refrigerators, building construction, and spray foam. CFCs were removed from polyurethane foam in the 1990s, however, due to their potential to destroy the ozone layer. Hydrochlorofluorocarbons (HCFCs) have a lower Ozone Depletion Potential (ODP) and are currently replacing CFCs, but were scheduled for phase out by 2010 in the United States.

Ecomate® (methyl formate) is a zero-ODP, zero Global Warming Potential (GWP) blowing agent designed to replace CFCs, HCFCs, and hydrofluorocarbons (HFCs). Ecomate® is also VOC-exempt, meaning it does not contribute to smog. With little or no modification of existing manufacturing processes, ecomate® foaming systems provide foam with insulating and structural characteristics equivalent to those of conventional polyurethane foams.

Foam Supplies, Inc. developed ecomate® as a green replacement for both HCFCs and the high-GWP hydrofluorocarbons (HFCs), which have GWPs of 725 to 1,810. Each pound of ecomate® replaces about two pounds of alternative blowing agents. Using ecomate® as a blowing agent in polyurethane foams has eliminated almost one million metric tons per year (mt-CO_2e) of high-GWP compounds such as HFC-134a and HFC-245fa. Using one million pounds of ecomate® would eliminate the equivalent of 1.4 billion–3.4 billion pounds of CO_2 emissions or 0.6 million–1.5 million mt-CO_2e.

Ecomate® blowing agent costs substantially less than HFCs, and there are usually no significant capital expenses associated with implementing the ecomate® technology. Ecomate® foaming systems allow manufacturers to help the environment without increasing their costs. Ecomate® has been demonstrated in pour-in-place, boardstock, and spray insulation systems as well as in boat flotation foam. Ecomate® currently has a variety of applications in several countries; its availability has allowed EPA to accelerate the phase out of HCFCs in the United States.

Gentle Power Bleach™: A Revolutionary Enzymatic Textile Bleaching System

Genencor

Currently, the textile industry faces major challenges in managing its use of natural resources. Traditional textile processing has a substantial impact on natural resources and requires potentially hazardous materials. Textile wet processing (e.g., bleaching) is the most environmentally hazardous stage in the textile supply chain. Regulatory and consumer pressure support reducing the environmental impacts of textile production; the future of the textile industry depends on reduced impacts.

Huntsman Textile Effects and Genencor, a division of Danisco A/S, collaborated to introduce Gentle Power Bleach™ (GPB), a first-to-market enzymatic textile pretreatment bleaching system. GPB uses Genencor's PrimaGreen™ Eco White liquid enzyme formulation containing a bacterial arylesterase. This unique, proprietary enzyme catalyzes the perhydrolysis of propylene glycol diacetate (PGDA) to propylene glycol and peracetic acid at neutral pH over a wide range of temperatures. Genencor engineered the enzyme to favor the perhydrolysis reaction to peracetic acid over the hydrolysis reaction to propylene glycol. The generation of peracetic acid in situ sets the GPB system apart from other enzyme systems and traditional chemical bleaching systems.

Using Genencor's enzyme formulation, Huntsman developed the GPB technology. Introduced in March 2009, GPB perfectly prepares cotton and elastane blends for dying. GPB enables low-temperature, neutral pH bleaching of fabrics and replaces harmful chemicals such as caustic soda. Gentler processing yields softer, bulkier, higher-quality fabrics than traditional bleaching and also reduces cotton loss during processing by 50 percent. An environmental lifecycle assessment (LCA) shows that GPB has a marked advantage over traditional textile bleaching for cotton fabrics. Lower treatment and rinsing temperatures and fewer rinse baths can result in water and energy savings of up to 40 percent for GPB. The LCA results demonstrate at least a 20 percent benefit in most categories, including climate change, human health, ecosystem quality, and water use, relative to a traditional bleaching system.

General Motors

Applying Green Chemistry Principles to Enable Zero-Waste Manufacturing

General Motors (GM) has created an environmentally sustainable process that eliminates GM's use of landfills for waste disposal. GM's process technology addresses environmental footprint reductions, potential long-term landfill impacts, and natural resource depletion. This process includes establishing goals; entering and analyzing data from all operations monthly; adhering strictly to a zero-landfill best practice; monitoring, maintaining, and reporting progress; and collaborating internally and externally. First, the process focuses on source reduction then works to retain all wastes (manufacturing byproducts) in use as long as possible. These priorities correspond to EPA's pollution prevention hierarchy.

On average, GM now recycles or reuses more than 97 percent of its waste materials and converts the remaining less than 3 percent to energy, replacing fossil fuels at waste-to-energy facilities. Within the United States, 13 facilities are landfill-free: they recycle, reuse, or convert to energy all wastes from their normal operations. During 2010, these facilities diverted over 385,000 tons of waste from landfills and avoided emissions equivalent to 2.1 million metric tons of carbon dioxide (CO_2e). Currently, GM's process is part of 76 global automotive manufacturing operations that reuse, recycle, or convert to energy all the waste they generate. During 2010, GM recycled or reused 2.5 million tons of byproduct materials worldwide.

Because environmental cross-industry collaboration and community stewardship are important, GM directs its engineers to mentor other companies, industries, and communities. For example, during the 2010 Gulf of Mexico oil spill, GM assembled an engineering team to recycle oil-soaked, absorbent polypropylene booms recovered from the Alabama and Louisiana coasts. To retain the chemical value of these booms, GM processed them into parts for the Chevrolet Volt. To date, this technology has prevented over 100 miles of oil booms and the oil retained in them from entering American landfills. It has also prevented 70 metric tons of CO_2e from entering the atmosphere.

Simplified Total Kjeldahl Nitrogen Method for Wastewater: A Green Alternative to Traditional Kjeldahl Methodology

Hach Company

The Total Kjeldahl Nitrogen (TKN) test is commonly performed at municipal and industrial wastewater treatment facilities to measure the concentrations of ammonia and organic nitrogen compounds. The TKN method is, however, one of the most challenging, dangerous, labor-intensive tests performed in wastewater treatment plants. This method requires digesting samples at high temperatures for several hours with strong sulfuric acid to convert the nitrogen to ammonium sulfate. Concentrated sodium hydroxide is then added to make the solution alkaline, and the liberated ammonia is distilled into a receiving solution where it is measured by back titration with sulfuric acid. The analysis requires equipment that is expensive, fragile, and space-consuming.

More recent TKN methods use metal catalysts such as mercury to speed the digestion and improve recoveries (EPA 351.2 Rev. 2.0, 1993). Ion-selective electrodes, the spectrophotometric phenate method, or the nesslerization method (which requires significant amounts of mercury) are often used to measure the ammonia. The TKN method also suffers from poorly understood interferences. Nitrate, the primary interference, can oxidize ammonia to form nitrous oxide (N_2O), causing negative interference. When sufficient organic matter is present, nitrate can be reduced to ammonia, causing positive interference. To date, traditional methodologies have not eliminated these interferences.

Hach Company has developed a rapid test that eliminates many of the weaknesses of traditional TKN tests. Their Simplified TKN (s-TKN) method uses two simple measurements to calculate the TKN value as the difference between the concentration of total nitrogen and that of nitrate plus nitrite. The method does not require mercury. Sample and reagent volumes are less than 10 milliliters per test. Based on the estimate that nearly 5 million TKN tests are performed annually, use of the s-TKN method could eliminate over 45 tons of mercury per year. In December 2009, Hach commercialized its s-TKN™ method and prepackaged chemistry.

HFO-1234yf Refrigerant for Automotive Air Conditioning with Low Global Warming Potential

Honeywell International, Inc. and DuPont

Driven by the European Union (EU) F-Gas Directive to phase out the automotive refrigerant HFC-134a, Honeywell and DuPont have jointly developed HFO-1234yf (i.e., $CF_3CF{=}CH_2$), a refrigerant with low global warming potential (GWP). This is the first hydrofluoro-olefin refrigerant developed for mobile air conditioning (MAC) systems. HFO-1234yf has a 100-year GWP of 4 versus that of HFC-134a at 1,430. A GWP of 4 easily meets the EU F-Gas mandate that automotive refrigerants achieve GWP values under 150. HFO-1234yf also has no ozone depletion potential. Due to its low GWP and high energy efficiency, it has excellent lifecycle climate performance (LCCP). Based on LCCP calculations using the EPA-supported GREEN-MAC-LCCP® Model, the potential global savings will be 5.2 million–5.9 million metric tons per year of CO_2 (carbon dioxide) equivalents (CO_2e) in 2017 when HFO-1234yf is fully implemented.

DuPont and Honeywell completed extensive testing of the toxicity, materials compatibility, stability, and air conditioning performance of HFO-1234yf. Tests also demonstrated its low potential for ignition. DuPont and Honeywell worked closely with automobile manufacturers and component suppliers to support refrigerant qualification programs of their customers. Results were very favorable, demonstrating that HFO-1234yf substitution requires only minor modifications to air conditioning systems designed for HFC-134a. Honeywell and DuPont have also registered or submitted the chemical under EU's Registration, Evaluation, Authorization and restrictions of Chemicals (REACH), EPA's Significant New Alternatives Policy (SNAP), and Toxic Substances Control Act (TSCA).

Honeywell and DuPont provided information for Society of Automotive Engineers (SAE) Cooperative Research sponsored by global automobile manufacturers to evaluate HFO-1234yf and other candidates. The program included performance testing, material compatibility testing, and assessments of environmental impact and risk. The SAE program found that HFO-1234yf is a safe, environmentally beneficial replacement that could be implemented globally. Global adoption of HFO-1234yf in all new vehicles would eliminate about 60 million pounds of HFC-134a.

IBM Corporation

Elimination of Perfluoroalkyl Sulfonates in IBM Semiconductor Manufacturing Processes and Development of PFAS-Free Photoacid Generators

In 2002, EPA restricted new applications of perfluorooctane sulfonate (PFOS) compounds because scientific evidence showed that PFOS persisted and bioaccumulated 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."

Due to increasing concern over the environmental impacts of these compounds, however, IBM began searching for alternatives to PFOS and perfluorooctanoate (PFOA). In 2006, IBM issued a corporate directive to eliminate all PFOS and PFOA from its 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, IBM completed replacing the PFOS surfactant in all BOE chemicals with perfluorobutane sulfonate (PFBS), which has overall lower environmental concerns according to EPA.

IBM targeted replacement of 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/PFOA lithographic chemicals. This change eliminates approximately 140 kilograms of PFOS and PFOA compounds per year. IBM's conversion occurred without decreasing the product final wafer test yield, increasing the volume of chemicals used in production, or increasing the cost of any chemicals except one. IBM believes it is the only company in the world to eliminate PFOS and PFOA compounds completely from semiconductor manufacturing. In February 2010, IBM announced the development of PAGs free of perfluoroalkyl sulfonates (PFAS) for both dry and immersion 193-nm semiconductor photolithography processes.

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. Treating wood with preservatives and insecticides can improve its durability significantly, but methods for delivering these protectants into wood are still largely based on old technologies that are environmentally damaging.

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, an environmentally positive building material in its own right.

In 2010, the Tru-Core® technology received a U.S. patent and EPA registered it as a wood preservative treatment. Because the Tru-Core® technology is effective, economical, and environmentally sound, it is having significant commercial success in the United States and other countries.

Kiehl's "Aloe Vera" Biodegradable Liquid Body Cleanser

L'Oreal USA

By developing and commercializing Kiehl's "Aloe Vera" Biodegradable Liquid Body Cleanser, L'Oreal launched the first ever Cradle to Cradle® certified biodegradable product within the cosmetic industry. Inspired by the Cradle to Cradle® philosophy and in collaboration with the Make It Right Foundation, L'Oreal formulated this product with green chemistry in mind. Cradle to Cradle® certification is a multi-attribute eco-label of McDonough Braungart Design Chemistry (MBDC). It assesses a product's safety to humans and the environment as well as its design for future lifecycles. Kiehl's "Aloe Vera" Biodegradable Liquid Body Cleanser received the Cradle to Cradle® silver certification. This product received a gold score in material reutilization and silver scores in the other four categories: material health, renewable energy use, water stewardship, and social responsibility.

The ingredients in the Kiehl's "Aloe Vera" formulation are water, sodium coco-sulfate, coco-glucoside, sodium benzoate, potassium sorbate, glycerin, *Aloe barbadensis* leaf juice, citric acid, sodium chloride, and fragrance. L'Oreal minimized the amount of ingredients to simplify and optimize the use of each ingredient and avoid unnecessary ingredients. In formulating this product, the company used ingredients in three main categories: coconut-derived surfactants for cleansing, preservatives commonly found in food, and fundamental moisturizing ingredients with known benefits. L'Oreal selected each ingredient not only to ensure biodegradability but also to ensure that the product was not ecotoxic.

The product is packaged in 100 percent post-consumer recycled poly(ethylene terephthalate) (PET) to minimize the production of plastic bottles from new materials. L'Oreal launched this product in 2008. It donates all of the net profits from sales of this product to the Make It Right Foundation.

Positive Environmental Impact of Novel Crankcase Lubricant Technology

The Lubrizol Corporation

Phosphorus in the form of zinc dialkyldithiophosphate (ZDP) is the most cost-effective antiwear, antioxidant, and anticorrosion agent available for engine oil. Phosphorus, however, can enter engine exhaust and decrease the ability of catalytic converters to reduce emissions. This effect, called catalyst deactivation, makes it difficult for automotive manufacturers to meet EPA's requirements for lengthy warranties on catalyst systems. To protect against wear and safeguard the catalyst, industry has restricted phosphorus in lubricants to 0.06–0.08 percent by weight. Even at these low levels, however, phosphorus can volatilize and deactivate the catalyst.

Lubrizol has developed the HyperZDP™ System, a low-volatility ZDP. In partnership with Valvoline, it has studied the performance of Hyper ZDP™ technology and that of conventional ZDP technology. In Valvoline motor oils, HyperZDP™ reduced phosphorus deposition on the exhaust catalyst by 30–50 percent after 100,000 miles. Road testing for 100,000 miles reduced non-methane organic gases by 20 percent, NO_X (nitrogen oxides) by 40 percent, and carbon monoxide (CO) by 35 percent. Chassis dynamometer testing showed NO_X reductions of 30 percent. Bench testing showed reductions in T50 across different catalysts. Lubrizol then modeled T50 values for total hydrocarbons (THC), CO, and NO_X as functions of catalyst characteristics and phosphorus levels on the catalyst. The models showed the strongly beneficial, statistically significant impact of Valvoline motor oils with HyperZDP™ on catalyst performance.

Environmental Resources Management Ltd. conducted a lifecycle analysis consistent with ISO 14040. Compared to conventional ZDP, HyperZDP™ produced very significant reductions in photochemical oxidation, acidification, global warming potential, and human toxicity along with a minor reduction in aquatic toxicity and a minor increase in resource depletion.

After Lubrizol introduced its API SM/ILSAC GF-4 low-volatility ZDDP technology in 2004, Valvoline began using it universally in passenger car motor oils. Lubrizol received a patent for this technology in 2010.

Monsanto Company

Revolutionizing Insect Control: Bacillus thuringiensis (Bt) Technology

Insect pests have limited food crop production for centuries. Insecticidal chemicals were the most technologically advanced tools for insect control until the 1980s. Unfortunately, these chemicals had undesirable environmental effects, were toxic to some nontarget organisms, and required repeated applications to crops.

Monsanto's successful scientific research in innovative biotechnology since the 1980s has led to replacing the chemical manufacturing of pesticides with biological manufacturing mechanisms that create natural pesticides in the crops themselves. Unlike traditional pesticide technology, Monsanto's recently patented technology uses effective insect control found in nature. *Bacillus thuringiensis* (*Bt*), a ubiquitous soil microbe, produces specific insecticidal toxins called Cry (crystal) proteins. Using biotechnology, Monsanto combined its knowledge of Cry proteins with pioneering plant molecular genetics to create plants that express these highly specific toxins. The resulting plants control pests by making *Bt* Cry proteins themselves. These plants reduce the need for chemical pesticides, and the specificity of Cry proteins ensures that only target organisms are affected and not humans, animals, or nontarget beneficial insects.

Monsanto is applying its *Bt* technology to many plant varieties, increasing crop yields, and reducing the need for harsh chemical pesticides. In 2006, *Bt* crops reduced pesticide use by 9.56 million pounds in the United States. From 1996 to 2006, the commercialization of *Bt* technology contributed to an increase in national farm income from $8.76 million to $707 million.

Farmers planting insect-resistant crops experience improved safety and health because they handle less pesticides and apply them less frequently. Farmers also handle fewer containers, use less fuel, and decrease their aerial spraying. These factors benefit the environment, increase yields, and enhance farmers' lives. In 2010, biotechnology-derived, insect-resistant crops developed with Monsanto's technology represented 63 percent of all corn and 73 percent of all cotton grown in the United States.

Enabling a Sustainable Biorefinery with Green Chemistry: Enzymatic Hydrolysis of Lignocellulosic Biomass for the Production of Advanced Biofuels and Renewable Chemicals

Novozymes North America, Inc.

Plant cell walls are a complex matrix of cellulose, hemicellulose, and lignin. Hydrolyzing this recalcitrant lignocellulosic material efficiently is critical to obtaining high-quality sugar streams as feedstocks for fermentation or chemical synthesis to make fuels and chemicals.

Novozymes has taken a major step towards enabling the commercial production of biofuels and renewable chemicals from biomass. The Novozymes Cellic™ CTec2 technology employs enzymes to achieve high sugar yields from a variety of feedstocks (e.g., corn stover, wheat straw, and perennial grasses). A key breakthrough was Novozymes's unexpected discovery that a family of proteins (GH61) from *Thielavia terrestris* plays a significant role in lowering the amount of cellulase enzymes needed to hydrolyze lignocellulose. Novozymes incorporated a highly active GH61 protein into the CTec2 enzyme cocktail secreted by genetically engineered *Trichoderma reesei*, a cellulolytic fungus. CTec2 significantly improves the efficiency of biomass conversion over previous enzyme cocktails. It enables the production of cellulosic biofuels that can reduce greenhouse gas emissions by 115–128 percent compared to gasoline. Novozymes also developed a companion product, HTec2, with increased xylanase for feedstocks with high levels of insoluble xylan.

In the near term, biofuels are the only form of renewable energy that can substantially reduce greenhouse gas emissions from transportation. Novozymes is supporting its partners in scaling up proven technologies to produce these biofuels. The Novozymes CTec2 enzyme technology, in combination with process improvements by its partners, allows major reductions in enzyme doses. This breakthrough makes Novozymes CTec2 the first commercially viable enzyme technology for cellulosic ethanol production. This technology supports U.S. goals articulated in the Renewable Fuels Standard by providing a practical way to expand ethanol production from corn starch to cellulose as a feedstock. In 2010, Novozymes launched CTec2, placing the cost of enzyme technology within the commercially feasible range of $0.24–0.50 per gallon of ethanol.

New Lead-Free Materials to Replace Existing Primary Explosives

Pacific Scientific Energetic Materials Co.

Lead azide (LA) and lead styphnate (LS) are widely used in ordinance as priming mixtures for propellants and as detonators for secondary explosives. Annually, the U.S. Army requires well over 1,000 pounds of LA. The United States uses 60,000–80,000 pounds of LS containing approximately 30,000 pounds of lead annually as percussion primers in military and commercial small-caliber ammunition. During use and disposal, these compounds release lead, a toxic heavy metal, into the environment. Further, their manufacture requires toxic or carcinogenic materials.

In 1993, President Clinton issued Executive Order 12856 to reduce or eliminate the procurement of hazardous substances and chemicals by federal facilities. In compliance, the CAD/PAD group (i.e., Cartridge Activated Device/Propellant Activated Device group) at the Naval Surface Warfare Center-Indian Head (NSWC-IH) began a program to replace LA and LS with substitutes free of mercury, lead, and barium. Pacific Scientific Energetic Materials Co. (PSEMC) in Chandler, Arizona has been a leader in developing drop-in replacements for LA and LS that incorporate no toxic or environmentally undesirable elements. Because LA and LS have specific and complex properties, PSEMC spent over ten years developing environmentally benign replacements for these materials from concept through synthesis to qualification.

DBX-1 (Cu^{I} 5-nitrotetrazolate) is an LA replacement that has undergone qualification testing and is being scaled up to production levels for commercial and military uses. DBX-1 offers high oxidative, hydrolytic, and thermal stability, improved safety characteristics and compatibility, and output performance equal to or exceeding that of LA.

KDNP (potassium 5,7-dinitro-[2,1,3]-benzoadiazol-4-oleate-3-oxide) is an LS replacement suitable for service use; it qualified for weapons development in 2009. KDNP has high thermal stability, improved safety and compatibility, and output performance equal to or better than that of LS. PSEMC has applied for several patents on both KDNP and DBX-1.

PPG Industries, Inc.

Waterborne Refinish Coatings Manufacture

Paints and solvents account for approximately 12 percent of all emissions of volatile organic compounds (VOCs). The traditional, solventborne paints that automobile body repair shops have used for automotive refinishing emit relatively large amounts of VOCs. The California Air Resources Board (CARB) enacted legislation in January 2010 to reduce VOCs for all automotive refinishing products. Most notably, it reduced the limit on VOCs in basecoat to 3.5 pounds per gallon (420 grams per liter). The rest of the United States is expected to adopt similar limits in the near future.

Waterborne and solventborne paints perform similarly in color accuracy, smoothness, and chip resistance. Although the main current motivators of market growth for waterborne coatings are VOC regulations in California and Canada, many automotive refinishers use PPG's waterborne finish products solely for their perceived superior performance.

PPG developed waterborne finish in Europe in the early 1990s. In spring 2010, PPG established an innovative waterborne manufacturing process and facility in Delaware, Ohio. This facility is designed such that all raw materials, production, filling, quality assurance, and utilities are located nearby. The design reduces product loss, contamination, and waste. The waterborne finish produced at this facility will contain approximately 0.15 pounds of VOCs per gallon.

The company's expansion to the North American market allows PPG to create an additional 3 million liters per year of its high-quality, environmentally friendly waterborne refinish paint. During 2012, this production volume will avoid the emission of 3,097 metric tons of carbon dioxide equivalents (CO_2e). PPG expects the use of waterborne finish to double in the next five years.

Any body shop that replaces solventborne finish with waterborne finish will release 80 percent fewer VOCs to the atmosphere. More than 25,000 auto body repair shops in 50 countries (nearly 5,000 in the United States) now use PPG's waterborne refinish coatings.

Rochester Midland Corporation

Enhance O2 Soil Remover for Commercial Fryers

Current technologies for cleaning commercial deep-fat fryers use acid, bleach, and caustic chemicals to break down the adhesion of protein-based fryer soils chemically and lift the soils away from the fryer surface. These technologies may leave hazardous chemical residues behind. They also may not remove all the original soils, which can then support additional bacterial growth and produce off-tastes. Traditional cleaning methods may also lead to employee contact with harsh acids, bleaches, or bases and to disposal problems after the cleaning process.

Rochester Midland Corporation's (RMC's) Enhance O2 formulation represents a revolutionary advance in the removal of charred soils from the surface of steel commercial fryers. These soiled fryers typically harbor baked-on hydrocarbon, protein-based surface contamination that both presents a potential food source for bacteria and limits effective heat transfer.

Enhance O2 uses environmentally friendly, renewable hydrogen peroxide and selected trace surfactants to oxidize and break down these protein-based fryer soils. Enhance O2 is a natural, green product. Once hydrogen peroxide does its soil removal job, it decomposes to water and oxygen gas, eliminating disposal issues at the plant. In addition, hydrogen peroxide is a known, traditional disinfectant for skin cuts and sterilization processes.

In one case study, Enhance O2 reduced caustic use by one-half in five large cookers and one chiller making pasta at Windsor Foods. Enhance O2 also eliminated an acid wash. Overall process improvements, including Enhance O2, reduced chemical, labor, and water costs by $25,000 annually.

RMC received a U.S. patent for its technology in March 2009 (Patent No. 7,507,697).

PRS Water Damage PreClean: Biological Cleaning for Restoration and Remediation

Rochester Midland Corporation

When common structural members such as wood and concrete become contaminated by gray or black water, they typically harbor residues that produce undesirable malodors and are a potential food source for bacteria, mold, and mildew. Current technology uses petroleum-derived detergents and harsh chemicals to penetrate interstitial structural pores, break down odoriferous residues chemically, and abate the proliferation of mold and mildew. After use, current technology may leave undesirable odors, residual harsh chemicals, and even residues of the original contaminants that may continue to grow bacteria and mold.

Rochester Midland Corporation (RMC) has developed PRS Water Damage PreClean (PRS PreClean) to remediate contaminated, waterlogged structures. PRS PreClean uses an environmentally friendly, renewable detergent and special nonpathogenic bacteria in a pH-neutral aqueous solution to access and digest malodor-causing residues. Unlike traditional cleaners, PRS PreClean penetrates porous structures easily, allowing its bacteria access to the residues. The bacteria germinate and metabolize the residues in situ.

PRS PreClean is a natural, green product: its active component is living, naturally occurring, noninfectious bacteria, and its principal surfactant is naturally derived. Because bacteria carry out the necessary chemical reactions, there is no need to introduce harsh acids or bases into the environment. As a result, PRS PreClean eliminates significant amounts of hazardous materials. In one case study, PRS Pre-Clean reduced both surface solids and bottom solids in septic tanks. In a second case study, Enviro Care Liqui Bac (a one-half concentrate of PRS PreClean) remediated damage to concrete floors, carpet, and wall cavities caused by a sewage leak in a house. After treatment, workers removed all porous building materials and cleaned nonporous materials thoroughly with disinfectant and vacuums. Subsequent testing showed no sewage bacteria.

In 2010, this technology received EcoLogo CCD-112 certification for Biological Digestion Additives for Cleaning and Odour Control.

Greener Chemistry Processes for Large-Scale Manufacture of Polyamino Acids

Sigma-Aldrich

Polyamino acids have properties that mimic proteins and make them ideal for targeted drug delivery. They are water-soluble, selective, biodegradable, low-toxicity molecules with a wide range of molecular weights. Their production, however, involves both unstable, intermediate amino acid *N*-carboxyanhydrides (NCAs) and polymer processing. Traditionally, these steps require large quantities of hazardous chemicals including phosgene, hydrogen bromide–acetic acid, acetone, and dioxane.

Sigma-Aldrich has developed novel manufacturing processes for polyamino acids that minimize hazardous chemicals, improve efficiency, and increase product quality. For NCA production, Sigma-Aldrich eliminated NCA recrystallizations and reduced manufacturing runs by over 30 percent. They reduced phosgene and tetrahydrofuran by 30 percent and ethyl acetate and hexane by 50 percent, which reduced hazardous waste. Finally, they increased consistency in quality and yield.

Sigma-Aldrich also applied green chemistry to manufacturing poly-L-glutamic acid, a major drug-delivery polymer, which requires hazardous operations with hydrogen bromide–acetic acid or hydrogenation as well as highly flammable solvents. Replacing a benzyl protecting group with an ethyl group allowed them to replace hazardous chemicals with water-based chemicals, decrease cycle time by over half, decrease energy use and greenhouse gas emissions, and improve the scale-up potential 10-fold.

Sigma-Aldrich achieved similar savings with new processes for polylysine polymers and polyamino acid copolymers. For polylysine polymers, Sigma-Aldrich used only half the previous amount of hazardous chemicals (dioxane, hydrogen bromide–acetic acid, and acetone), but increased the yield from 10–30 percent to 43–53 percent. Sigma-Aldrich halved production runs, which is saving hundreds of gallons of hazardous chemicals, generating less waste, and saving energy. They also switched polyamino acid copolymer production to water-based systems that eliminate benzyl bromide, a hazardous lachrymator byproduct.

Sigma-Aldrich believes its contributions will lead to efficient chemotherapeutic treatments for diseases such as cancer, multiple sclerosis (MS), and diabetes and pave the way for greener chemical industry practices.

Tandus Flooring

Ethos™ Modular Commercial Floor Coverings

For years, recyclers have recovered glass from recovered windshields and sold it into other markets. In contrast, most of the polymeric poly(vinyl butyral) (PVB) film recovered from used-car windshields and other safety glass has been sent to landfills or burned for energy. PVB is a thermoplastic terpolymer of vinyl acetate, vinyl alcohol, and vinyl butyral.

Tandus Flooring is the first manufacturer to use the abundant PVB waste stream and recycle it into a high-performance carpet backing. Ethos™ secondary backing is made from PVB film reclaimed from windshields and other safety glass. Tandus has developed a patented technology for recycling post-consumer carpet and manufacturing waste into recycled-content backing for new floor coverings. Ethos™ backing is an alternative to other structured carpet backings such as poly(vinyl chloride) (PVC), ethylene–vinyl acetate (EVA), polyurethane, polyolefin, and bitumen. Producing carpet 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 and has very low volatile organic compounds (VOCs). In a fire, ethos™ does not generate hydrochloric acid (HCl) or dioxins, as do other carpet backings.

Initially, Tandus successfully introduced a six-foot-wide ethos™ cushion backing to meet the needs of Kaiser Permanente for high-performance, PVC-free carpet. This product is recyclable into Tandus's existing carpet-recycling process. More recently, the company introduced ethos™ modular, which has been commercially available since November 2009 at a price equivalent to PVC-containing modular products.

UOP LLC

Diesel and Jet Fuel from Renewable Resources That Is Fungible with Petroleum Fuels

Two roadblocks preventing the widespread use of renewable sources in transportation fuel are the incompatibility of current renewable fuels with the existing fuel distribution infrastructure and their incompatibility with current petroleum-based fuels. The primary components of current renewable transportation fuel are ethanol and fatty acid methyl esters (FAMEs). Because neither of these components is compatible with the existing infrastructure, they must be splash-blended at fuel distribution terminals. Further, their incompatibility with current gasoline, jet, and diesel engines limits them to about 10 percent by volume. This presents a huge hurdle to their commercial acceptance.

Scientists and engineers at UOP (a Honeywell Company) have developed the innovative approach of hydroprocessing biofeedstocks into transportation fuels. Hydroprocessing uses hydrogen to remove the oxygen from biofeedstocks by decarboxylation and hydrodeoxygenation, producing fuel and leaving propane, water, and carbon dioxide (CO_2) as byproducts. With new catalysts and process-flow schemes, UOP can produce both diesel and jet fuels from many biofeedstocks including jatropha, camelina, algal oil, animal fats, and used cooking oil. Their products are compatible with the existing refinery infrastructure, technology, and distribution network. Even more important, UOP's bioproducts can be blended directly into current fuels without modifying the jet or diesel engines or the delivery infrastructure. Although the processes to make diesel and jet fuels are similar, the detailed flow schemes and catalysts are different because the two fuels have different specifications. A lifecycle analysis (LCA) estimates greenhouse gas (GHG) savings at 84 percent for Green Jet Fuel™ and 89 percent for Green Diesel™.

In developing the UOP/Eni Ecofining™ process for Green Diesel™, UOP and Eni SpA took these inventions from concept to full process design. They have now licensed their process to four refiners. Several organizations are partnering with UOP to bring renewable jet fuels to market. UOP and Eni have filed 30 U.S. patent applications for their Ecofining™ technologies.

Klean-Strip® Green™ Safer Paint Thinner

WM Barr & Company, Inc.

Petroleum distillates present risks to human health and the environment, such as air pollution from volatile organic compounds (VOCs), health hazards from inhalation and skin contact, and fire hazards during manufacture, use, storage, and transport. Although consumers can foresee these hazards and government regulators, industry, and the marketplace deem them to be acceptable and reasonable, Barr sought to develop a safer, more environmentally friendly alternative.

Klean-Strip® Green™ Safer Paint Thinner is a formulation of Type IIC mineral spirits suspended in water with a small amount of oleic acid emulsifier. It contains 67 percent lower VOCs than regular paint thinner. The mineral spirits are a safer petroleum distillate without any hazardous air pollutants (HAPs). Consumers of Klean-Strip® Green™ Safer Paint Thinner report lower odors and less skin irritation than with regular paint thinner. Klean-Strip® Green™ Safer Paint Thinner is nonflammable and noncombustible; therefore, it poses no fire hazards. Its lower VOC content means that it is less volatile than regular paint thinner, so indoor air pollution is less of a problem for consumers. Unlike regular paint thinner, Klean-Strip® Green™ Safer Paint Thinner is not a hazardous waste under the Resource Conservation and Recovery Act (RCRA), not a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA), and not a hazardous material under Department of Transportation regulations.

Other environmental benefits include less dependence on nonrenewable resources such as petroleum because 67 percent of the product is water, a renewable resource. Because water is readily available at Barr's manufacturing site, there are fewer transportation risks and environmental impacts (i.e., air pollution) associated with raw material supply. Since its introduction in 2007, this product has had average annual sales of 8 million pounds, eliminating the use and VOC emissions of 5 million pounds of petroleum distillate.

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