



Presidential Green Chemistry Challenge Awards Program: Summary of 2014 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 19 years of the awards program, EPA has received 1,606 nominations and presented awards to 98 winners. By recognizing groundbreaking scientific solutions to real-world environmental problems, the Presidential Green Chemistry Challenge has significantly reduced the hazards associated with designing, manufacturing, and using chemicals.

Each year our 98 winning technologies are together responsible for:

- Reducing the use or generation of 826 million pounds of hazardous chemicals
- Saving 21 billion gallons of water
- Eliminating 7.8 billion pounds of carbon dioxide releases to air

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

This booklet summarizes entries submitted for the 2014 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 2014 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 October 16, 2014, 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 abstracts in this document were submitted in nominations for the 2014 Presidential Green Chemistry Challenge Awards. They were copied directly from the nominations and have only been edited for stylistic consistency. They are not written or officially endorsed by the Agency. These abstracts represent only a fraction of the information provided in the nominations from which they were copied; judging was conducted on all information in the nominations. Claims made in these abstracts have not been verified by EPA. Mention of trade names, products, or services does not convey official EPA approval, endorsement, or recommendation.

Academic Award

Aerobic Oxidation Methods for Pharmaceutical Synthesis

Innovation and Benefits

Oxidation reactions are widely used in the production of organic chemicals, but they often form wasteful byproducts. Professor Stahl has developed catalytic methods that replace hazardous chemicals with oxygen from air as an environmentally benign oxidant. The methods operate under mild conditions, can be performed safely on a large scale, and are highly selective, even with complex building blocks for pharmaceuticals, potentially saving time and money and reducing hazardous waste.

Molecular oxygen (O₂) is the least expensive and most environmentally benign chemical oxidant available, but it is rarely used because of safety concerns and poor reaction selectivity. Rather than using oxygen, industrial chemists typically choose between using more toxic oxidizing agents or employing alternative synthetic routes that avoid oxidation altogether, even if the routes are less efficient.

Professor Stahl and his group specialize in the development and investigation of catalytic aerobic oxidation reactions, and they recently developed several practical and synthetically useful aerobic alcohol oxidation methods. In 2011, post-doctoral researcher Dr. Jessica Hoover showed that a copper(I) salt and TEMPO (2,2,6,6-tetramethylpiperidiny-N-oxyl) mediate selective oxidation of primary alcohols to aldehydes at room temperature with ambient air as the oxidant. The method is compatible with both activated and unactivated alcohols, tolerates heterocycles and diverse oxygen-, nitrogen-, and sulfur-containing functional groups, and enables selective oxidation of primary alcohols within the molecules containing unprotected secondary alcohols. Mechanistic studies of these reactions led to the subsequent discovery of a new catalyst system by graduate student Janelle Steves that exhibits broader scope and efficiently oxidizes both primary and secondary alcohols. The simplicity of these catalyst systems and lack of stoichiometric reagents other than oxygen greatly simplifies product isolation and reduces waste. Chlorinated solvents, which are commonly needed with other classes of oxidation reactions, are not required.

Professor Stahl has partnered with Professor Thatcher Root (Dept. of Chemical and Biological Engineering, University of Wisconsin-Madison) and scientists at several pharmaceutical companies (Drs. Matthew Yates, Martin Johnson, Joseph Martinelli at Eli Lilly; Dr. Christopher Welch at Merck; Dr. Joel Hawkins at Pfizer) to explore strategies for safe and scalable implementation of aerobic oxidation reactions for pharmaceutical synthesis. One approach involves a continuous-flow process, which has been used to achieve aerobic oxidation of alcohols to aldehydes in near-quantitative yields with reactor residence times as low as five minutes.

The development of practical, safe, and scalable oxidation methods of this type provides a foundation for widespread adoption of oxidations using molecular oxygen by pharmaceutical, fine, and specialty chemical manufacturers.

**Professor
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Small Business Award

Amyris

Farnesane: a Breakthrough Renewable Hydrocarbon for Use as Diesel and Jet Fuel

Innovation and Benefits

Renewable fuels are needed to help achieve global sustainability. Amyris took a step toward this goal by engineering yeast to make a chemical called farnesene instead of ethanol. Farnesene is a building block hydrocarbon that can be converted into a renewable, drop-in replacement for petroleum diesel without certain drawbacks of first-generation biofuels. Use of Amyris's renewable diesel may produce 82 percent less greenhouse gas emissions than use of petroleum diesel.

Transportation is second only to generating electricity as a source of greenhouse gas (GHG) emissions in the United States. Gasoline consumption by automobiles is responsible for more than half of all greenhouse gas emissions from transportation, while other uses, such as diesel fuel for trucks, trains, or maritime use and jet fuel for aircraft, account for the remainder. Increases in fuel prices have led many countries, including the United States and Brazil, to begin modern large-scale production of biofuels. Locally-produced biofuels have the potential to be a significant contributor to global sustainability, including providing local employment, ensuring access to energy resources, and reducing GHG emissions.

First generation biofuels, notably ethanol and biodiesel (i.e., fatty acid methyl esters), suffer from limitations, such as limits on how much can be blended with gasoline or poor cold-weather performance. To address the known shortcomings of first generation biofuels, Amyris developed an advanced renewable fuel compatible with the existing vehicle and distribution infrastructure that is now used in heavy-duty diesel engines and commercial aircraft.

Amyris used state-of-the-art strain engineering to make yeast that converts sugars into the hydrocarbon farnesene rather than ethanol. Farnesene can then be hydrogenated to farnesane, a renewable drop-in replacement for petroleum diesel and a blend-stock for jet fuel. A recent lifecycle analysis estimated an 82 percent reduction in GHG emissions for farnesane, compared with the EPA baseline fossil diesel—including indirect effects. Farnesane can also have land-use benefits for heavy-duty transportation: a hectare of land growing soybeans to produce traditional biodiesel generates enough fuel for a bus to travel about 600 miles. If the same land is instead used to grow sugarcane to make ethanol, a bus adapted to run on ethanol could travel about 4,000 miles. However, if the sugarcane is used to produce farnesane, the unmodified diesel vehicle can travel about 5,500 miles. Breakthroughs in converting lignocellulosic biomass to fermentable sugars will further increase this benefit.

Amyris has demonstrated industrial-scale production using its proprietary yeast strains to ferment sugars into renewable fuels that meet petroleum fuel specifications. Its renewable diesel, which has been approved by EPA for blends up to 35 percent, contains no sulfur or particulates, has a higher cetane number than diesel, and has improved low-temperature performance. More recently, in June 2014, ASTM revised its standard for jet fuel to include the use of renewable farnesane as a blending component in jet fuels for commercial aviation.

Greener Synthetic Pathways Award

Tailored Oils Produced from Microalgal Fermentation

Solazyme, Inc.

Innovation and Benefits

Vegetable oils derived from plants can replace petroleum as building blocks for many industrial chemicals. Solazyme has engineered microalgae to produce oils tailored to customers' needs that can mimic or enhance properties of traditional vegetable oils. These micro-algae-derived oils are consistent regardless of season, geographic origin, and feedstock source.

For thousands of years, civilization has used approximately 12 natural triglyceride vegetable oils, including palm, soy, peanut, corn, olive, sunflower, and coconut, for food, energy, and as building blocks to make a wide variety of chemicals. However, those oils may not have the ideal composition for any particular use. Vegetable oils are isolated from their source, refined, fractionated, distilled, and often chemically modified. Achieving the desired compositions from plant oils is often energy intensive, expensive, can be wasteful, and, in some cases, requires use of hazardous chemicals.

While some companies have turned to traditional biotechnology organisms, such as *E. coli* and *Saccharomyces*, to engineer to produce triglyceride oils, Solazyme recognized that the pathways that make oil in canola, soybean, palm, and coconut first evolved in microalgae. Solazyme took advantage of the inherent oil-producing ability of microalgae and developed a process to make oils via fermentation.

Solazyme's technology combines the innate oil-producing machinery of algae with genetic engineering to express the unparalleled diversity of oil production genes. Consequently, Solazyme has the potential to produce a nearly unlimited variety of differentiated triglyceride oils while dramatically reducing the time required to produce these oils. Solazyme has screened tens of thousands of microalgae to identify the unique oils they produce with a broad array of chemical and physical properties. In several commercial applications, Solazyme demonstrated that their oils and lubricants reduce volatile organic compound (VOC) emissions and waste compared to use of regular vegetable oils. Solazyme's oils are currently being tested and sold commercially for use in a broad array of applications, including food, fuel, home and personal care, and industrial products.

Oils produced at Solazyme's joint venture facility in Brazil are expected to have a lower carbon and water footprint than many current triglyceride oils and have a far lower environmental impact than the petroleum-based products they replace.

Greener Reaction Conditions Award

QD Vision, Inc.

Greener Quantum Dot Synthesis for Energy Efficient Display and Lighting Products

Innovation and Benefits

QD Vision makes higher-quality quantum dots—nanoscale LED components—using an innovative greener process. These quantum dots make possible cost-effective full-spectrum color in flat-screen displays and solid-state lighting. Historically, making quantum dots involved hazardous chemicals and low yields. QD Vision's process has increased efficiency, uses less hazardous building blocks, and eliminates nearly 40,000 gallons of highly toxic solvent each year.

Most white light sources include a primary light source and a “downshifting” phosphor which converts some or all of the primary light into the desired white light spectrum. In a typical fluorescent bulb, electrified mercury gas produces the primary light in the ultraviolet (UV) range, and phosphors (the whitish powder on the inside of the bulb) convert that UV light into white light. Similarly, today's light emitting diodes (LEDs) produce a blue primary light, and phosphors convert some of that light to make it appear whiter to the human eye. However, these LED phosphors emit light in a broad band and result in a tradeoff between color quality and efficiency. As a result, display manufacturers must either make displays that cannot show the full range of colors found in nature, or greatly reduce the product's efficiency. Lower efficiency means that more LEDs are required to achieve the same brightness, and hence cost more to make and need more energy to run.

Semiconductor nanocrystal quantum dot technology offers high-quality color to the solid-state lighting (LED light bulbs) and liquid-crystal display (TVs, mobile devices) markets with high system efficiency. While developing these energy-saving materials, QD Vision also developed a much greener synthesis. QD Vision estimates that they avoid using 150,000 liters (40,000 gallons) of highly toxic solvent per year and avoid 100 kilograms of cadmium waste in production in the United States. QD Vision achieved these improvements by replacing alkyl phosphine- and alkyl phosphine oxide solvents with long-chain hydrocarbons, reducing both the hazard and amount of solvent used. They also replaced highly hazardous organo-cadmium and organo-zinc building blocks with less hazardous precursors. Finally, they improved their purification by switching from centrifugation to filtration saving time and energy, and reducing waste. QD Vision has implemented all of these changes while simultaneously improving material performance. As such, QD Vision quantum dots were the first to be implemented in mainstream commercial devices, including ten different models of Sony TVs in 2013.

Using QD Vision Color IQ™ components in 20 million TVs (equivalent to roughly 10 percent market penetration) is projected to save 600,000,000 kilowatt-hours (kWh) of electricity per year worldwide—enough electricity to power 50,000 average homes in the United States. Although QD Vision quantum dots do still use cadmium, the amount of cadmium used in a device is less than the amount of cadmium emissions prevented through reduced electricity production, resulting in a net decrease in cadmium waste.

Designing Greener Chemicals Award

The Solberg
Company

RE-HEALING™ Foam Concentrates-Effective Halogen-Free Firefighting

Innovation and Benefits

Fluorinated surfactants are critical components of firefighting foams, but they are persistent chemicals and have the potential for environmental impacts. In developing RE-HEALING™ Foams (RF), the Solberg Company has replaced fluorinated surfactants in its firefighting foam concentrates with a blend of non-fluorinated surfactants and sugars. The new foam works well with far less environmental impact.

Firefighting foams suppress combustion by smothering burning fuels and cooling fires. For years, these foams have used long-chain fluorinated surfactants as the “active ingredient”. In 2006, EPA established a voluntary stewardship program to reduce uses of long-chained fluorosurfactants because they are persistent, bioaccumulative, and toxic. As a result, foam formulators switched from long- to short-chain fluorosurfactants. However, almost 40 percent more fluorosurfactant is required to meet the Underwriter Laboratories (UL) 162 firefighting foam performance standard when using short-chain rather than long-chain fluorosurfactants. While less bioaccumulative and less toxic, short-chained fluorosurfactants are still persistent, and, given the greater amounts used, greater quantities of these short-chained fluorochemicals are expected to be released to the environment.

Rather than simply switching to the short-chain fluorosurfactant, the Solberg Company developed a line of halogen-free foam concentrates. After several years of research and testing on fires, Solberg developed products that are equal, and in many cases superior, to their fluorinated counterparts. Solberg’s foams have achieved full regulatory compliance with existing fire protection standards, while eliminating persistent chemicals. In particular, RE-HEALING™ Foam (RF) is a very effective firefighting foam concentrate for flame knockdown, fire control, extinguishment, and burnback resistance. Control, extinguishing time, and burnback resistance are paramount to the safety of firefighters everywhere, and RF has excellent performance in each.

RE-HEALING™ Foam concentrates are a blend of hydrocarbon surfactant(s), water, solvent, sugars, a preservative, and a corrosion inhibitor. Concentrates are formulated to be used as 1 percent, 3 percent, or 6 percent products to fight “Class B” hydrocarbon fuel fires. The presence of complex carbohydrates gives the foam significantly more capacity to absorb heat than fluorine-containing foam. This improves the extinguishing property of RF and adds to the burnback capacity. The renewable hydrocarbons used in RF concentrates are the same products used in the health care industry. The use of these blends results in a product that has very favorable hygiene and environmental properties (including 93 percent degradation in 28 days, and complete degradation by day 42). The RF concentrates are also easy to retrofit into existing foam systems as a replacement to existing fluorosurfactant foams.

Entries from Academia

Green Biological Production of Short and Medium Chain Esters

Increasing global demand and reliance on petroleum-derived chemicals will necessitate alternative sources for chemicals and all the products made possible by them. Currently, 99 percent of chemicals are derived from petroleum and natural gas. The ester classes of small molecules are used for fragrances and cosmetics due to their fruity and floral aromas but are also heavily used in paints, coatings, and solvents. In 2012, the global market for flavors and fragrances was \$16 billion. Small esters are commonly produced by acid-catalyzed esterification synthesis of an organic acid and alcohol substrate that are usually sourced from petroleum under harsh conditions. Synthetic biology and metabolic engineering enables the renewable production of fuels and chemicals from microorganisms by constructing unique metabolic pathways. Professor Atsumi and his team developed a new strategy for ester production that is cleaner and more sustainable. The alcohol *O*-acyltransferase (ATF) class of enzyme utilizes acyl-CoA units for ester formation, which takes advantage of the stored energy in the thioester bond of the acyl-CoA molecule. The release of free CoA upon esterification with an alcohol provides the free energy to facilitate ester formation under green conditions. Thus, Professor Atsumi and his team engineered the industrial production host, *Escherichia coli*, to produce various esters under green conditions (water and ambient temperatures) and from a renewable carbon source (glucose). They achieved high-yield and titer production of isobutyl acetate, which demonstrates the commercial potential of this platform. Ultimately, Professor Atsumi and his team demonstrated production of 13 different ester compounds using the strategy. This renewable technology can potentially replace petroleum-derived ester synthesis, greatly reducing carbon emissions and the associated health hazards.

The Scalable Production of Edge-Functionalized Few Layer Graphene Oxide

Edge-functionalized few layer graphene oxide (EFGO) can be rapidly prepared in large quantities by mechanochemical means. Grinding graphite with urea hydrogen peroxide adduct produces a highly delaminated product with an oxygen content of 5-20 percentage by weight. The only byproducts of this synthesis are water and urea. This process does not require toxic reagents and it produces byproducts generally considered safe. The edge-functionalized graphene produced by this method is hydrophilic and easily suspended in water, allowing for convenient processing of films and epoxy composites. It can also be electrodeposited to form uniformly smooth coatings. This material is electrically conductive and free from manganese impurities that often plague graphite oxides prepared by Hummers'-type methods. Analyses show that the graphite is fully oxidized to -COOH groups along the edges of individual graphene sheets. This approach offers a scalable, environmentally benign route to large quantities of EFGO.

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Enzyme-Free Biomass Depolymerization Using GVL

The need for renewable alternatives to petroleum-based resources has never been greater. Reliance on fossil fuel extraction currently poses environmental, economic, and political threats worldwide. Biomass-derived fuels and chemicals provide a renewable alternative to products traditionally generated from fossil fuels and yet previous efforts to transform cellulose-containing biomass into fuels and other products have often relied on expensive, energy-intensive, and sometimes toxic chemical protocols. Developing environmentally sustainable and economically viable biofuels and bio-based products thus depends on developing greener and more streamlined ways of breaking down cellulose into sugar.

Researchers at the University of Wisconsin-Madison have shown that γ -valerolactone – a small molecule solvent that can be renewably sourced from biomass – promotes efficient and selective thermal breakdown of cellulose in the presence of dilute aqueous acid. The researchers have successfully performed laboratory-scale production of soluble carbohydrates from corn stover, hardwood, and softwood at high yields (70 to 90 percent) in a solvent mixture of biomass-derived γ -valerolactone (GVL), water, and dilute acid (0.05 weight percent H_2SO_4). A key advantage to this process is that it replaces enzymes and significant quantities of acid with a green solvent easily producible from biomass itself. GVL can also be easily separated by adding small amounts of liquid carbon dioxide.

An initial economic assessment indicates that this technology could produce ethanol, and perhaps other biofuels, at a cost savings of roughly 10 percent when compared with current state-of-the-art technologies. Through Wisconsin Alumni Research Foundation's Accelerator Program, University of Wisconsin researchers are now constructing a high-efficiency biomass reactor that will use GVL to produce concentrated streams of sugars and intact lignin solids for use by scientific collaborators optimizing the conversion into valuable chemicals and fuels. With the use of this technology, it turns out that the secret to success in creating plant-based fuels was within the plants themselves.

Catalytic Cross-Couplings Using a Sustainable Metal and Green Solvents

The nominated technology involves one of the most important classes of organic reactions used in modern research: transition metal-catalyzed cross-coupling reactions. These reactions are amongst the most effective and widely used means of constructing carbon-carbon (C-C) and carbon-heteroatom (C-X) bonds. The importance of cross-coupling methodology is underscored by the 2010 Nobel Prize given “for palladium-catalyzed cross-couplings in organic synthesis.” Arguably, the most widely used and reliable coupling methodology is the Suzuki-Miyaura coupling to forge C-C bonds. These couplings have transformed the landscape of drug discovery and development.

Given the importance of the Suzuki-Miyaura coupling, the development of “greener” variants has been a topic of great interest. The American Chemical Society's Green Chemistry Institute's Pharmaceutical Roundtable has highlighted the limitations associated with these couplings and, more recently, has incentivized academic research in this area by making it the focus of their 2012 grant cycle. Since 2008, the Garg laboratory at the University of California-Los Angeles has pursued the development of “greener” and more sustainable Suzuki-Miyaura couplings for use in academic and industrial applications. The key green chemistry challenges targeted include: (a) developing Suzuki-Miyaura couplings that do not require the use of the precious metal palladium, (b) discovering conditions that proceed in green solvents, rather than less attractive solvents (source reduction), and (c) uncovering a unified set of reaction conditions to enable the Suzuki-Miyaura coupling of an unprecedented range of substrates.

Professor Neil Garg, Department of Chemistry and Biochemistry, University of California-Los Angeles

By targeting the aforementioned challenges systematically, the Garg laboratory has developed Suzuki–Miyaura couplings that use inexpensive nickel-catalysis, proceed in “greener” solvents such as alcohols, and are tolerant of a vast range of substrates, including heterocycles, in addition to a variety of electrophiles (e.g., halides and pseudohalides). These studies have led to discoveries in fundamental chemical reactivity and new tools for cross-coupling chemistry. Finally, these efforts have fueled educational initiatives in green chemistry where undergraduate students have performed “green” Suzuki–Miyaura couplings in an instructional laboratory.

Green Approaches of Nanocomposite Material Synthesis for Energy Storage, Environmental Surveillance and Sustainable Food Systems

Graphene sheets have high specific surface area, large electrical conductivity, and robust mechanical strength. It is readily produced in tons. Current economical and effective production of graphene in mass from graphene oxide (GO) requires reducing reagents such as hydrazine, alkaline, ethylenediamine, NaBH_4 , and urea, which are toxic, corrosive, or even explosive. The process with reducing reagents and stabilizers to improve reduced GO dispersion are time-consuming and usually undesirable due to their damage on electronic properties. Graphene nanocomposites with metal nanoparticles can have synergistic effects for use in different applications such as energy storage, biosensors, and optical electronics. However, the synthesis of these nanoparticles from their salt precursor solutions also needs hazardous reducing reagents. Therefore, a large-scale greener and more effective synthetic route of graphene and graphene nanocomposites is an unmet need. A facile, controllable, and cheap electrochemical approach was used to perform rapid and green synthesis of graphene and graphene-based nanocomposite materials for energy storage, environmental surveillance, and sustainable food systems. Compared to reduction by constant potential or current, a repetitive cathodic potential cycling reduction was designed, which can completely remove unfavorable electrochemically unstable oxygenated groups and generate a two-dimensional, defect-free homogeneous graphene film with excellent stability and electronic properties. The synthesis can be successfully conducted on different flat and rough substrates such as indium tin oxide glass, glassy carbon, and graphitic carbon. Applications of graphene and graphene nanocomposites from this green route without generating any hazardous wastes are exhibited as supercapacitor, oxygen reduction reaction, and biosensing in food and environmental samples. By using a patented replaceable technology for the developed solid-state electrodes, wastes such as alumina slurry and water from electrode washing can be avoided.

Ultrasound Induced, Copper Mediated Homo-Coupling Using Polymer Supported Aryltrifluoroborates

The homocoupling of aryl compounds is an important reaction used in the formation of fundamental building blocks for numerous industrial and pharmaceutical materials. Unfortunately, many of the widely used homocoupling reactions require expensive catalysts or use harsh reaction conditions with large quantities of metal while producing only modest product yields. In an attempt to improve the negative aspects of these reactions, researchers have employed a variety of tactics including the use of different metals, ultrasound or microwave energy sources, various solvent systems, and different ligands, all with varying degrees of success. There are a number of reports that indicate successful synthesis of biaryl compounds using polymer supports. Benefits of the modification include successful reactions run in water and under atmospheric conditions with good product yields. Regrettably, these reactions are not atom efficient, and require extensive preparation of the polyethylene glycol, with harsh chemicals and environmentally toxic solvents, before it can be used in the reaction. Since Dowex is commercially available, the Kabalka group attempted a homocoupling reaction similar to the reported polyethylene glycol methods.

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Palladium(II) acetate was chosen as the survey metal, following the reported methods. Initial survey reactions using heat and stirring indicated only minimal product yield (seven percent) after 72 hours. It was decided to carry out the reaction using an ultrasound energy source, which provided a significantly improved yield of 92 percent while decreasing reaction time to six hours. To develop a more environmentally friendly reaction, the copper acetate replaced the palladium salt, and the aqueous tetrahydrofuran solvent was changed to aqueous ethanol. Product yields remained excellent at 96 percent. The reaction is green, atom efficient, and, in later reactions, shown to be scalable as compared to currently used industry reactions.

Highly Efficient and Practical Monohydrolysis of Symmetric Diesters

Water is the least expensive solvent and among the most environmentally friendly solvents. Among various synthetic conversions, desymmetrization of symmetric compounds is one of the most atom-economical and cost-effective reactions, because the starting symmetric compounds are typically obtained easily on a large scale from inexpensive sources, or are commercially available inexpensively. Therefore, water-mediated desymmetrization of symmetric organic compounds is of tremendous synthetic value, and makes a significant contribution to creating greener reaction conditions.

Dr. Niwayama pioneered water-mediated desymmetrization. In particular, she has been developing monohydrolysis of symmetric diesters as the water-mediated desymmetrization reaction. Half-esters, which are produced by such monohydrolysis of symmetric diesters, are versatile building blocks in organic synthesis applied to synthesis of polymers and dendrimers with applications to industrial products of commercial value. Unfortunately, since the two ester groups in symmetric diesters are equivalent, the statistically expected yield of half-esters would be a maximum of only 50 percent. Classical saponification usually affords complex mixtures of dicarboxylic acids, half-esters, and the starting diesters, which are difficult to separate, yielding a large amount of undesirable dirty waste. Ring-opening reactions of cyclic acid anhydrides require hazardous organic solvents. However, Dr. Niwayama discovered a highly efficient and practical ester monohydrolysis of symmetric diesters. In this reaction, an aqueous base such as NaOH or KOH is added to a symmetric diester suspended in water at 0°C. With this simple reaction, pure half-esters are obtained in high to near-quantitative yields without production of dirty waste and without use of hazardous organic solvents. This reaction, which is anticipated to significantly contribute to green chemistry, has been licensed by three companies, and several half-esters produced by this reaction have been commercialized.

Utilization of Elemental Sulfur as a New Chemical Feedstock for Polymeric Materials

The nominated technology focuses on the development of new polymerization methods to convert elemental sulfur into useful polymeric materials. A new generation of sulfur-based plastics has resulted from these new synthetic advances, where these materials have been demonstrated to possess useful electrochemical and optical properties. The surfeit of elemental sulfur (S₈) generated from petroleum refining has created an incredibly abundant and inexpensive supply of sulfur. However, there remain only limited uses for elemental sulfur toward the production of other chemicals (e.g., sulfuric acid), and there is a paucity of synthetic chemical methods to modify, or directly convert elemental sulfur into useful polymers and alternative materials. This challenge arises from the incompatibility and limited miscibility of sulfur with the majority of chemical reagents and solvents. To obviate these fundamental synthetic challenges, the team of Pyun and Glass has developed a new concept of using molten liquid sulfur as an unconventional solvent and

Professor Jeffrey Pyun and Professor Richard Glass, Department of Chemistry & Biochemistry, University of Arizona

reagent for chemical reactions used to prepare gold nanoparticle nanocomposites and high content sulfur polymers. To convert sulfur into a chemically stable and useful plastic, Pyun and Glass' team has developed a new polymerization method termed inverse vulcanization that for the first time uses molten liquid sulfur as the reaction medium and comonomer for the synthesis of sulfur-rich copolymers. They demonstrated that these sulfur-based plastics possess unique electrochemical and optical properties, which enabled their application in devices for enhanced lithium-sulfur batteries and infrared thermal imaging. These collective findings point to the creation of a new field of sustainable sulfur chemistry for advanced materials with significant environmental and technological benefit through the use of excess sulfur. This work has generated five publications and one patent application.

Bacteriophage-Based Bacterial Identification and Antibiotic Resistance Test

Antibiotic-resistant bacterial infections are a serious and growing global health problem. Conventional antibiotic resistance determination techniques typically require laborious and time-intensive culture-based assays, which take up to 96 hours and expend an inordinate amount of disposable plastics and bacterial growth media. In contrast, the Colorado School of Mines (CSM) bacteriophage amplification platform enables rapid simultaneous identification and antibiotic resistance determination without the need for extensive culturing, minimizes the use of disposable plastics, and reduces overall environmental impact. More importantly, with respect to its impact on human health diagnostics, these attributes result in more user-friendly tests with significantly reduced testing times of less than five hours. First described, developed, and patented by the Advanced Biodetection Technologies Laboratory (ABTL) at CSM, the intellectual property covering this technology was licensed by MicroPhage in 2002 for commercial development. MicroPhage advanced the technology through the Food and Drug Administration (FDA) 510(k) approval process, but then filed for bankruptcy in 2012 and returned all licensed technology and intellectual property to CSM. During that time and continuing to the present, the ABTL has advanced the technology through several key breakthroughs that allow even more sensitive and rapid bacterial detection with a focus on green chemistry practices while maintaining the technology's minimal environmental footprint.

Phages are viruses that infect targeted bacteria in a species-specific fashion. The phage amplification process can generate as much as a 5-log signal amplification versus detection of bacteria alone. In addition, because of the reliance of phages on a viable bacterial host, simultaneous drug resistance determination is achieved through parallel, multiplexed phage amplification reactions with and without the addition of any given antibiotic. The CSM approach has miniaturized the process to a milliliter level and has incorporated modern green chemistry technologies for detection of progeny phage on a dual track lateral flow immunoassay strip, which is analogous and read like a typical home pregnancy test. A positive result from the first drug-free reaction indicates the presence of target bacteria. A positive result from the second, drug-containing reaction shows that the target bacteria were antibiotic resistant. The phage amplification platform was the first FDA-approved *in vitro* diagnostic for direct identification of bacteria and determination of antibiotic resistance or susceptibility. The CSM rapid bacterial identification and antibiotic resistance determination test embodies the tenants of green chemistry by benefiting human health with advanced diagnostic capacity using natural phage products and greener reagents, and by significantly reducing environmental waste and power consumption.

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UCR Co-Solv Technology Achieves Unprecedented Yields of Fuel Precursors from Lignocellulosic Biomass

Professor Wyman and his team has developed an integrated biomass pretreatment and conversion strategy, named “Co-Solv,” to promote the production of fuel precursors furfural and 5-hydroxymethylfurfural (5-HMF) directly from lignocellulosic biomass as a future platform for sustainable biofuel production. These fuel precursors have been considered by the U.S. Department of Energy as top platform chemicals for the production of renewable chemicals and liquid transportation fuels if they can be obtained at high yields and at low cost from lignocellulosic biomass. As biomass feedstocks costing \$60/dry ton are equivalent in energy cost to petroleum at about \$20/barrel, they are distinctive in being the only sustainable resource sufficiently inexpensive and abundant to make a large impact on liquid fuel use. Green processes that can economically convert low-cost biomass into compatible transportation fuels that have enormous benefits for addressing global climate change, national energy security, economic growth and employment, trade deficits, and global competitiveness issues. Co-Solv is a highly tunable and scalable process to simultaneously solubilize lignocellulosic biomass and catalytically convert hydrolyzed sugars into fuel precursors. In one arrangement, Co-Solv technology employs a one-pot monophasic reaction combining a renewable solvent with non-corrosive solid acid catalysts to produce the highest overall yields furfural (>90 percent) and 5-HMF (>45 percent) directly from biomass. Co-Solv is greener and more effective than other competing strategies such as biphasic reactions, ionic liquid systems, and other co-solvent systems because it is low-boiling, relatively non-toxic, and can be renewably produced from furfural as a final product to supplement a continuous reaction strategy. Professor Wyman and his team has also successfully compared these results with current industrial methods to show an impressive product yield advantage, which could result in low-cost, largescale production. Lignin removal is also extensive, achieving ~90 percent delignification of hard woods to maximize the utility of all major fractions of lignocellulose reducing solid waste products.

Professor Yi-Heng Percival Zhang, Department of Biological Systems Engineering, Virginia Tech

High-Yield and High-Purity Hydrogen Production from Carbohydrates via Synthetic Enzymatic Pathways

Hydrogen is one of the most important chemical intermediates produced from fossil fuels and will become one of the best transportation fuels and energy storage compounds in the future. The production of carbon-neutral hydrogen from renewable resources and the storage of high-density hydrogen are the two greatest challenges for the hydrogen economy. Carbohydrates, including cellulose, hemicellulose, starch, and sucrose, are the most abundant renewable bioresources. They are produced through plant photosynthesis. Professor Zhang has designed non-natural synthetic enzymatic pathways that can release all of the hydrogen from a variety of carbohydrates and water under mild reaction conditions (e.g., 30–60°C, atmospheric pressure, and aqueous solution), that is, the production of 12 H₂ per hexose and 10 H₂ per pentose. These synthetic enzymatic pathways are comprised of more than 10 enzymes from different sources, such as archaea, bacteria, animals and plants, as well as coenzymes, including biomimetic analogs. Furthermore, Professor Zhang suggested the use of carbohydrates as a high-density hydrogen carrier with a gravimetric density of up to 14.8 H₂ mass percent, far higher than the Department of Energy’s hydrogen storage goals. To decrease its production costs, Professor Zhang has developed a number of ultra-stable enzymes with total turnover numbers of up to 1,000,000,000 mole of product per mole of enzyme and succeeded in changing the coenzyme preference of redox enzymes to low-cost and ultra-stable biomimetic coenzymes from costly and unstable natural ones. Also, Professor Zhang has increased its production rates by 800 times, 75 times the best algal biohydrogen production rate. Current carbohydrate-to-hydrogen rates are fast enough for small-size distributed hydrogen generator systems that utilize local biomass resources. This work was done in collaboration with Professor Mike Adams of the University of Georgia, Drs. Jonathan Mielenz and Barbara Evans at the Oak Ridge National Laboratory, and Dr. Joseph Rollin at Cell Free Bioinnovations Inc.

Entries from Small Businesses

A S Filtration™, LLC

Pathex®/PathShield™ Antimicrobial Filter Media for the Control of Bacteria in Stormwater and Industrial Process Waters

A S Filtration™, LLC developed Pathex® Antimicrobial Filter Media (PathShield™ is an Alternate Brand Name) for the reduction and control of coliform bacteria in stormwater, industrial waste water, recirculating cooling towers, heat transfer systems (evaporative condensers, hydrostatic sterilizers and retorts, brewery and other pasteurizers, and warmers), industrial fresh water systems, service water and auxiliary systems, and municipal waste water treatment. Commercial applications demonstrate 20 percent water savings, enhanced temperature exchange capacity by reducing biofilm resulting in energy savings up to 40 percent, and significant decreases in traditional chemical biocide use by at least 75 percent.

Our technology confirms the 1970s theory that the unique surface bond of an organosilicon quaternary ammonium chloride compound to siliceous materials, without release of chemical, offers a new approach to water treatment. Efficacy is achieved at high loading rates up to 20 gpm/ft² without releasing, discharging, or leaching any antimicrobial agents, chemicals, or heavy metals. Pathex®/PathShield™ kills coliform bacteria as the organisms physically move over the hostile surface of filter media granules. The antimicrobial filter media is stable, non-toxic, not consumed, requires no power source for efficacy, non-corrosive, and not affected by temperature changes. There are no harmful disinfection byproducts such as total trihalomethanes, haloacetic acids, bromate, or chlorite formed by using Pathex®/PathShield™ filter media for treating water.

Independent laboratory testing and field demonstrations support the significant health and environmental benefits achieved through the use of Pathex®/PathShield™ filter media. Laboratory challenges achieved up to log 4 reductions in *E. coli*, total aerobic bacteria, *Legionella pneumophila*, sulfate reducing bacteria, and iron fixing bacteria. Stormwater field demonstrations further support high efficacy against *E. coli*, enterococci, and total coliform bacteria. Long-term suppression of total aerobic bacteria and total coliform bacteria in industrial cooling towers using PathShield™ within a high efficiency side-stream filter has been documented.

A Greener, Safer and More Energy Efficient Antifreeze

ACTA Technology Inc.

Ethylene glycol, the main ingredient in antifreeze, smells and tastes sweet, attracting both children and pets to consume it. Ethylene glycol should not be confused with propylene glycol, a common food additive. Drinking ethylene glycol antifreeze will cause heart and breathing difficulties, kidney failure, brain damage, and even death. The major cause of toxicity is not the ethylene glycol antifreeze itself but its metabolites. The American Association of Poison Control Centers reported that there were 5,784 poisonings due to ethylene glycol antifreeze in 2012. There were 431 reported cases of children under the age of 5 years old and some of these cases were fatal.

ACTA's product improves the heat transfer capability of propylene glycol and is 58 percent better than ethylene glycol antifreeze in a circulating cooling system. Therefore, heat transfer performance and cost should no longer be reasons to use the potential lethal ethylene glycol antifreeze.

ACTA's additive to propylene glycol antifreeze can reduce dependence on foreign oil and reduce greenhouse gas emissions because of improved energy efficiency. ACTA's product covers a greener and non-toxic chemical.

Consumer Viable and Environmentally Friendly Solvent Replacements Developed From Food Grade Compounds

The BODYGUARD is a new, water-based and environmentally friendly, multi-surface treating emulsion developed to replace solvents, degreasing agents, and cleaning agents that use chlorofluorocarbons, specifically methylchloroform, CFC-13, and HCFC-225. The BODYGUARD uses cavitation, capillary attraction, and encapsulation to protect and clean surfaces from bonding materials such as epoxies, frozen loads, wet soils, clays, wet concrete, ice, asphalt, and biofouling. The patented formula controls surfaces and creates a bridge across the millions of micropores on surfaces that allow bonding.

In 2013, Bay State Tech, LLC completed its 12-month field testing of the BODYGUARD and secured manufacturing of the product. In 2014, Bay State Tech, LLC began responding to procurement opportunities from different municipalities across the United States. The BODYGUARD is a USDA certified Bio-Preferred product and tested to be 96 percent bio-based. The technology is a combination of water with food grade additives including a boron compound, a gelling compound, and an inorganic alkali compound.

Novel, Effective, Safe Delivery System for Antimicrobial Agents Derived from Sustainable Vegetable Monoglycerides

Biopolysan[®] is a novel antimicrobial composition derived from coconut oil. The patented manufacturing process is a relatively low temperature, single vessel reaction wherein monoglycerides are heated in the presence of a polyhydric alcohol and an alkaline catalyst. The result of processing is a liquid crystal mixture of glycerol and propylene glycol esters and salts thereof with drastically improved solubility, stability and efficacy. Biopolysan[®] is composed of generally recognized as safe (GRAS) food-grade ingredients. The active ingredient, glyceryl laurate, is derived from coconut oil, a renewable source. There is no waste stream and no harmful byproducts are produced by the process. Biopolysan[®] has applications in numerous industrial and medical settings including as a preservative and other anti-microbial applications.

Commercialization of Biopolysan[®] as a multifunctional ingredient for use in various formulations began in 2012. The benefits to the formulator are many, and include green preservation, greener chemistry, emolliency, improved penetration and skin feel as well as cost savings and simplification of the manufacturing process when Biopolysan[®] replaces a plurality of ingredients in some products. Current products on the market formulated with Biopolysan[®] include both animal and human products. Once Biopolysan[®] 120 (Copperhead's standard Biopolysan[®] formulation) receives its FIFRA registration, commercialization of Biopolysan[®] as a preservative is expected to replace a portion of the annual 40,000 metric ton traditional preservative market.

Naturama—Oil Surfactant, Green Degreaser, and Cleaner

Naturama is a naturally-derived, plant-based feedstock that is a water soluble solution utilized in an array of industries to remove grease and clean surfaces, without leaving the harmful environmental impact evidenced in other comparable products. The benefits of Naturama are extensive. It is 100 percent biodegradable, non-enzyme-based, non-toxic, and non-ionic. It is hypo-allergenic, non-caustic, and non-flammable.

Other industries' products contain toluene, tetrachloroethylene, hexane, heptanes, and other toxic chemicals that pose extreme fire hazards as well as both short- and long-term health hazards. Additionally, the cost of these competitor products extend beyond the product to regulatory compliance, training, protective gear, environmental controls, waste management services, and employee cost. With Naturama, the oil molecules quickly degrade through a much expedited photosynthesis process ranging from minutes to a few weeks.

The primary industrial applications targeted for Naturama are automotive and food service. Specifically, degreasing and cleaning of automotive parts and cleaning facilities. Significant opportunities have been identified in manufacturing, drilling, marine, and even household applications.

When compared to other toxic products, Naturama saves a tremendous amount of energy because it does not require a heat source when used. Being non-toxic, employee safety is not compromised, and no special storage is required. The volume of material needed is reduced to very small quantities. The waste of particulate matter, after filtration, is the only hazardous material to be disposed of, reducing the waste stream. Naturama is not hazardous in its initial component, nor in its life cycle after filtration. Naturama can be used completely during its life as a cleaner/degreaser in various applications and industries.

Cooling Tower Water Conservation & Chemical Treatment Elimination

Properly engineered electrolytic extraction of calcium carbonate from recirculating cooling water has successfully controlled deposit formation on heat exchange and other surfaces in practical systems such as industrial and HVAC cooling tower systems. Electrolysis of ionic-rich water produces exploitable *in situ* chemistry requiring no external chemical reagent other than electricity. A *Green Machine* consists of a series of steel tubes that are made the cathodic element of an electrolytic cell where water is reduced to form molecular hydrogen and hydroxide ion, and calcium carbonate is subsequently made to accumulate. Centered in each tube typically is a titanium rod coated with a mixture of ruthenium and iridium oxides, which make the anode of the electrolytic cell. The common name for an anode of this type is “dimensionally stable anode,” or DSA. It is the coating of the anode that is critical in driving the oxidation of water to produce molecular oxygen, hydrogen ion, and higher oxygen species such as hydroxyl free radical and ozone. DSA technology allows for the efficient splitting of water at a low practical voltage potential above that theoretically required, the difference being termed “overpotential.” DSAs have been responsible for past Green Machine success. Supplementing DSAs with anodes coated with boron-doped, ultrananocrystalline diamond (BD-UNCD) now allows not only control over troublesome calcium carbonate deposition, but more efficient *in situ* chlorine formation and degradation of organic contaminants. Microbiological control in cooling water is significantly more efficient.

High Performance Solvent-Free Coating Technology

Corrosion is a tremendous problem and cost to society, with a staggering annual cost of \$400 billion in the United States. Many primers and paints used to coat metal surfaces for corrosion resistance and decoration pose environmental hazards from cradle to grave. Conventional epoxy-based coatings commonly contain corrosive components, hazardous air pollutants (HAPs), volatile organic compounds (VOCs), and other solvents, and often contain chromium compounds. Urethane-based paints contain isocyanates and often contain HAPs, VOCs, and other solvents. Because isocyanates are strong irritants to mucous membranes, they can sensitize exposed individuals, in some cases causing severe asthma attacks. The hexavalent form of chromium is carcinogenic, particularly for lung cancer.

Light Curable Coatings has developed pollution-free coating technology for high performance protection of industrial and aerospace surfaces, including corrosion resistance, solvent resistance, and weathering resistance. Light Curable Coatings technology also provides the advantages of efficiency and economy, with fast cure under an ultraviolet (UV) light and with improved properties with much less material usage than conventional materials. The green chemistry of Light Curable Coatings does away with chromium compounds, isocyanates, and other HAPs,

**H-O-H Water
Technology, Inc.**

**Light Curable
Coatings**

solvents, and VOCs completely, producing high-performance, corrosion-resistant, solvent-free technology without using any toxic chemicals. Field application and fast UV cure of Light Curable Coatings technology has been demonstrated with good performance on large structures at temperatures as low as 34°F. Customer studies show savings of over 90 percent in the time required for painting operations for maintenance activities and factory processes.

Light Curable Coatings technology is a green alternative to current systems that contain toxic components, and provides a significant positive societal impact in terms of a better quality of life for industrial workers and for citizens through safer workplaces and a cleaner environment.

AirCarbon: Carbon-Negative Plastic Made from Greenhouse Gas

Newlight Technologies has developed a carbon sequestration technology that uses air and greenhouse gas emissions to produce a plastic material called AirCarbon. AirCarbon has been independently verified by Trucost and NSF Sustainability as a carbon-negative material, and is being used to directly replace oil-based plastics in a wide range of market segments. Based on Newlight's high yield biocatalyst breakthrough, AirCarbon can be produced for significantly less than the cost to produce oil-based plastics, representing a market-driven solution to reducing greenhouse gas emissions.

Founded in 2003 out of Princeton University and Northwestern University, the founding principle of Newlight was that climate change can be solved if carbon emissions are used as a resource to produce products that out-compete oil-based products on price and performance. After nearly a decade of research, Newlight achieved a breakthrough in the company's greenhouse gas conversion technology that increased the yield of the process by over nine times relative to previous efforts, a breakthrough that fundamentally shifted the economics of greenhouse gas sequestration. Today, Newlight is able to use that technology to harness carbon emissions as a resource to produce plastics for significantly less than the cost to produce plastics from oil.

In 2012, nine years after the company's founding, Newlight began selling AirCarbon for the first time, and by the end of 2012, had generated executed letters of intent to purchase AirCarbon in excess of 12.5 million pounds. In August 2013, Newlight scaled up the AirCarbon production technology to commercial scale, using air and carbon emissions from an agricultural operation to manufacture AirCarbon thermoplastic. In November 2013, Newlight launched the world's first carbon-negative furniture made with AirCarbon to market. Today, Newlight is working with over 25 partners in nine market segments to use AirCarbon to replace oil-based plastics.

Disruptive 1,1-Disubstituted Alkene (1,1-DA) Green Chemistry Platform, Step Change in Manufacturing: Breakthrough High Performance, Energy Efficient, Sustainable and Green Polymer Platform to Transform Industrial Manufacturing

Sirrus advances manufacturing technology through chemistry relating to the synthesis, stabilization, activation and formulation of a unique and reactive class of monomers commonly known as 1,1-DAs. These monomers, their derivatives and resulting polymer platforms provide the foundation for meeting customers' needs through game-changing technology.

**Newlight
Technologies, LLC**

Sirrus, Inc.

Specifically, Sirrus is advancing chemistry relating to the isolation, stabilization, activation, and formulation of 1,1-DAs. These monomers, their derivatives, and resulting polymers provide fast cure speeds at ambient temperatures to significantly reduce cycle times, increase throughput, reduce energy costs, and enable new material selection in a broad range of customer and consumer applications, including auto, electronics, packaging, and hygiene.

Moreover, Sirrus' technology enables improved features such as increased temperature, water, environmental, and solvent resistance in downstream products. Sirrus' green chemistry platform reduces pollution at its source by minimizing and eliminating the hazards of chemical feedstocks, reagents, solvents, and products.

1,1-DAs are molecules that embody a platform with a wide variety of substituents or side-chains. The overall chemistry and behavior of 1,1-DAs are analogous to cyanoacrylates (super glue); e.g., both cure anionically. However, 1,1-DAs possess superior environmental resistance for enhanced product application compared to traditional cyanoacrylates. This chemistry also suggests potential synthesis of monomers specifically designed for a given functionality; e.g., adhesives, inks, sealants, stains, coatings, etc. Similar compounds have been investigated since 1886 without notable synthetic improvement. Limited in-depth understanding of system stabilization and inherent monomer reactivity precluded chemists from obtaining sufficient yields needed for commercialization. Sirrus' platform provides variability and derivitized resin development that translate to appealing features and benefits; e.g., high speed and zero-energy polymerization, tailored solvent and thermal resistance, and increased product life.

CIRKIL Biopesticide

Pesticides are critical to society, increasing agricultural output, managing disease, and enhancing human comfort. Despite these benefits, Conventional Chemical Pesticides (CCPs) are under increasing scrutiny. For years, CCP producers have created small-molecule pesticides, delivering efficacy primarily through toxicity. Regrettably, these pesticides can be toxic to target and non-target pests, humans, and other animals. Insects also develop resistance to CPPS and CPPs typically biodegrade slowly becoming persistent in the environment. Put simply, CPPs are important but indiscriminately toxic, are easily "outsmarted" by the target insect, and persist in the environment. The conventional approach to deal with these challenges has been to "double-down" and create more synthetic pesticides.

Terramera has a significantly different approach. Rather than creating novel molecules, the company has created a novel, patent pending formulation technology that stabilizes and potentiates the natural efficacy of plant bioactives. Terramera has shown that plant biochemicals are effectively delivered into the insect's organism as a result of this technology, enabling development of plant-based biopesticides that perform as well or better than CCPs.

Terramera has successfully commercialized a bio-pesticide targeting bed bugs with this technology potentiating cold pressed neem oil to deliver superior efficacy to CCPs, in a minimally toxic formula. Terramera is extending this technology into agriculture developing novel products using botanical bioactives to treat insects, plant parasites, and fungi with field trials in progress. By substituting with Terramera, a single large strawberry grower in California could annually displace 540,000 pounds of methyl bromide/chloropicrin, a CCP being phased out in the United States.

Terramera Inc.

Entries from Industry and Government

SAFEN: A Low Cost Nematicide and Fungicide That is Generally Regarded as Safe by the FDA, Which Biodegrades into Two Naturally Occurring Substances, with No Lasting Detrimental Effects to Air, Soil, and Water

The nominated technology is for the production and use of SAFEN, a green chemical nematicide and fungicide that is environmentally friendly to air, soil, and water. The Montreal convention emphasized the need for pesticides which were environmentally friendly and eliminated the use of methyl bromide, an ozone depleting agent commonly used worldwide. SAFEN represents a green alternative to methyl bromide. SAFEN's components are made from low cost raw materials. Its primary component ethyl formate is made from ethanol, a renewable resource. SAFEN's simple molecules biodegrade into naturally occurring substances after effective use. SAFEN was applied to plots of up to 4 hectares with the capability of surface spraying or drip feeding to enable studies of complexities associated with different field operations. The analytical services of University of California-Davis, the University of Guanajuato, and Cinvestav were essential to the study together with attendant advice and field operations.

The eVOLV™ System, a Clean, Sustainable Solution to Electronic Waste

The eVOLV system was created to help solve the global issue of electronic waste (e-waste). While laws in developed nations have been pushing to regulate or eliminate dirty, harmful e-cycling practices and scrap piling, underdeveloped nations are seeing their lands being used as dumping sites. These sites host opportunities for people, including children, to use dangerous open burning techniques and toxic chemicals to extract metals for resale. While these conditions are deplorable, the piles themselves are growing and are polluting the soil and groundwater.

A United Nations report states that e-waste will grow by one-third by the year 2017 to total about 65.5 million metric tons. According to the report, the United States produced 9.4 million metric tons in 2012—the most of any country. In all, e-waste is the fastest-growing municipal waste stream in the world.

The eVOLV process is the first of its kind to safely reclaim base and precious metals at a large scale with a 98 percent recovery rate and virtually zero waste. The system consists of three process tools and a series of chemistries. It operates at or near room temperature and uses very little energy. It processes printed wiring boards, cell phones, and integrated circuits, or computer chips. Traditional shredding or grinding of boards, which leads to the loss of precious metals and/or the formation of dangerous contaminants, is eliminated. The chemistries are engineered for selectivity to dissolve different metals for easy recovery. Each chemistry was designed using the 12 Principles of Green Chemistry and is less toxic than common orange juice. In addition, each chemistry – and all process water – can be infinitely reused, generating no waste. All metals recovered are at a purity of 98 percent or better and can be re-inserted into manufacturing processes.

**Acid-Amine
Technologies, Inc.
(AAT)**

**Advanced
Technology
Materials, Inc.
(ATMI), an Entegris
Company**

Improved Performance and HSE Profile of a Novel Stimulation Fluid for Oil and Natural Gas Wells

Well stimulation is a process to improve oil or gas well productivity as the well's output naturally declines. Stimulation typically involves the injection of hydrochloric acid (HCl) or hydrofluoric acid (HF) based fluids at high pressure into the well. These corrosive acids dissolve portions of the rock near the well bore and allow more oil or gas to freely flow. While stimulation can significantly improve the productivity of a well, safely handling these corrosive acids is a significant challenge – e.g., HF is a contact poison. Additionally, additives needed to mitigate the corrosive impact of HCl further aggravate the safe handling and environmental impact due to these additives' poor ecotoxicological profiles. Wells at high temperature and pressure require a greater number and concentration of these additives, further emphasizing the need for both safe handling and ecotoxicological profiles of the treatments. As wells trend toward off-shore with higher temperatures and pressures, there are greater health, safety and environmental considerations and safer stimulation fluids are desired.

Recent lab studies and field applications with a new stimulation fluid based on the chelating agent GLutamic Diacetic Acid (GLDA) has shown that GLDA can improve oil and gas flow in carbonate and sandstone petroleum reservoirs. Even at high temperature and pressure, additives are not needed with GLDA to prevent corrosion of carbon steel or chrome-based well pipes. Contrary to conventional stimulation fluids used in the industry, GLDA is a biodegradable, non-toxic and non-hazardous chemical. GLDA was recently recognized by EPA's Design for the Environment (DfE) program as a safer chemical ingredient and is certified as 58 percent bio-based by the USDA's Bio-Preferred Procurement Program. The successful application of GLDA in four high temperature gas wells in the Gulf of Mexico resulted in a doubling of production using this safe and environmentally friendly stimulation fluid based on GLDA.

Archroma

Earthcolors Technology

Nowadays, all raw materials currently used for the production of textile dyestuff at commercial scale are derived from petroleum via a complex process of oil extraction, refining, and synthesis. Archroma is using a key raw material derived from biomass to produce soluble dyestuffs that are capable of dyeing cellulosic fibers such as cotton, viscose, paper, and Tencel with high strength and color fastness properties. For this purpose, the term "biomass" is defined as the residual product obtained from the usual human crop activities in agricultural and forestry sectors.

Archroma R&D has been working for the past five years on the technology resulting in two patents: EP 2 527 407 (WO 2012163498) & EP2546310 (WO 2013007358) (patent pending). Abundant, globally available, and renewable, the different agriculture crop waste is directly used as raw material and 100 percent transformed to final dyestuffs. A range of six dyes have been developed at this stage: two dyes are synthesized using 100 percent biomass while the other four dyes are 90 percent biomass + 10 percent petrol due to the limitation of color range when using 100 percent biomass. The first bulk batches were produced in 2013, and the full range will be available at the end of May 2014. The recent implementation of these dyes showed equal performance to the conventional dyes using standard and the best available wet processing techniques.

There are two main benefits for the new technology:

- The massive reduction of the use of aromatic toxic compounds and of the generation of CO₂ in comparison with present known procedures of the petroleum aromatic chemistry. The technology also eliminates the high environmental risks of oil extraction and further processing; and
- The use of waste from another industry (circular economy).

SYLVAROAD™ RP 1000 Performance Additive: A Sustainable, Pine-Based Additive to Enable High Re-Use of Reclaimed Asphalt Pavement

In January 2014, Arizona Chemical Company, LLC commercially launched the SYLVAROAD™ RP 1000 performance additive for asphalt pavement. Arizona Chemical produces this new, bio-based additive from pine trees using a green production process. This product enables Arizona Chemical's customers in the paving industry to incorporate significantly higher percentages of reclaimed asphalt pavement in their hot mix asphalt, thus preventing waste and reducing the use of virgin materials such as aggregate and binder while still maintaining the specified performance of the pavement. Enabling higher aged pavement recycling not only saves virgin raw materials, but also makes economic sense due to reduced raw material costs. Arizona Chemical's technology upgrades a byproduct from the paper pulping industry into a value-added specialty chemical for improving infrastructure in the United States.

Boegel Surface Activation Technology Suite

The Boegel Surface Activation Technology Suite is an environmentally friendly alternative to hazardous surface preparation methods for metallic structures. Invented by a team of Boeing chemists, the process is based on sol-gel condensation polymerization and utilizes tailored molecules which link metals to resins by covalently bonding with both surfaces and resins in order to create a strong, durable chemical bond between critical layers. The Boegel Suite includes a number of related sol-gel formulations that can be used on aluminum, titanium, stainless steel, nickel, tungsten, and many other alloys. It has been leveraged for painting, bonding, and sealing surface preparations across the Boeing Enterprise, including commercial, military, and space vehicles. Hazardous materials that Boegel successfully replaces include acidic and hexavalent chromium – containing conversion coatings such as Alodine, Phosphate Fluoride, Pasajel 105 and 107, and Chromic Acid Anodizing. In addition to ridding Boeing manufacturing processes of many major environmental concerns, Boegel has also simplified work and increased efficiencies in numerous paint operations, increased performance and durability, reduced chemical inventories, and has become a key enabling technology for metal bonding and sealing, with improved adhesion and durability performance.

Cylinderized Phosphine as Safer, More Environmentally Friendly Alternatives to Traditional Stored Product Fumigants

Cytec Industries Inc. has developed and commercialized technology for the stored product fumigation market. Traditional fumigants such as methyl bromide and metallic phosphides have significant safety and environmental shortcomings in their use, application, and disposal. Methyl bromide is an ozone depleting chemical and is partially being phased out under the Montreal Protocol. Metallic phosphide suffers from worker safety and environmental issues created by the residues. Cytec's cylinderized phosphine products, ECO₂FUME (a non-flammable blend of two percent phosphine and 98 percent CO₂) and VAPORPH₃OS® (phosphine fumigant), offer inherently safer alternatives as they involve less worker exposure and do not significantly impact the environment. The use of Cytec's cylinderized products for fumigations in 24 hours allows for greatly expanded use of these products as drop-in replacements for methyl bromide and they are now being used commercially in a number of 24-hour applications across the United States. To date, this technology has resulted in an annual global waste reduction of 900,000 pounds of solid chemical residue and 600,000 aluminum flasks. In addition, this technology has annually eliminated 620,000 pounds of methyl bromide use and 1,500,000 pounds of metallic phosphide use globally.

**Arizona Chemical
Company, LLC**

**The Boeing
Company; Boeing
Research &
Technology**

**Cytec Industries
Inc.**

BETAMATE™ and BETAFORCE™ Structural Adhesives Improve Automotive Fuel Efficiency and Emissions

Environmental impact is a central consideration in vehicle development. Since the Kyoto Protocol, more countries and industries have committed to reducing their greenhouse gas footprint. In parallel, fuel economy regulations are becoming more stringent and increasing attention is being paid to vehicle safety. With strong growth in vehicle production projected in the coming years and a shift of vehicle ownership and road congestion towards emerging markets, these sustainability aspects are commanding ever increasing attention globally. Reducing vehicle weight by incorporating lightweight materials has become a key route to improving fuel economy and reducing greenhouse gas emissions. Automakers today face the additional challenge of producing lightweight vehicles that also meet consumer expectations and government standards for safety, comfort, and performance. One of the key requirements for successfully implementing lightweight materials in vehicles is the selection of effective joining technologies, especially for dissimilar, lightweight substrates such as high strength steel, aluminum, magnesium, and composites. BETAMATE™ and BETAFORCE™ structural adhesives enable joining of lightweight and dissimilar materials, where traditional joining techniques such as welding and riveting have limited applicability. These structural adhesives also increase load bearing capability, static and dynamic stiffness, driving and handling characteristics, and optimized ride, leading to improved safety and crash behavior, longer vehicle life span, and improved durability.

As a result, BETAMATE™ and BETAFORCE™ structural adhesives represent a breakthrough solution addressing energy and climate change, as well as safety and health – two pressing world challenges. For example, structural adhesives have enabled 10 kg weight savings per vehicle, which translates to an estimated 1.8MM gallons of fuel saved and 16.3 MM kg CO₂ avoidance for a typical 100,000 vehicle build program over the five year life of program.

Dow Polymeric Flame Retardant

Polystyrene (PS) foam is widely used as insulation in the building and construction market, thus it must meet rigorous building code and fire safety performance standards. The Dow Polymeric Flame Retardant is an innovative technology that is essential for the preservation of the PS foam insulation industry, which annually produces foam that avoids service lifetime totals of 1.7 gigatons of CO₂ equivalent greenhouse gases. With impending global regulation and restriction of hexabromocyclododecane (HBCD), the incumbent flame retardant, the PS foam industry needed an alternative flame retardant that could provide a significantly improved environmental, health, and safety (EH&S) profile while cost-effectively matching HBCD's fire safety performance and foam properties and processing performance. The Dow Polymeric Flame Retardant was scientifically engineered to achieve this set of requirements by using a combination of chemistry, polymer science, process technology, application know-how, and EH&S expertise. Success was achieved by designing a flame retardant polymer, which is inherently more sustainable than small molecule flame retardants, with a controlled stability to survive under foam processing conditions and specific chemistry designed to release the active flame retardant agent under fire conditions. The Dow Polymeric Flame Retardant has met the challenge, leading the global PS foam industry to select it as the new standard flame retardant. This breakthrough technology is enabling the industry to meet increasingly stringent building and construction energy efficiency codes while continuing to meet fire safety performance standards.

FORMASHIELD™ Formaldehyde Abatement Technology

FORMASHIELD™ is a breakthrough polymeric binder technology that abates gaseous formaldehyde from the surrounding ambient environment. FORMASHIELD™ Binders incorporate novel technology that imparts smart functionality to interior architectural paints. The walls of homes and buildings painted with architectural paints incorporating FORMASHIELD™ are well positioned to abate a carcinogenic pollutant like formaldehyde thereby improving indoor air quality for occupants.

According to the United States Green Building Council, buildings in the United States consume 36 percent of the total energy usage and generate 30 percent of all waste. The green movement is motivated by the desire to conserve energy usage and reduce natural resources utilized by this market. Consequently, main building codes used in the United States have made energy codes the priority which increases “occupant risk of exposures to indoor generated contaminants.” It is believed that this trend of reducing ventilation and sealing buildings has led to indoor air containing 2-5 times the levels of many outdoor pollutants.

FORMASHIELD™ Binder Technology seeks to address the growing concern over the most carcinogenic pollutants by enabling an indoor house paint to ameliorate the health and wellness of occupants in buildings. Additionally, FORMASHIELD™ Polymers help facilitate a more robust paint film with improved performance properties. This is achieved by means of reactive cross-linking technology that enhances adhesion and overall paint durability while further improving the sustainability profile. Commercial paints containing FORMASHIELD™ Binders are now sold in the United States and are expanding the credibility of green movement products. It is expected that FORMASHIELD™ Technology will become a standard feature in common commercial paints in the United States whereby formaldehyde reductions provide improved health and wellness benefits for residents in homes and offices.

SOLDERON™ BP Lead-free Solder Plating Chemistry

SOLDERON BP products eliminate lead in advanced semiconductor packaging applications, such as solder bumping and pillar capping. SOLDERON BP tin-silver plating chemistries provide electrical and mechanical connections that are equivalent to industry-standard lead-based solder.

Bumping is an advanced wafer level process technology where solder “bumps” or “balls” are formed during wafer processing. These bumps, formed before the wafer is diced into individual integrated circuits, will ultimately electrically and mechanically connect the die and the substrate together into a single package. Solder bumps are deposited using electroplating, and the process must produce very uniform bumps in terms of size and composition. Electronics manufacturers use them to join semiconductors together, to a substrate, or directly to a circuit board in flip chip or controlled collapse chip connection (C4) packaging.

Solder is a critical element in electronics and must provide connections that are durable and reliable. Tin-lead is an ideal solder because it is malleable and has a low melting point. It has been used for decades and much of the electronics infrastructure was designed around it. Tin is combined with lead to provide greater tensile and shear strength and higher conductivity. The combination resulted in an ideal balance of electrical and thermal conductivity and cost. Regulations limiting lead have been enacted due to its high toxicity, especially when electronics reach end of life and are deposited in landfills or recycled.

Materials suppliers have spent most of a decade searching for a lead-free chemistry to match the reliability of tin-lead solders and tin-silver has emerged as the most viable solution. Technology is what differentiates Dow's SOLDERON BP tin-silver – patented additives that provide manufacturers with superior performance and low cost of ownership, which will drive wider adoption of lead-free solders in electronics.

Sustainable Microbial Control Treatments for Hydraulic Fracturing

The sustainability of hydraulic fracturing operations is of vital concern to the United States. Chemistry is a critical factor in the success of hydraulic fracturing, enabling technology breakthroughs and allowing energy producers to maximize well performance and hydrocarbon quality. To successfully advance sustainable hydraulic fracturing, enabling chemistries must be designed to not only improve performance, but also improve the safety and environmental impact of the fracturing operation.

The use of microbial control agents is critical for sustainable operations, ensuring the minimization of biogenic hydrogen sulfide and acid production. Hydrogen sulfide causes corrosion, hydrocarbon souring, and, most critically, is a human exposure health concern. Therefore, effective microbial control is required to ensure worker and public safety, asset integrity, and to preserve the quality of hydrocarbons, resulting in reductions in overall drilling, re-work, and re-fracturing.

The safety and environmental impact of chemicals used in hydraulic fracturing, including microbial control agents, are often of critical concern to the industry and public. To date, attempts to introduce chemistries or technologies perceived as less harmful have not proven to be effective. Therefore, the Dow Chemical Company purposely and systematically designed and developed a microbial control program that enables the advancement of sustainable hydraulic fracturing operations. This program is based on innovative, sustainable chemistry to dramatically reduce the environmental impact of current technologies, ensure worker safety, and improve overall effectiveness of microbial control. The new patent-pending treatment, utilizing glutaraldehyde and 4,4-dimethyloxazolidine in synergistic combination, provides enhanced microbial control at lower dosage with excellent biodegradability and low environmental toxicity to offer advanced treatment of fractured reservoirs. Proven performance in lab and field testing has been validated through rapid commercial adoption of this chemistry. The implementation of this technology enables improved asset integrity and improved quality of hydrocarbon production, thus reducing the overall environmental footprint of hydraulic fracturing.

G-Clean® Line of Green Cleaning Products Designed to Clean Hydrocarbons Safely and Effectively

In all industries that deal with cleaning hydrocarbons, maintaining profitability while ensuring safety of people and the environment are top priorities. Increasing regulations, media attention, public perspective, fears of climate change, and water and energy conservation are only adding to the importance of staying ahead of the curve on how companies approach production and maintenance.

G-Clean® combines domestically sourced renewable feedstocks with proprietary technologies molded around the multiple green ideologies including biodegradable, recyclable, renewable, and environmentally safe as well as being commercially viable. G-Clean® offers companies effective and environmentally safe cleaning products that substantially lower their carbon footprint but ultimately offers companies a lower cost of cleanups or an increase in revenues (sometimes both).

Each of the products in the G-Clean® product line is based on proprietary colloidal chemistry processes at the nanoscale. Food grade ingredients, such as soy, corn, grain, potatoes, and trees are processed to form a particle called a micelle. Micelles work to breakdown long chain hydrocarbon bonds in fats, oils, and grease and hold them in suspension when mixed with water. Ultimately, the wash off is completely biodegraded by bacteria resident in the crude oil.

G-Clean[®], developed by Inventek, all have “zero” ratings according to National Fire Protection Association: zero reactivity, zero flammability, zero health hazard, and no special hazards. These 100 percent biodegradable and non-toxic products can be used instead of solvents and other hazardous materials like diesel that are commonplace when cleaning oil. G-Clean[®] cleaners in their organic form are safe for the skin, the air, water, animals, and ground.

According to studies done in the oilfields of E&B Natural Resources and other oil companies, G-Clean[®] has proven to reduce water needed to clean a typical storage tank by over 50 percent. Therefore, waste disposal is also reduced substantially. G-Clean[®] is listed on the EPA National Contingency Plan list and was highlighted as being successful in the BP Deepwater Horizon cleanup. Other industry validations have come from the Oil & Gas Awards, the Louisiana Gulf Coast Oil Exposition “spotlight on new technology award,” as well as winning a “Pollution Prevention” award from Kern County (California) Green Awards.

Eastman Omnia[™] Solvent – Changing the Chemistry of Clean. New, Safe, Highly Effective Solvent for Cleaning Applications

To enable development of cleaners that are safer for humans and the environment, cleaning product formulators need safer ingredients. It is rare, however, for a solvent used in cleaning products to be safe for people, the environment, and surfaces being cleaned - and still enable efficient cleaning and compliance with air quality requirements. With this in mind, Eastman developed a solvent offering an exceptional combination of safety, performance, and value throughout the industry - from formulators to cleaning staff to customers.

With thousands of molecules under consideration, Eastman narrowed the solvent universe using computer modeling based on human health and environmental safety criteria and specific physical/chemical properties to predict good performance. The minimum safety criteria for candidates were based on EPA’s DfE Solvent Screen.

The final candidate, Eastman Omnia[™] solvent, has an excellent safety profile, as evidenced by meeting DfE’s Solvent Screen criteria, listing in GreenBlue’s CleanGredients[®] database with no restrictions, and inclusion in DfE’s Safer Chemical Ingredients List with highest rating. Performance testing demonstrates Omnia’s excellent cleaning ability: neutral-pH formulations with Omnia[™] were highly effective at cleaning and outperformed competitive alternatives.

Prior to making Omnia[™] commercially available, Eastman satisfied requirements for TSCA Inventory listing and began its first commercial manufacture of Omnia[™] in October 2013. Shortly thereafter, the first sales of Eastman Omnia[™] solvent were made.

Omnia[™] has a unique chemistry that offers an exceptional combination of performance, safety, and value. Effective in a variety of light- and heavy-duty cleaners formulated at neutral pH, Omnia[™] works on a wide range of soils—from greasy dirt and tar to soap scum. The combination of powerful cleaning and excellent safety profile makes it an excellent choice for formulators challenged to comply with increasingly stringent safety, regulatory, and market demands. Eastman Omnia[™] solvent is changing the chemistry of clean.

Environmentally Preferable Biocide for Water Treatment in Hydraulic Fracturing

In the past years, unconventional oil and natural gas production has steadily increased in the United States. Driven by the development of new technologies such as horizontal drilling and hydraulic fracturing, shale gas has led to major increases in reserves of oil and natural gas. During hydraulic fracturing, water and chemicals are injected, at high pressure, into the geologic formation

**Eastman Chemical
Company**

Ecolab

to increase the fractures in the rock layers and allow hydrocarbons to flow. Because large quantities of water are used during this process, the need for water treatment and reuse has become critical. Water treatment prevents the introduction of microorganisms in the formation, which can result in problems such as reservoir souring, biofouling and microbiologically induced corrosion. Additionally, facilitating the reuse of produced water through cleaning reduces the constant demand for fresh water. Based upon these concerns, Ecolab has developed an improved formulation of the oxidizing biocide peracetic acid (PAA). This chemistry shows superior results when compared to other conventional biocides (e.g., glutaraldehyde, chlorine dioxide), including faster and persistent microbial kill, water cleanup properties, solids dropout, and less corrosion. Importantly, PAA had no adverse effects on other chemistries present in the hydraulic fracturing fluids, such as friction reducers and scale inhibitors. Ecolab's peracetic acid biocide is an environmentally preferable chemistry as it breaks down into innocuous components, water and acetic acid (e.g., vinegar).

A concern associated with hydraulic fracturing is impacts on surface water quality. Ecolab's EC6734A peracetic acid biocide enables the reuse of produced water brine, reducing fresh water draw. Use of this biocide facilitates safe, cost-effective, onsite water disposal by minimizing emissions, and reduces plugging by controlling biological growth and thus maintaining hydraulic conductivity. These benefits contribute significantly to better quality and management of surface waters.

Environmentally Responsible Spore Control Program through Effective Cleaning and Sanitizing of Heat Exchange Dairy Process Equipment

Explosive population growth, massive growth of technology, and accelerating change is occurring globally. For example; between 1960 and 2010, global population has increased two-fold, the economy seven-fold, food consumption three-fold, water use three-fold, and fossil fuel use four-fold. Food is one resource lost throughout the supply chain. The recent FAO (Food and Agricultural organization of the UN) study reports that roughly one third of food produced for human consumption is lost. This waste is compounded by lost resources (e.g., water and energy) associated with food production.

In this context, production methods such as Ecolab's novel spore control program that minimize water and energy requirements while producing safe high quality food that is free of spoilage-inducing contaminants is an important step forward. To meet current and future demands, food must be able to be efficiently processed without waste while leveraging renewable energy and working with a minimum amount of water that can be reused or recycled.

The Ecolab spore control program combines technologies described in two separate patents to solve a very difficult food and beverage manufacturing problem. This novel cleaning and sanitizing process employs environmentally responsible biocides that decompose to organic acids and water after reaction and dilution. Given this positive environmental profile, it is even more surprising that this product effectively kills thermophilic spores, which are among the most resistant living organisms. Commercialization of these patented technologies enhances food security by enabling products suitable for direct human consumption, increasing the value of the product, and bolstering the economic sustainability of producers in the United States.

Targeted Chemotherapy for Solid Tumor Cancer Treatment

Kadcyla® (INN: trastuzumab emtansine) is an antibody drug conjugate approved by the FDA for treatment for HER2-positive metastatic breast cancer patients who have received prior treatment with Herceptin® and a taxane chemotherapy. Antibody drug conjugates combine the targeting capabilities of antibodies with the potency of chemotherapy. Kadcyla®, specifically, links

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trastuzumab, a monoclonal antibody that binds to HER2-positive cancer cells, via a stable linker to DM1, an antimicrotubule agent that blocks cell growth by stopping cell division. In clinical studies, patients treated with Kadcyła[®] lived nearly six months longer and lived over 3 months longer without their cancer getting worse compared to the standard treatment. In addition, fewer patients who received this medication experienced severe (≥grade 3) adverse events. Environmental studies have shown that Kadcyła[®] is readily degradable (84 percent in 28 days). In wastewater treatment facilities, the antibody portion of the conjugate is readily degraded leaving the linker-DM1 (MCC-DM1) portion of the molecule. Ready and inherent biodegradation tests have shown that MCC-DM1 is not toxic to activated sludge bacteria nor does it bioaccumulate, thus Kadcyła[®] does not pose a pharmaceutical in the environment risk.

Kadcyła[®] has been shown to be less toxic to patients than the standard treatment (as defined by the number of adverse events experienced) because it delivers the chemotherapeutic agent directly to the cancer cells. Additionally, Kadcyła[®] is biodegradable and does not bioaccumulate. Antibody-drug conjugate technology generally has the potential to reduce the amount of toxic agents used in the clinic as these therapeutics provide a targeted alternative to systemic chemotherapy dosing.

Low Global Warming and Energy Efficient Polyurethane Foam Insulation Blowing Agent

Solstice[®] Liquid Blowing Agent (LBA) (1-chloro-3,3,3-trifluoropropene) has a Global Warming Potential (GWP) that is 1,000 times lower than the hydrofluorocarbons (HFCs) it is designed to replace, is non-flammable, non-toxic, non-ozone depleting, and classified by EPA as VOC exempt. Honeywell's extensive testing proves that Solstice[®] LBA is more environmentally friendly, safer, more energy efficient, and more cost-effective to implement compared to existing blowing agents such as cyclopentane and HFCs.

Solstice[®] LBA is being adopted globally in appliances, transport, and construction. It is currently being used in the United States, European Union, Japan, China, Korea, and India. Whirlpool started producing refrigerators with Solstice[®] LBA in 2013. Widespread use of Solstice[®] LBA to replace HFCs in polyurethane foam applications in the United States alone will result in a reduction of more than 18M tonnes per year of CO₂-equivalent; globally this number would exceed 67M tonnes according to a Honeywell internal analysis. This new product will not only help reduce global warming, but it will spur economic growth and job creation in the United States. The first plant will start production in Louisiana in May 2014, and Honeywell is currently working on a second, world-scale plant in the United States.

An Innovative Catalytic Intramolecular Asymmetric Reductive Amination of a Dialkyl Ketone Enables a Highly Efficient, Green Synthesis of Suvorexant (MK-4305)

A highly efficient and environmentally responsible synthesis of suvorexant has been discovered and demonstrated. Suvorexant is a new treatment for insomnia which is currently under review in a number of countries. The first scalable route to the molecule was based on a classical resolution, and used to prepare material for early drug development. Although this approach could have been the basis of a viable manufacturing process, it did not meet Merck's high green chemistry goals and hence Merck researchers decided to totally revise the synthesis. A highly selective and previously unprecedented catalytic intramolecular reductive amination reaction of a dialkyl ketone with an alkyl amine was discovered and used to introduce the challenging stereocenter. Detailed kinetic studies led to understanding of the reaction mechanism and hence optimization of catalyst loading, yield, and enantiomeric excess. The fundamental knowledge gained from this work greatly expands the utility of the reductive amination, a ubiquitous transformation in fine chemical production, and can be applied to the large scale synthesis of other chiral molecules.

**Honeywell
International**

Merck & Co., Inc.

In addition, the entire synthesis of suvorexant was scrutinized with respect to amount and type of solvents and reagents used, number of operations and isolations, and process robustness. This allowed the complete removal of the undesirable solvent dichloromethane and led to a 56 percent reduction in the amount of waste produced by the process. The technology discovered, developed and implemented by Merck for the manufacture of suvorexant is an excellent example of scientific innovation resulting in significant benefits to the environment.

Bt Technology, Transforming Insect Control

Insect pest infestation of crop species have limited food production for centuries. Until the 1990s, chemical insecticides were the most advanced tools for insect control. However, they created significant challenges, including undesirable environmental consequences, toxic effects against non-target organisms, and often required repeated applications. The vision of biotechnology as a solution for these challenges became a reality in the mid-1990s.

Biotechnology means pesticide manufacturing and chemical pesticide applications are needed less frequently. Unlike traditional pesticide manufacturing, some *Bacillus thuringiensis* (*Bt* - a ubiquitous soil microbe) bacteria contain genes expressing proteins that naturally control insect pest species. Monsanto used biotechnology to take advantage of the characteristics of these toxins – Cry (crystal) proteins – combining this knowledge with plant molecular genetics to create plants that express specific toxins to control crop plant pests by producing the crystal protein through naturally occurring biological mechanisms within the plants. In addition to reducing the use of pesticides, the specificity of Cry proteins ensures only target organisms are affected, and avoids pesticide exposure of humans, animals, and non-target beneficial insects.

Bt technology continues to be applied across many plant varieties, increasing yields and reducing the need for chemical pesticides. All *Bt* traits in commercial use have been created through the use of Monsanto's patented synthetic *Bt* gene technology, and many of Monsanto's traits developed using this technology have been licensed to and sold by numerous seed companies. In 2013, three quarters of all corn and cotton grown in the United States included one or more *Bt* traits.

Farmers planting insect-resistant crops experience improved safety and health because of reduced pesticide use, and spending less time applying insecticides. This reduced number of applications mean fewer containers, less fuel and decreased aerial spraying, and reduced costs per acre farmed, all benefiting the environment while increasing yields and enhancing farmers' lives.

Evotherm[®] Warm Mix Asphalt Technology

Traditional hot mix asphalt paving is a significant source of greenhouse gas emissions. MWV Specialty Chemicals, a division of MeadWestvaco Corporation, developed Evotherm warm mix asphalt technology. Evotherm is a unique, bio-based surfactant that enhances the ability of asphalt mix to be produced at temperatures 60°- 90°F lower than conventional hot mix asphalt. This reduction in temperature enables plant energy savings of 55 percent, resulting in lower carbon dioxide (CO₂) and nitrogen oxide (NO_x) emissions. Since Evotherm was introduced to the marketplace in 2005, over 50 million tons have been used on United States roadways, creating a savings of 27 million gallons fuel and 605 million pounds of CO₂. The lower temperature asphalt mix also creates a safer and more pleasant work environment by reducing the temperature of the mix at the paving site to limit vapor and thermal worker exposure.

Evotherm technology, derived from renewable tall oil fatty acids and distilled tall oil, was developed by MWV Specialty Chemicals in Charleston, South Carolina as a part of the Innovation Strategy to support the transportation industry. The technology also allows for increased utilization of recycled materials. As states seek to maximize transportation funding dollars, utilizing recycled materials provides economical, high-performance roadways. Evotherm improves the workability recycled materials, allowing for up to 75 percent more recycled content.

Monsanto Company

MWV Specialty Chemicals, a Division of MeadWestvaco Corporation

Amended Silicates[®] HgX

Amended Silicates[®] HgX (AS-HgX) is a non-carbon mercury capture reagent that removes mercury from coal-fired power plant flue gas, enabling utilities to comply with the EPA's soon-to-be-implemented Mercury & Air Toxic Standards (MATS). This mineral-based product removes mercury via a chemical reaction, providing economic and environmental advantages unavailable with carbon-based products. AS-HgX is currently being used in 14 coal-fired power generation units.

AS-HgX consists of a bentonite substrate that is amended with a metal sulfide that acts as the reagent to capture mercury from coal-fire flue gas. A chemical reaction forms mercuric sulfide on the reaction sites of particle surfaces in flue gas. Mercuric sulfide is the most stable form of mercury, occurring naturally as the mineral metacinnabar. Mercuric sulfide is extremely insoluble and does not leach into the environment.

Prior to the availability of Amended Silicates, coal-fired power plants had little choice but to use carbon-based products (Powdered Activated Carbon – PAC) to remove mercury. However, PAC contaminates fly ash (a byproduct of burning coal), necessitating landfill burial of millions of tons of fly ash annually. AS-HgX does not contaminate fly ash thus preserving its resale value to concrete manufacturers, eliminating landfill disposal, and avoiding an estimated one million tons annually of CO₂ emissions related to Portland cement production.

AS-HgX removes mercury three times more efficiently than PAC products. Extensive testing demonstrated that compared to PAC products, AS-HgX provides a 25-50 percent cost savings, reduced operating expenses and consistent MATS compliance. AS-HgX is non-flammable, noncorrosive, and compatible with a power plant's existing injection equipment with few or no modifications.

The carbon footprint for producing AS-HgX is about 90 percent less than that created by PAC production (a potential reduction in CO₂ emissions of 175,000 metric tons per year if just 10 percent of the market used AS-HgX instead of PAC).

Polyethylene Terephthalate (PET) Derived Polymers for Coatings

PET is a polymer with a polyester backbone. This class of compounds relies upon a reversible reaction: the substitution at saturated carbonyl. This reaction is usually accomplished through elimination of a leaving group that is in most cases water or methanol for industrial production. This esterification in appropriate conditions can be reversed to go back to the starting raw material, with different methods existing to do so. For this green chemistry technology, glycolysis was chosen to reverse the esterification. Using an appropriate polyfunctional glycol, the polymer is broken down to lower molecular weight portions and, with appropriate stoichiometric conditions, is possible to leave a hydroxyl active functionality at the end. Those lower molecular weight fractions can further react with other acids or anhydrides to obtain a new polymer in which they represent part of the backbone mixing up physical-chemical properties with those of other raw material. In a process invented by PPG Industries, the final polymer is produced using the PET as starting raw material with a simple and compact process.

The polymer produced can have multiple characteristics depending on the raw materials and process chosen. A number of different polymers can be obtained from this process including: polyester resins, alkyd resins; polyester or alkyd acrylated resins; and urethane polymers. Many of these polymers are suitable for use in various coatings chemistries. Currently, the most significant use of this technology is in the production of a 2K polyurethane primer for use in automotive refinish coatings. The 2K polyurethane is produced by reaction of a hydroxyl functionalized polymer with a polyisocyanate to obtain a cross-linked film. While PPG is using the recycled-PET based polymer in a 2K polyurethane primer paint, there are many other potential uses of this technology within the coatings industry.

Cold-Water Enzyme: Reducing the Environmental Footprint of Residential Laundry through Low Temperature Cleaning

Each day, Americans do 123 million loads of laundry. They have become accustomed to a certain level of cleaning and ease in performing this essential everyday activity. And when it comes to stain removal, most choose to set their dials to warm or hot to ensure a quality clean. The research teams at DuPont have invented an entirely new enzyme which allows consumers to wash their clothes at significantly lower temperatures with dramatically improved performance. The enzyme helps reduce energy use by 50 percent with each load.

This superior enzyme technology, cold water protease, is available now in Tide Coldwater Clean. Both companies felt passionate about pursuing because success meant significant environmental benefits due to the sheer scale of use. Current laundry washing creates 40 million metric tons of emissions of carbon dioxide. If the loads were cleaned instead in cold water, the energy savings would reduce those emissions by 80 percent. In other words, that is the equivalent of taking 6.3 million cars from the road, based on annual United States emissions. Use of this cold-water protease has equivalent performance and stability compared to the traditional technology used. DuPont's Genencor scientists applied novel protein engineering methods to invent an optimal protease enzyme that at 60°F matches the cleaning performance of the previous incumbent generation product at 90°F. Joint commercialization of this breakthrough technology means it has the potential to become the number one selling engineered enzyme in the world – greening one of the most common household chores on a macro scale.

STEPOSOL® MET-10U: A Bio-Derived, Nonionic Surfactant Solution for Solvent Replacement: Source Reduction and Inherently Lower Health Hazards in Hard Surface Cleaning and Adhesive/Paint Removal

Highly toxic solvents and corrosive formulations represent a health hazard and environmental concern. There have been, for example, 14 recorded deaths since the year 2000 attributed to paint strippers formulated with methylene chloride, a suspected human carcinogen. Additionally, N-methyl pyrrolidone raises concerns regarding reproductive hazards. Stepan Company has recently introduced STEPOSOL® MET-10U, an efficient, effective, and low toxicity solution to these problems. This surfactant, developed through a joint effort with Elevance Renewable Sciences (ERS), realizes commercialization of ERS' novel bio-derived, unsaturated short-chain methyl ester to achieve the same level of adhesive and paint removal performance in 5 percent aqueous formulations as 100 percent solvent-based materials. The unsaturated ester raw material is produced from renewable feedstocks via Nobel-prize winning metathesis technology that generates 50 percent less greenhouse gases.

The performance of this groundbreaking surfactant stands in stark contrast to previously available green solvent options. The cleaning power of a solvent is often measured through its Kauri Butanol value. In external labs, STEPOSOL® MET-10U scored >1,000 on this scale while d-limonene, a weaker green alternative solvent, rated a 67. STEPOSOL® MET-10U is 75 percent renewable, non-VOC (boiling point = 297°C), non-flammable, less toxic, readily biodegradable, effective in aqueous solution at more neutral pH than current formulations, and cost-effective in use. The performance of STEPOSOL® MET-10U is attributable to its metathesis-enabled double bond, its derivatization as an amide, and its wide ranging formulation compatibility.

STEPOSOL® MET-10U is the first of a new generation of bio-derived, high-performance chemicals that Stepan Company and joint development partner ERS have brought to both commercial and consumer markets as an alternative to less sustainable and more hazardous chemicals. In this manner, Stepan is providing superior performance while also delivering source reduction and inherently lower hazards to workers, consumers, and the environment.

A Novel High Efficiency Process for the Manufacture of Highly Reactive Polyisobutylene (PIB) Using a Fixed Bed Solid State Catalyst Reactor System

Polyisobutylene (PIB) is an isobutylene polymer containing one double bond per polymer molecule. In high-reactive PIB, the double bond is at or near the end of the polymer chain making product more reactive. When the double bond is located at internal positions, PIB is less reactive, creating low-reactive PIB.

Traditional processes to make high-reactive PIB use a liquid polymerization catalyst. The catalyst is continually fed to the reactor and mixed with isobutylene monomer. The liquid catalyst is toxic, hazardous, and requires special handling systems and procedures to avoid exposure and vapor release. As the reaction mixture leaves the reactor, the catalyst must be immediately neutralized and separated. The separation process involves washing the neutralized catalyst complex from the reaction mixture with copious amounts of water to remove all catalyst residues. Trace amounts are corrosive to subsequent processing steps and detrimental to product quality and stability. Neutralized catalyst cannot be recycled. This process substantially increases plant capital investment, increases operating costs, and generates approximately as much wastewater as product.

Soltex's new process is based on a novel solid catalyst composition using a fixed bed reactor system. A solid catalyst, in the form of a bead or other convenient geometrical shapes and sizes, is packed into a tubular reactor to form a stationary, completely contained bed. Isobutylene monomer is fed to the reactor at a controlled rate and passes over the solid catalyst allowing polymerization reaction to occur. The polymer mixture exits the reactor at the same controlled rate. This reactor effluent contains no catalyst residues, therefore no subsequent catalyst separation or water wash is required.

The Soltex process, using this solid catalyst composition, produces high yields of high purity product through a simplified, highly efficient operation with substantially reduced capital investment, low operating and catalyst costs, and no waste generation.

Green Detergents for Industrial Laundries

Since 2005, Washing Systems made the commitment to develop washing chemistry for industrial laundries across the United States that would enable customers to improve their environmental profile and financial well-being. This endeavor began in 2007, through the company's voluntary phase out of nonylphenol ethoxylates (NPEs) in laundry detergents, a known endocrine disruptor and toxic chemical. Through diligently incorporating strict success criteria, consisting of formulating a more environmentally friendly detergent capable of reaching the same quality, chemical usage, and cost for the customer, Washing Systems efficaciously eliminated NPEs from the laundry formulations. In addition, the new formulations (industrial and two linen detergents) were developed without the addition of other harmful chemical of concern. From the projects inception, Washing Systems customers have reduced over 21.6 million pounds (an average of 3.6 million pounds/year) of NPEs discharged into the environment.

**Synthetic Oils and
Lubricants of Texas,
Inc. (Soltex)**

**Washing Systems
LLC**

In order to fully align with Washing Systems new corporate commitment, the three new detergents were submitted for DfE recognition and approved in 2008. As part of this new partnership with DfE, Washing System continued to evaluate alternate chemistry to create the best products and further reduce the environmental impact for all customers. This initiative and desire has led to the development of another DfE-recognized detergent in 2009, Pinnacle Liquid Detergent, and two additional products in 2013 (Spectrum and Supreme).

An Application of Hybrid Multispectral Analysis: Real-Time Wastewater Chlorine Pacing Control

Hybrid Multispectral Analysis (HMA) is a unique combination of advanced optical, photonic, and statistical technologies applied to the challenge of providing synchronized high frequency data for complex water matrixes. Such information is required for real-time treatment process control. HMA allows plants to continuously adjust treatment based on current and on-line historical data to eliminate over and under treatment, provide real-time water security, and enable closer compliance with and more effective enforcement of environmental laws.

HMA utilizes a single optical probe to conduct over 3.3 million *in situ* measurements per day, collecting direct molecular data on absorption, reflectance, and fluorescence. Molecular data is used to virtually instantaneously quantify critical water quality parameters such as biochemical oxygen demand (BOD), chloramine, chemical oxygen demand (COD), *E. coli*, fluorescent dissolved organic matter (FDOM), NH₃, NO₃, specific UV absorbance (SUVA), trihalomethanes (THMs), total Kjeldahl nitrogen (TKN), total organic carbon (TOC), total free chlorine (HOCl+OCl⁻), pH, total suspended solids (TSS), mixed liquor suspended solids (MLSS), and turbidity; ranging from ppb to over 10,000 ppm. Approximately every two minutes, parameter values and/or control signals are broadcast for real time control of processes that determine the chemical load or energy consumption of a plant and quality of water it discharges, such as chlorine injection, UV lamp settings, aeration blower speeds, or nutrient injectors; or to stop pumps when water security parameters are violated.

Green aspects of HMA are that it eliminates reagents, eliminates sample preparation and storage, minimizes treatment guard bands used to compensate for delays in conventional data, and requires only 72 watts to operate. HMA is sold under the trade name LiquID™, where over 65 LiquID™ stations shipped to date have proven useful in the fields of municipal water, wastewater treatment, water reuse, and industrial process control. The HMA methodology was developed through support in part by EPA, Office of Naval Research, Oregon State University, and Oregon Nanoscience and Microtechnologies Institute.

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