EPA
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Agency

GREEN CHEMISTRY CHALLENGE

A U.S. EPA Program

Presidential
Green Chemistry Challenge

Award Recipients
1996-2016




The Presidential Green Chemistry Challenge

Award Recipients

1996—2016

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Introduction

The Presidential Green Chemistry Challenge Awards Program enables individuals, groups, and organizations to compete for annual presidential-rank awards that recognize innovations in cleaner, cheaper, smarter chemistry. By honoring and highlighting outstanding chemical technologies that incorporate principles of green chemistry into chemical design, manufacture, and use, this awards program better enables industry to meet its pollution prevention goals.

This booklet presents the 1996 through 2016 Presidential Green Chemistry Challenge Award recipients and describes their award-winning technologies. Each winner demonstrates a commitment to designing, developing, and implementing a green chemical technology that is scientifically innovative, economically feasible, and less hazardous to human health and the environment.

Winner Categories

EPA typically honors six winners in each of the following categories:

- Academia
- Small Business
- Greener Synthetic Pathways, such as the use of innocuous and renewable feedstocks (e.g., biomass, natural oils); novel reagents or catalysts including biocatalysts and microorganisms; natural processes including fermentation and biomimetic syntheses; atom-economical syntheses; and convergent syntheses
- Greener Reaction Conditions, such as the replacement of hazardous solvents with greener solvents; solventless or solid-state reactions; improved energy efficiency; novel processing methods; and the elimination of energy- and material-intensive separations and purifications
- Designing Greener Chemicals, such as chemicals that are less toxic than current alternatives; inherently safer chemicals with regard to accident potential; chemicals recyclable or biodegradable after use; and chemicals safer for the atmosphere (e.g., do not deplete ozone or form smog)
- Specific Environmental Benefit: Climate Change for a technology in any of the three focus areas that reduces greenhouse gas emissions (added in 2015)

Environmental Results

The Presidential Green Chemistry Challenge has had 109 winners over its 21 years. Collectively each year these winning technologies:

- Eliminate 826 million pounds of hazardous chemicals and solvents
- Save over 21 billion gallons of water
- Eliminate 7.8 billion pounds of carbon dioxide releases to the air

Added together, the environmental, health, and cost benefits of over 1,714 technologies nominated for these awards over the past 21 years are huge. Congratulations to all of our winners and nominees! In the future, EPA looks forward to honoring many more nominees and winners on the cutting edge of pollution prevention.

Academic Award

Professor Paul J. Chirik
Princeton University

Catalysis with Earth Abundant Transition Metals

Innovation and Benefits

Hydrosilylation is a chemical process that is critical for the production of a wide range of consumer goods. It relies on some of the least abundant elements in the Earth's crust, which results in high cost and significant environmental consequences. Professor Chirik discovered a new class of hydrosilylation catalysts based on earth abundant transition metals such as iron and cobalt that have superior performance to existing platinum catalysts.

Metal-catalyzed chemical reactions have enabled many of the technological innovations of modern society with applications ranging from the synthesis of advanced materials to new medicines. For decades, catalyst technology has relied on some of the least abundant elements in the Earth's crust – palladium, platinum, rhodium, and iridium. In addition to their high cost, price volatility, and toxicity, extraction of these elements has significant environmental consequences. Obtaining one ounce of a precious metal, for example, often requires mining approximately 10 tons of ore which creates a CO_2 footprint that is estimated to be 6,000 times that of abundant metals such as iron.

Alkene hydrosilylation is an example of a metal-catalyzed chemical reaction that is used on an industrial scale in the manufacture of silicones from alkenes and silanes. Silicones are found in a range of consumer products including adhesives, household utensils, medical devices, health care products, and low rolling resistance tires. The platinum catalyst used in alkene hydrosilylation reactions is often not recovered, however, which results in a significant environmental footprint for this commercially important process.

Professor Chirik and his research group, in collaboration with Momentive Performance Materials, discovered a new class of hydrosilylation catalysts based on earth-abundant transition metals such as iron and cobalt that have superior performance to existing platinum catalysts. This base metal catalyst technology offers the opportunity to enable new chemical processes that provide the desired product exclusively, eliminate distillation steps, and avoid generation of byproducts and unnecessary waste. This technology is based upon "metal-ligand cooperativity," a broad catalysis concept pioneered by the Chirik group, where electron changes occur concomitantly between the metal and the supporting ligand.

Hydrosilylations to produce various commercial silicone products have been conducted on multi-gram scales using this new technology. The discovery of these air-stable, readily-synthesized iron and cobalt catalysts with unprecedented activity and selectivity may ultimately transform the industrial approach to commercial silicone products.

Verdezyne

Renewable Nylon Through Commercialization of BIOLON™ DDDA

Innovation and Benefits

Dodecanedioic acid (DDDA) is used to manufacture nylon 6,12 for high performing engineered plastics, as well as in numerous other applications. DDDA is traditionally produced from petrochemicals via a multi-step chemical process using heat and nitric acid. Verdezyne developed a technology platform for producing BIOLON™ DDDA and other industrial chemicals from biobased and renewable raw materials.

Verdezyne developed a yeast fermentation technology platform to provide manufacturers and consumers with renewable alternatives to existing petroleum-based chemical intermediates. This technology focuses on the production of dicarboxylic acid chemical intermediates such as adipic acid, sebacic acid and dodecanedioic acid (DDDA). The first of these to be commercialized will be BIOLON™ DDDA, which will be used primarily in the manufacture of nylon 6,12 for engineered plastics that require special properties such as high chemical, moisture, or abrasion resistance. Other uses for DDDA are in the manufacture of adhesives, coatings, corrosion inhibitors, lubricants, and fragrances.

The current global demand for DDDA is estimated to be 100 million pounds per year. All DDDA currently on the market is produced from fossil-based sources, with the largest volume manufactured via trimerization of butadiene, followed by hydrogenation and oxidation with nitric acid. Verdezyne's process for production of BIOLON™ DDDA uses fatty acid feedstocks sourced from the co-products of vegetable oil refining as the starting raw material. In addition to providing a renewable alternative, this process offers a higher level of manufacturing safety since high temperature and pressure and concentrated nitric acid are no longer needed. Moreover, Verdezyne's process also results in reduced greenhouse gas emissions.

Verdezyne's production of BIOLON™ DDDA is an aerobic fermentation process integrated with downstream product isolation and crystallization. The fermentation converts the twelve carbon fatty acid, lauric acid, to DDDA through the activity of Verdezyne's proprietary, genetically engineered *Candida sp.* yeast. The biochemical pathway involved is the three-step ω-oxidation pathway that sequentially oxidizes the terminal end of an alkane (or a fatty acid) to a carboxylic acid. Verdezyne scientists specifically engineered this yeast to enable rapid, high-yield production of DDDA while minimizing the accumulation of pathway intermediates that can be toxic to the organism and detrimental to final product purity.

Verdezyne's proprietary method for producing renewable BIOLON™ DDDA has been successfully demonstrated on a larger scale, enabling the production of over 70,000 pounds thus far. The product has met all industry quality specifications and has also earned the USDA Certified Biobased product label. The company's first commercial production facility is scheduled to open in 2017.

Greener Synthetic Pathways Award

CB&I and Albemarle

AlkyClean® Technology: An Inherently Safer Technology for the Production of Gasoline Alkylate

Innovation and Benefits

Alkylate is a clean gasoline component and is produced from light olefins and isobutane. Despite being a cleaner product, traditional alkylate production uses toxic and corrosive liquid acid catalysts. CB&I, Albemarle, and Neste developed an inherently safer solid acid catalyst alkylation technology that produces gasoline alkylate with a lower environmental impact.

Alkylate is a highly valued "clean fuels" blending component for motor gasoline. It consists of clean-combusting isoparaffins that have low vapor pressures and high octane values. Alkylate also does not contain toxic components such as aromatics, olefins, or sulfur compounds. Alkylate is the preferred gasoline blending component for compliance with relevant environmental regulations.

Alkylate is produced from the reaction of isobutane and light olefins (C3-C5). Alkylate production is currently about 30 billion gallons/year worldwide, of which 60% is located in North America. A challenge facing refineries today is that alkylate production requires the use of liquid acid catalyzed processes, typically hydrofluoric acid or sulfuric acid. Hydrofluoric acid, in particular, is extremely toxic and, upon release, forms clouds that can be lethal for up to five miles.

For more than 40 years, scientists have been trying to replace liquid acid technologies with a greener solid acid catalyst technology. Prior approaches failed because of poor product selectivity and/or excessively rapid catalyst deactivation, coupled with the lack of an acceptable catalyst regeneration procedure. In some cases, these catalysts used leachable corrosive components such as halogens, triflic acid, and boron trifluoride, which could migrate into product streams.

Albemarle and CB&I developed a catalyst-process combination technology, the AlkyClean® solid acid alkylation process, which coupled with CB&I's novel reactor scheme, produces high quality alkylate without the use of liquid acid catalysts. Additionally, neither acid-soluble oils nor spent acids are produced, and there is no need for product post-treatment of any kind.

Albemarle's AlkyStar™ catalyst was designed for use exclusively with the AlkyClean® alkylation process. It uses a type of zeolite catalyst that is well-proven in the industry. The strength and the number of acid sites on the catalyst have been optimized to enhance hydrogen transfer reactions over multiple alkylation reactions. The catalyst particle size and porosity were also optimized using a pilot plant and a demo unit that allowed the investigation of regeneration procedures as well.

The world's first commercial-scale, solid catalyst alkylation unit was started up in August, 2015. The unit employs the AlkyClean® technology and has a capacity of 2,700 BPD alkylate production. The plant has met or exceeded all performance expectations and is producing an alkylate product of quality that is on par with existing technologies.

Greener Reaction Conditions Award

Dow AgroSciences LLC

Instinct® Technology – Making Nitrogen Fertilizers Work More Effectively for Farmers and the Planet

Innovation and Benefits

Agricultural activity introduces a significant amount of nitrate into ground and surface waters. Dow Agrosciences developed Instinct® nitrogen stabilization technology which protects nitrogen fertilizer in the ammoniacal form, thereby reducing nitrate leaching to ground and surface waters as well as atmospheric nitrous oxide emissions. Instinct® also results in longer retention of applied nitrogen in a plant's root zone for optimal crop utilization and yield.

The demand for higher crop yields and agricultural productivity is ever increasing, and so are concerns for the negative impacts on the environment caused by agricultural activities. Human activities related to farming account for a significant percentage of nitrate in ground and surface waters as well as nitrous oxide emissions. An estimated 75% of all nitrous oxide emissions, for example, come from agricultural activities such as applied nitrogen fertilizers and manures.

Crop genetics and precision application methods have improved the efficiency of applied nitrogen fertilizers, but losses to the environment are still significant after soil bacteria quickly convert nitrogen from the applied urea or ammoniacal form to nitrate. In the nitrate form, nitrogen fertilizer is susceptible to losses through leaching or as emissions in the form of nitrous oxide. Furthermore, nitrate fertilizer that leaches out of a plant's root zone is no longer available to provide nutrients to the crop.

Scientists at The Dow Chemical Company discovered a powerful nitrification inhibitor that can inhibit soil bacteria from rapidly converting nitrogen in the ammoniacal form to nitrate, thereby retaining more nitrogen in the more stable ammoniacal form. By keeping nitrogen in the root zone for a longer period during the season, Dow's nitrogen stabilizers improve Nitrogen Use Efficiency and reduce nitrogen loss through leaching and nitrous oxide emissions. N-Serve® was the first commercial product introduced by Dow in 1974, but it is only suitable for use with anhydrous ammonia fertilizer applications due to the limitations of its physical-chemical properties.

In 2010, Dow AgroSciences launched a novel, aqueous microcapsule suspension product, Instinct®. This patented technology can be conveniently used with other commonly used nitrogen fertilizer sources, enabling adoption of the product for multiple crops in the U.S. and around the world. As an aqueous suspension of a microencapsulated active ingredient, Instinct®, also provides additional environmental benefit by significantly reducing the amount of petroleum-based solvents used per treated acre.

In less than five years, acres treated with stabilized nitrogen have grown more than five-fold. In 2014 alone, based on calculated adoption of Instinct® in the U.S., it is estimated that use of the technology reduced carbon dioxide equivalent emissions by about 664,000 metric tons and increased U.S. corn production by about 50 million bushels, equating to about $205,500,000 additional production revenue for U.S. corn growers.

Designing Greener Chemicals Award
Specific Environmental Benefit: Climate Change Award

Newlight Technologies

AirCarbon: Greenhouse Gas Transformed into High-Performance Thermoplastic

Innovation and Benefits

Fossil fuels are refined, cracked, and then polymerized at high temperature and pressure in petro-based processes to make plastics. Newlight Technologies developed a technology that produces high performance, carbon-negative AirCarbon™ resins from captured greenhouse gases. AirCarbon™ uses a p6oprietary biocatalyst to produce plastics at lower cost compared to plastics from petrochemicals.

Methane is emitted by natural sources such as wetlands. It is also the second most prevalent greenhouse gas emitted in the U.S. from human activities, such as leakage from natural gas systems and the raising of livestock. Methane's lifetime in the atmosphere is much shorter than carbon dioxide, but methane is more efficient at trapping radiation. Pound for pound, the comparative impact of methane on climate change is more than 25 times greater than carbon dioxide over a 100-year period.

Newlight Technologies developed and commercialized a carbon capture technology that combines methane with air to produce AirCarbon™, a high-performance thermoplastic material that matches the performance of a wide range of petroleum-based plastics while out-competing on price. Newlight's biocatalyst combines air and methane-based carbon to produce polymers at environmentally friendly, ambient conditions. Despite the conceptual simplicity, previous technologies utilizing carbon capture to manufacture plastics resulted in production costs that were significantly higher than petroleum-based manufacture of plastics.

To overcome this long-standing cost challenge, Newlight developed a biocatalyst that does not "turn itself off" based on the amount of polymer being produced. To do this, Newlight developed a process to disable the negative feedback receptors on polyhydroxyalkanoate polymerase, the central polymer production enzyme in the biocatalyst. As a result, the biocatalyst is able to continue to polymerize significantly beyond previous maximum limits and generate a yield of nine kilograms of polymer for every one kilogram of biocatalyst (9:1) – nine times more material compared to previous technologies. Newlight's AirCarbon™ technology also reduces unit operations by a factor of three and capital cost by a factor of five, resulting in a net operating cost that enables AirCarbon™ to be cost and performance advantageous compared to petrochemical incumbents.

Within 24 months of scaling in 2013, AirCarbon™ was adopted by a range of leading companies including Dell, Hewlett-Packard, IKEA, KI, Sprint, The Body Shop, and Virgin to make packaging bags, containers, cell phone cases, furniture, and a range of other products. These products use a greenhouse gas in a carbon-negative process as a cost-effective replacement for petroleum-based plastics.

Academic Award

Professor Eugene Y.-X. Chen
Colorado State University
Greener Condensation Reactions for Renewable Chemicals, Liquid Fuels, and Biodegradable Polymers

Innovation and Benefits

Condensation reactions are necessary for the production of chemicals, pharmaceuticals, fuels, and materials. However, they generate a large amount of waste and are commonly metal-mediated. To address these problems, Professor Chen developed a condensation reaction using a biomass platform chemical (5-hydroxymethylfurfural) for the production of renewable chemicals, fuels, and polymeric materials. Additionally, he developed a polycondensation using acrylic monomers to create biodegradable unsaturated polyesters. This new technology offers two novel synthetic pathways that are catalytic, waste-free and metal-free.

In condensation reactions, as two molecules combine to form a larger molecule, small molecules split off. Because of the loss of this small molecule, such as water, hydrogen chloride, ethylene, methanol, or acetic acid, these reactions are intrinsically waste-generating. Additionally, condensation reactions are often mediated by metals. For the production of jet or other transportation fuels, fine chemicals, and bioplastics, biomass platform chemicals, such as 5-hydroxymethylfurfural (HMF), need to be upgraded through the C–C bond forming, condensation reaction into chain-extended, higher energy-density substances, such as 5,5′-dihydroxymethylfuroin (DHMF). The twelve-carbon DHMF is a new bio-derived building block that can be catalytically transformed into renewable fine chemicals, polymeric materials, and oxygenated biodiesel or premium alkane jet fuels.

Direct HMF coupling is not possible through aldol self-condensation of HMF because it lacks a necessary hydrogen atom in the α-position to the carbonyl group. Existing alternative methods, such as metal-mediated cross-aldol condensation, have to use other enolizable petrochemicals. These methods also suffer from the unavoidable waste inherent in conventional condensation reactions. Professor Chen and his graduate student Dajiang (DJ) Liu developed a new condensation technology that uses an organic catalyst, such as an *N*-heterocyclic carbene (NHC), to reverse the polarity of the HMF carbonyl (umpolung), to enabling a solvent-free direct condensation coupling of HMF into DHMF with quantitative yield and 100% atom-economy.

Professor Chen and his postdoctoral fellow Dr. Miao Hong also developed a polycondensation method, called "Proton-Transfer Polymerization" (HTP), which uses an NHC catalyst to polymerize dimethacrylates uniquely into biodegradable polyesters with 100% atom-economy. The resulting unsaturated polyesters are of interest for producing tailor-made biodegradable polyester materials through post-functionalization and cross-linking. The synthesis of such polyesters from dimethacrylates is not possible by a metal-based process, such as the Ru or Mo-mediated acyclic diene metathesis, because such methods are ineffective for polymerization of electron-deficient, conjugated or sterically demanding diolefins such as dimethacrylates. In contrast, existing methods polymerize dimethacrylates through non-condensation, polyaddition pathways into non-biodegradable polymethacrylates.

The new condensation technology not only offers two novel condensation synthetic pathways towards the HMF upgrading and polyester production from acrylic monomers, both processes of which are not possible by any existing technologies, it also exhibits important hallmarks of a green technology by being catalytic, metal-free and 100% atom-economical as well as solvent-free (for the HMF upgrading) or biodegradable (for the polyester production).

Small Business Award

Renmatix

The Plantrose® Process: Supercritical Water as the Economic Enabler of Biobased Industry

Innovation and Benefits

The biobased industry requires access to high volume, low cost sugars from a wide variety of biomass. Technologies that extract these second generation sugars from cellulose are typically more expensive than first generation sugars, like corn and cane. Renmatix developed the Plantrose® process, a technology that uses supercritical water to deconstruct biomass and produce cost-advantaged cellulosic sugars. Plantrose® technology enables affordable renewable materials as alternatives to petroleum-derived chemicals and fuels.

Traditional sugar sources, like corn and cane, are expensive feedstocks for producing relatively low value, high volume products like fuels and chemicals. Unfortunately, the traditional second generation technologies (acid, enzymes, and solvents) that were designed to extract these low value cellulosic sugars lack the practical economics to even compete with first generation sugars, let alone traditional petrochemical sources. In part, this is due to the capital expense of historical technologies like mineral acids and enzymatic processes that hydrolyze cellulosic feedstocks. This reality has severely limited the market adoption and broad integration of cellulosics.

Renmatix's Plantrose® process, which uses supercritical water to deconstruct biomass, provides cost-advantaged cellulosic sugars by using primarily water for conversion reactions. The two-step continuous process deconstructs a range of plant material into renewable feedstocks to produce separate streams of xylose and glucose. After sugar extraction, remaining lignin solids can be burned to supply the bulk of the heat energy required for the process (or utilized in higher value applications like adhesives or thermoplastics).

In the first step, biomass and water are pumped together, heated, and fed into a fractionation reactor, where the hemicellulose is solubilized into a five-carbon sugar stream. In the second step, the cellulose and lignin that were filtered away from the initial sugar steam are pumped into the supercritical hydrolysis reactor. In the reactor, water acts as both a solvent and catalyst, decrystalizing and dissolving the cellulose and hydrolyzing the cellulose polymers. The temperature and pressure of the supercritical water system can be adjusted for very specific reaction condition control, enabling the use of smaller continuous reactors for large-scale commercial production.

Renmatix's technological innovation, the use of water-based chemistry instead of enzymes, and/or acids, provides a cleaner, faster, and lower-cost method for deconstructing biomass into cellulosic sugars. Those sugars become the building blocks for a multitude of renewable downstream technologies to serve significant biochemical market demand – and begin providing meaningful volumes of plantrochemicals, in lieu of the conventional petroleum-derived equivalents. Renmatix partners and customers will build their own biorefineries by licensing the Plantrose process to convert locally available biomass into cellulosic sugars, enabling profitable scale-up of biochemical, cellulosic ethanol, and advanced biofuels markets worldwide.

Greener Synthetic Pathways Award

LanzaTech Inc.

LanzaTech Gas Fermentation Process

Innovation and Benefits

Waste gas is an attractive resource for fuel and chemicals production due to its low value and high production. LanzaTech microbes utilize waste gas streams with a range of compositions to produce fuels such as ethanol and chemicals such as 2,3-butanediol at high selectivities and yields. Combining robust microbes, innovative bioreactor design, and process development has enabled rapid scale-up to take place, with two 100,000 gallon/year demonstration scale facilities in China using steel mill off gases for ethanol production.

Carbon gas streams are often byproducts of established processes. When they cannot be utilized efficiently they are wasted, normally through venting or flaring. The conversion of carbon monoxide-rich gases through synthetic chemical pathways, for example Fischer-Tropsch or methanol synthesis, requires that H_2 be available in the synthesis gas. Waste industrial gases often do not contain H_2 and therefore cannot be converted using conventional synthetic pathways. Gas fermentation technologies have also stalled because gas toxicity requires expensive microbe conditioning and leads to gas solubility limitations.

LanzaTech developed a method to utilize gas streams with a range of CO and H_2 compositions to produce fuels such as ethanol and chemicals such as 2,3-butanediol at high selectivities and yields. While both CO/CO_2 and H_2 are utilized in the process, LanzaTech's proprietary microbes are also able to consume H_2-free CO-only gas streams, due to the operation of a highly efficient biological water-gas shift reaction occurring within the microbe. The process is facilitated by the enzyme-catalyzed chemistry of the Wood-Ljungdahl pathway whereby CO_2 and CO can be converted in a water-gas shift reaction catalyzed by carbon monoxide dehydrogenase (CODH). Through a series of intermediates, CO and CO_2 are ultimately fixed as acetyl-CoA by the CODH/ACS complex.

The process is a highly efficient conversion of acetyl-CoA to ethanol, as this is actually linked to growth of the organism. LanzaTech has also manipulated the organism for high yields of specific products (e.g. the microbes can make a single enantiomer of 2,3-butanediol), eliminating the need to separate and find markets for co-products. These microbes operate close to ambient temperature and atmospheric pressure and are tolerant to high levels of toxicity. LanzaTech has overcome the gas solubility limitations through proprietary bioreactors that increase volumetric mass transfer by creating more interfacial area per volume bubble size. This results in higher product yield and productivity.

Life cycle analysis studies performed in partnership with MTU, E4Tech, and Tsinghua University have shown that the LanzaTech gas fermentation process can produce fuels from steel mill off-gases with GHG emissions that are 50-70% lower than those of fossil fuels. Particulate matter and NO_x emissions are also reduced. LanzaTech's gas fermentation simultaneously makes valuable fuels and/or chemicals while mitigating the environmental effects of waste and residual industrial emissions. LanzaTech has partnered with over 10 global Fortune 500 Companies across a variety of sectors, including chemicals companies, INVISTA and EVONIK.

Greener Reaction Conditions Award

Synthetic Oils and Lubricants of Texas (Soltex)

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

Innovation and Benefits

Polyisobutylene (PIB), an intermediate used to produce additives for lubricants and gasoline, is made using a liquid polymerization catalyst. This catalyst is hazardous and must be separated and washed after use which generates substantial amounts of wastewater. Soltex has developed a new process that is based on a solid catalyst in a fixed bed reactor. Soltex produces a high purity product with significantly reduced catalyst usage and no water wash, which reduces capital investment.

Polyisobutylene (PIB) is used in the production of dispersants and detergents for lubricants and gasolines. 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 in a branched position making the product more reactive. When the double bond is located at internal positions in the backbone of the polymer, 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 and corrosive 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 to stop the reaction 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 vessel 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 the polymerization to occur. The polymer mixture exits the reactor at the same controlled rate. This reactor effluent contains minimal 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 with significantly lower catalyst usage. It is a simplified, highly efficient operation with substantially reduced capital investment, low operating and catalyst costs, and no water wash generation.

Designing Greener Chemicals Award

Hybrid Coating Technologies/Nanotech Industries

Hybrid Non-Isocyanate Polyurethane/Green Polyurethane™

Innovation and Benefits

Green Polyurethane™ is a hybrid non-isocyanate polyurethane (HNIPU) manufactured by Hybrid Coating Technologies that does not use isocyanates at any point in the production process. Isocyanates irritate the eyes, lungs, skin and throat, are a potential carcinogen, and can cause occupationally-induced asthma. Green Polyurethane™ applications provide a reduction in health and environmental hazards with simultaneous improvements in mechanical and chemical resistance properties. Green Polyurethane™ is also cost competitive compared to conventional polyurethane coatings and foam.

Isocyanates are critical components used in conventional polyurethane products such as coatings and foam. However, exposure to isocyanates is known to cause skin and respiratory problems and prolonged exposure has been known to cause severe asthma and even death. Isocyanates are also toxic to wildlife. When burnt, isocyanates form toxic and corrosive fumes including nitrogen oxides and hydrogen cyanide. Due to these hazards, isocyanates are regulated by the EPA and other government agencies.

To address the health and environmental hazards associated with conventional polyurethanes, Hybrid Coating Technologies (HCT) has developed a hybrid non-isocyanate polyurethane (HNIPU), also called "Green Polyurethane™." HNIPU is formed from a reaction between mixture of mono/polycyclic carbonate and epoxy oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. The result is a crosslinked polymer with β-hydroxyurethane groups of different structure.

HCT developed a novel concept for generating new multifunctional modifiers for "cold" cure epoxy-amine compositions, namely hydroxyalkyl urethane modifiers (HUM), and subsequently developed HUMs based on renewable raw materials (vegetable oils), which are now used for SPF and UV-cured acrylic polymer based coatings. Utilizing HUM provides the cured composition with superior coating performance characteristics including pot life/drying times, strength-stress properties, bonding to a variety of substrates and appearance. Other characteristics, such as weathering and chemical resistance, are also strengthened while HNIPU is not sensitive to moisture in the surrounding environment. HCT also developed a version of its epoxyamine hydroxyurethane grafted polymer that replaces corrosive low molecular weight amines with less hazardous high molecular weight amines.

HNIPU is a safer chemical formulation for use in polyurethane and epoxy applications such as coatings and foam. It also has improved mechanical and chemical resistance properties, replaces up to 50% of its epoxy base with renewable resources (vegetable derived) and is cost competitive compared to other conventional polyurethane and epoxy products.

HCT is currently manufacturing coatings in California with a production capacity of 100,000 tons. Applicators using HNIPU coatings report cost savings between 30-60% due to the product's improved safety profile and excellent properties. HCT expects to see similar benefits for applicators using its spray polyurethane foam once it becomes commercially available in the next 1-2 years.

Specific Environmental Benefit: Climate Change Award

Algenol

The Algenol Biofuel Process: Sustainable Production of Ethanol and Green Crude

Innovation and Benefits

Algenol has developed genetically enhanced strains of cyanobacteria for production of ethanol and "green crude" that can then be converted into replacements for petroleum-derived chemicals and fuels. Algenol's cyanobacteria (blue-green algae) are able to divert over 80% of the carbon that they capture through photosynthesis into the ethanol production pathway. The Algenol technology utilizes waste CO_2 from industrial emitters and relies on patented photobioreactors and proprietary separation techniques for low-cost and low-carbon footprint fuel production.

Ethanol can be used as a transportation fuel directly or blended with gasoline. Algenol has developed technologies for the recombinant and classical genetic improvement of cyanobacteria (blue-green algae), leading to strains that divert more than 80% of the photosynthetically fixed carbon into ethanol without a decrease in overall photosynthetic yield. This has led to improved biofuel productivity, higher economic returns, minimal waste production, and a lower carbon footprint.

Algenol's hybrid algae are grown in saltwater in proprietary photobioreactors (PBRs) which minimize heterotrophic contamination and reduce water use. Photosaturation is a common limiting feature in aquatic photosynthesis and occurs when the rate of photon absorption exceeds the rate that the algae can use the energy for product formation (i.e., carbon fixation), such that the energy of the excess photons is wasted through non-photosynthetic processes. Algenol's vertical PBR system offers a productivity advantage over horizontal systems by delivering a more dilute irradiance over a greater surface area of the PBR, thereby limiting photosaturation.

Algenol has also developed proprietary downstream processes for energy-efficient recovery of fuel-grade ethanol. In collaboration with Pacific Northwest National Laboratory (PNNL), Algenol has applied hydrothermal liquefaction technology to convert the spent biomass into green crude. Algenol is also working with PNNL, National Renewable Energy Laboratory, and Georgia Tech on development of higher-value green chemical production concepts.

Algenol has demonstrated about 15–20 times the productivity of corn-based ethanol on a per acre basis. In the past five years, Algenol moved this technology from laboratory scale to pilot scale and is currently completing the construction and commissioning of a 2-acre facility as part of the IBR Project ($52 million project with a $25 million grant from the U.S. Department of Energy). The overall process reduces the carbon footprint relative to gasoline by 60–80% according to peer-reviewed published work from Georgia Tech. A single 2,000 acre commercial Algenol module is the equivalent of planting 40,000,000 trees or removing 36,000 cars from the road. Broad deployment of this technology, with its low carbon footprint, can contribute to CO_2 emission reduction targets and lower dependence on fossil fuel resources.

Academic Award

Professor Shannon S. Stahl
University of Wisconsin-Madison
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 (O_2) 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-tetramethylpiperidinyl-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.

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

Solazyme, Inc.

Tailored Oils Produced from Microalgal Fermentation

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 *Saccromyces*, 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 LEDs—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 U.S. homes. 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 PBTs. 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 chemicals 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 to 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 burn-back resistance. Control, extinguishing time, and burn-back resistance is 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.

Academic Award

Professor Richard P. Wool
University of Delaware
Sustainable Polymers and Composites: Optimal Design

Innovation and Benefits

Professor Richard Wool has created several high-performance materials using biobased feedstocks, including vegetable oils, chicken feathers, and flax. These materials can be manufactured using less water and energy, and producing less hazardous waste compared to petroleum-based processes. Professor Wool's products can be used as adhesives, composites, foams, and even as circuit boards and as a leather substitute.

Many advanced composite materials use hazardous chemicals in the adhesive resin and use inorganic fibers for strength. A typical composite like fiberglass might use a styrene-polyester co-polymer, a polyurethane, or an epoxy resin. While the cured resin is unreactive, the uncured form may be quite toxic, posing risk during manufacturing. Furthermore, the resources used to make traditional composites are non-renewable: petroleum, natural gas, and minerals.

Professor Wool has developed several new biobased materials that can be used as substitutes for toxic substances used to make high-performance materials, like adhesives, composites, and foams. The processes to create these biobased materials yield less waste, require less water and energy, and are well-suited to mass production. His materials start with vegetable oils triglycerides and vegetable oil free fatty acids, cellulose and lignin from wood or plant stalks, and fibrous materials such as flax and chicken feathers.

To design these new biobased materials, Professor Wool evaluates the mechanical and thermal properties of the resins, integrates molecular design, and selects products with minimal toxicity. He developed the Twinkling Fractal Theory (TFT) to help predict the functional properties of a material based on its molecular properties, enabling a more focused design approach. He then evaluates the potential toxicity of the materials using the U.S. EPA's EPI Suite™ software. Using these design and predictive methods, Professor Wool has synthesized a number of lignin-based replacements for styrene and identified three of these as being less toxic. Other products that Professor Wool has designed include chemically functionalized high oleic soy oil used in pressure sensitive adhesives and elastomers, composite resins, a thermoplastic polyurethane (TPU) substitute, and an isocyanate-free foam from plant oils. The TPU substitute was developed in collaboration with Professor Epps, also of the University of Delaware. In addition to its reduced toxicity, the biobased foam is also compatible with living cells and supports the growth of human tissue. One of Professor Wool's more recent inventions is a breathable, bio-based "Eco-Leather", which avoids the traditional leather tanning process and can be entirely vegan. This work was done in collaboration with Professor Huantian Cao of the Fashion and Apparel Department at the University of Delaware.

Since 1992, Professor Wool has been awarded five patents for his safer materials and has applied for three additional patents. As of 2012, Dixie Chemical began producing Professor Wool's bio-based composite resins for a worldwide market. His discoveries led to the development of soy-based composites used to make boats, tractor panels, and wind turbine parts. He developed the biobased foam replacement for polyurethane in collaboration with Crey Bioresins Inc. This biobased foam is now being considered as a replacement component by several packaging and automotive suppliers. Professor Wool's start-up company, Eco-Leather Corp., has entered into collaborations with Nike and Puma to use his leather substitute in their products.

Faraday Technology, Inc.

Functional Chrome Coatings Electrodeposited from a Trivalent Chromium Plating Electrolyte

Innovation and Benefits

Chrome plating in many high-performance uses, such as some aircraft parts, still requires hexavalent chromium, a carcinogen, to achieve the necessary performance. Various chrome-free replacements have limitations that preclude widespread adoption. Faraday has developed a plating process that allows high-performance chrome coatings to be made from the less toxic trivalent chromium. This nearly drop-in replacement can reduce millions of pounds of hexavalent chromium without comprising performance.

High-performance, functional chrome coatings plated from a hexavalent chromium [Cr(VI)] plating bath are widely used in industrial applications for military and commercial markets. These coatings provide resistance to abrasives and sliding wear in heavy-duty machinery, especially pneumatic tubing. However, Cr(VI) is the most toxic form of chromium due to its carcinogenic properties. Reducing or eliminating the use of Cr(VI) has been a priority for governments and industry for years. A number of alternative non-chrome plating technologies have been developed, but do not provide the performance required for the full range of industrial or military applications.

The FARADAYIC® TriChrome Plating process uses trivalent chromium [Cr(III)], a much less toxic and non-carcinogenic form of chromium, in place of Cr(VI) in the plating baths. This approach maintains the advantages of a functional chrome coating but vastly reduces the hazards associated with the plating process. In the past, Cr(III) had been used for decorative coating when only a thin layer of plating was needed, such as on a car bumper, but such coatings are not suitable for heavy-duty applications where hardness and wear resistance are required.

The conventional Cr(VI) electrodeposition process uses a constant direct current during the entire process. Faraday designed a new electrodeposition process that alternates between a forward (cathodic) pulse followed by a reverse (anodic) pulse and an off period (relaxation). Not only does this process allow for thicker coatings from Cr(III), but it can also be adjusted to affect the structure and properties of the coating. This new process results in a product that exhibits equivalent or improved wear and fatigue performance compared to chrome coatings plated from a Cr(VI) bath. In addition, this new Cr(III) plating process is more efficient that the Cr(VI) plating process and does not produce any Cr(VI) as a byproduct. Yet another advantage to this technology over non-chrome alternatives is that it is a true drop-in replacement technology for Cr(VI) coatings. Only new plating bath electrodes are required. Unlike many non-chrome technologies, Faraday's process can plate both the inner and outer surfaces of a tube.

Development of the FARADAYIC® TriChrome Plating process has been supported by EPA, through its Small Business Innovation Research program, the National Center for Manufacturing Sciences, The Boeing Co., Messier-Bugatti-Dowty, United Technologies Research Center and other potential commercial clients. Commercialization of the FARADAYIC® TriChrome Plating process will occur via the existing metal finishing supply chain via partnerships with chemical formulators and chemical vendors. Use of Faraday's technology could eliminate about 13 million pounds of hexavalent chromium waste each year in the Unites States and as much as 300 million pounds worldwide.

Greener Synthetic Pathways Award

Life Technologies Corporation

Safe, Sustainable Chemistries for the Manufacturing of PCR Reagents

Innovation and Benefits

Polymerase Chain Reaction (PCR) is the process used to perform genetic testing. Manufacturing the key chemicals required for PCR tests is quite wasteful, often producing thousands of times more waste than product. Life Technologies has developed a three-step, one-pot synthesis, which is much more efficient. The new process prevents about 1.5 million pounds of hazardous waste a year.

Polymerase chain reaction (PCR), the process of amplifying genetic material, is used in basic research, genetic engineering, forensics, infectious disease identification, food safety, and, most recently, personalized medicine. The expanding role of PCR in science and medicine highlights the need to create safe and sustainable chemistries for the manufacture of reagents for these applications. Deoxyribonucleotide triphosphates (dNTPs) are the individual building blocks for the DNA that is made during PCR. Conventional syntheses of dNTPs are inefficient, involve multiple steps that require isolation and purification of intermediates, and use excessive volumes of toxic or hazardous solvents and reagents.

Researchers at Life Technologies have devised synthetic routes for the manufacture of dNTPs that are only three steps in a single pot, eliminating the need to transfer reaction material. These synthetic routes also eliminate the need for a variety of hazardous reagents and solvents, including zinc chloride, triphenyl phosphine, aldrithiol, dimethyl formamide (DMF), and dichloromethane. By using these new dNTP routes, worker exposure to hazardous materials is minimized and the process E-factor (the ratio of amount of waste to amount of product) is improved by about a factor of 10.

In 2011, Life Technologies implemented these greener synthetic routes for the full-scale production of dNTPs and their analogues at their Austin, Texas manufacturing site. Organic solvent consumption has been reduced by up to 95 percent and other hazardous waste up to 65 percent compared to conventional protocols. By improving the yields and specificity of reaction, process E-factor (the ratio of the mass of waste to the mass of product) has been reduced from approximately 3200 to 400, almost a full order of magnitude, leading to a savings of 1.5 million pounds of hazardous waste per year.

Greener Reaction Conditions Award

The Dow Chemical Company

EVOQUE™ Pre-Composite Polymer Technology

Innovation and Benefits

Titanium dioxide (TiO_2) is added to paint as the base white pigment that hides color on the painted surface. TiO_2 is energy intensive to make, so increasing the amount added increases the cost of paint as well as the emissions from TiO_2 production. Dow has developed a polymer that when applied to TiO_2 improves its dispersion, thus decreasing how much TiO_2 is needed.

Titanium dioxide (TiO_2) is added to most paint as the base white pigment that hides the color of the painted surface. TiO_2 is employed due to its high refractive index and light scattering power. However, the high levels of TiO_2 commonly found in paint formulations come at a cost to the paint formulator and the environment. TiO_2 is often the most costly and energy-consuming component in a can of paint, and has the largest impact on the eco-profile of the finished paint formulation.

Dow Chemical has developed a pre-composite polymer called EVOQUE™ that coats the TiO_2 particles and improves their dispersion in the paint, allowing better hiding at lower pigment loading. The polymers bind to the pigment, improve the pigment interaction with the rest of the paint formulation, and result in a more even, contiguous dry paint layer. Once dry, paints formulated with EVOQUE™ polymers provide better hiding, reducing the appearance of stains or colors on the painted surface and improved durability as a result of less pigment clumping.

EVOQUE™ polymers are compatible with a wide range of paint formulations, including zero-VOC waterborne paints, reduce the need for rheology additives, and allow up to 20 percent lower TiO_2 loading. A third-party validated Life Cycle Assessment (LCA) showed that TiO_2 reductions allowed by EVOQUE™ polymers in exterior house paint reduces the paint's carbon footprint by over 22 percent, water consumption by 30 percent, NO_x and SO_x emissions by 24 percent, and the potential impact on water eutrophication (algae bloom) by 27 percent. Other benefits found in the LCA include a 30 percent reduction in potential chemical oxygen demand (COD) and a 35 percent reduction in non-methanic volatile compounds, two factors that degrade water quality and air quality. These benefits are in addition to the improved performance of the paint.

Designing Greener Chemicals Award

Cargill, Inc.

Vegetable Oil Dielectric Insulating Fluid for High-Voltage Transformers

Innovation and Benefits

High-voltage electric transformers require an insulating fluid to prevent short circuiting and provide cooling. Polychlorinated biphenyls (PCBs) were used as transformer fluids until they were banned in the 1970s, and mineral oil became the primary replacement. Unfortunately, mineral oil is flammable and may be toxic to fish. Cargill has developed a vegetable-oil-based transformer fluid that is much less flammable, provides superior performance, is less toxic, and has a substantially lower carbon footprint.

High-voltage electric transformers must be filled with an insulating fluid that absorbs heat and prevents short-circuiting. For many years, most transformers were filled with polychlorinated biphenyls (PCBs) or, especially after PCBs were banned, petroleum-based mineral oil. While mineral oil is significantly less hazardous than PCBs, it is quite flammable and may be toxic to aquatic species. Furthermore, mineral oil is very hydrophobic, so any water in the system is taken up by the solid insulating material inside the transformer, usually cellulose (wood, paper, or cardboard). Cellulose degrades when exposed to water and the operating temperatures of a typical transformer. The service interval for transformers is largely dependent on the operational life of the solid cellulose insulators, so preventing the degradation of those insulators can significantly extend the service life of the transformer.

Cargill has developed Envirotemp™ FR3™ dielectric fluid based on vegetable oil instead of petroleum. These biobased oils can be used in replacement of mineral oil for retrofilling transformers. If used in newly designed transformers, the transformers can be made smaller owing to better thermal performance of Cargill's oils. The FR3™ fluid is significantly less flammable than mineral oil, greatly reducing the risk of fire or explosion. Cargill's oils also increase the service life of the cellulose insulation by 5-8 times longer than mineral oil thus extending the insulation life as well as the transformer life.

According to a lifecycle assessment using BEES® 4.0, a transformer using FR3™ fluid has a lower carbon footprint across the entire life-cycle of a transformer, with the largest reductions occurring in the raw materials, manufacturing, and transportation phases. The total carbon foot print of an electric transformer is about 55-times lower when using FR3™ fluid compared to mineral oil. This is all in addition to the low toxicity, high biodegradability, and the fact that FR3™ fluids are based on a renewable resource. Furthermore, there have been no known explosions or fires in the hundreds of thousands of transformers filled with FR3™ fluid since the product launched.

FR3™ fluid has achieved numerous industry validations including EPA's Environmental Technology Verification, the lowest environmental impact performance score in a BEES lifecycle assessment, USDA Bio-based Product certification, and certification as a less flammable fluid by both Underwriters Laboratory (UL) and Factory Mutual Research Corporation.

Academic Award

Professor Geoffrey W. Coates
Cornell University

Synthesizing Biodegradable Polymers from Carbon Dioxide and Carbon Monoxide

Innovation and Benefits

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

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

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

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

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

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

Academic Award

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

Organic Catalysis: A Broadly Useful Strategy for Green Polymer Chemistry

Innovation and Benefits

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

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

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

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

Small Business

Elevance Renewable Sciences, Inc.

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

Innovation and Benefits

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

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

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

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

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

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

Greener Synthetic Pathways Award

Codexis, Inc.
Professor Yi Tang, University of California, Los Angeles

An Efficient Biocatalytic Process to Manufacture Simvastatin

Innovation and Benefits

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

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

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

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

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

Greener Reaction Conditions Award

Cytec Industries Inc.

MAX HT® Bayer Sodalite Scale Inhibitor

Innovation and Benefits

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

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

Cytec developed its MAX HT® Bayer Sodalite Scale Inhibitor products for the Bayer process. There are no other scale inhibitors on the market for this application. The active polymeric ingredient contains silane functional groups that inhibit crystal growth by incorporation into the crystal or adsorption onto its surface. The polymers have molecular weights in the range 10,000 and 30,000. Their synthesis involves polymerizing a monomer containing a silane group or reacting polymer backbone with a reagent containing the silane group. Dosages range from 20 to 40 ppm. Assessments of these polymers under EPA's Sustainable Futures Program indicate low overall concern for human health and the aquatic environment.

Eliminating sodalite scale from heater surfaces has many benefits. Heat recovery from the steam produced in various unit operations is more efficient. Increased evaporation makes the countercurrent washing circuit more efficient and reduces caustic losses. Reducing the use of steam reduces emissions from burning carbon-based fuels. Finally, reducing the sulfuric acid used to clean heaters reduces both worker exposure and waste. Typically, MAX HT® inhibitor increases the on-stream time for a heater from 8–10 days to 45–60 days for digestion and from 20–30 days to over 150 days for evaporators.

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

Designing Greener Chemicals Award

Buckman International, Inc.

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

Innovation and Benefits

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

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

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

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

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

Academic Award

Professor Bruce H. Lipshutz
University of California, Santa Barbara

Towards Ending Our Dependence on Organic Solvents

Innovation and Benefits

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

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

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

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

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

BioAmber, Inc.

Integrated Production and Downstream Applications of Biobased Succinic Acid

Innovation and Benefits

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

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

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

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

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

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

Greener Synthetic Pathways Award

Genomatica

Production of Basic Chemicals from Renewable Feedstocks at Lower Cost

Innovation and Benefits

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

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

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

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

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

Greener Reaction Conditions Award

Kraton Performance Polymers, Inc.

NEXAR™ Polymer Membrane Technology

Innovation and Benefits

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

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

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

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

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

The Sherwin-Williams Company

Water-based Acrylic Alkyd Technology

Innovation and Benefits

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

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

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

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

2010 Winners

Academic Award

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

Recycling Carbon Dioxide to Biosynthesize Higher Alcohols

Innovation and Benefits

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

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

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

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

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

Small Business Award

LS9, Inc.

Microbial Production of Renewable Petroleum™ Fuels and Chemicals

Innovation and Benefits

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

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

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

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

Greener Synthetic Pathways Award

The Dow Chemical Company
BASF

Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide

Innovation and Benefits

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

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

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

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

Greener Reaction Conditions Award

Merck & Co., Inc.
Codexis, Inc.

Greener Manufacturing of Sitagliptin Enabled by an Evolved Transaminase

Innovation and Benefits

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

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

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

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

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

Clarke

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

Innovation and Benefits

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

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

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

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

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

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

2009 Winners

Academic Award

Professor Krzysztof Matyjaszewski
Carnegie Mellon University

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

Innovation and Benefits

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

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

Professor Matyjaszewski has been working continually to increase the environmental friendliness of his process. During the last four years, he and his team at CMU have developed new catalytic systems that dramatically decrease the concentration of transition metal, while preserving good control over polymerization and polymer architecture. The latest improvements are activators generated by electron transfer (AGET, 2004), activators regenerated by electron transfer (ARGET, 2005), and initiators for continuous activator regeneration (ICAR, 2006). These methods allow the preparation, storage, and use of the most active ATRP catalysts in their oxidatively stable state as well as their direct use under standard industrial conditions. The recent discovery of ARGET ATRP reduces the amount of copper catalyst from over 1,000 ppm to around 1 ppm in the presence of environmentally friendly reducing agents such as amines, sugars, or ascorbic acid. AGET and ARGET ATRP provide routes to pure block copolymers. The new processes allow oxidatively stable catalyst precursors to be used in aqueous homogeneous, dispersed (miniemulsion, inverse miniemulsion, microemulsion, emulsion, and suspension), and solventless bulk polymerizations. Professor Matyjaszewski's work is opening new "green" routes for producing many advanced polymeric materials.

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

Small Business Award

Virent Energy Systems, Inc.

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

Innovation and Benefits

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

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

Compared to other biomass conversion systems, Virent's technology broadens the range of viable feedstocks, provides more net energy, and produces fuels compatible with today's infrastructure. The process uses either food or non-food biomass; it is scalable to match feedstock supply. Unlike fermentation, Virent's robust process can use mixed sugar streams, polysaccharides, and C_5 and C_6 sugars derived from cellulosic biomass. By using more plant mass per acre, the process provides better land use and higher value for farmers. The technology needs little energy input and can be completely renewable. Virent's energy-dense biofuels separate naturally from water; as a result, the process eliminates the energy-intensive distillation to separate and collect biofuels required by other technologies. The hydrocarbon biofuels from Virent's process are interchangeable with petroleum products, matching them in composition, functionality, and performance; they work in today's engines, fuel pumps, and pipelines. Preliminary analysis suggests that Virent's BioForming® process can compete economically with petroleum-based fuels and chemicals at crude oil prices of $60 a barrel.

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

Greener Synthetic Pathways Award

Eastman Chemical Company

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

Innovation and Benefits

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

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

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

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

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

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

Greener Reaction Conditions Award

CEM Corporation

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

Innovation and Benefits

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

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

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

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

Designing Greener Chemicals Award

The Procter & Gamble Company
Cook Composites and Polymers Company

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

Innovation and Benefits

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

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

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

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

Academic Award

Professors Robert E. Maleczka, Jr. and Milton R. Smith, III
Michigan State University

Green Chemistry for Preparing Boronic Esters

Innovation and Benefits

One way to build complex molecules, such as pharmaceuticals and pesticides, is with a Suzuki "coupling" reaction. This versatile coupling reaction requires precursors with a carbon–boron bond. Making these precursors, however, typically requires harsh conditions and generates significant amounts of hazardous waste. Professors Maleczka and Smith developed a new catalytic method to make these compounds under mild conditions and with minimal waste and hazard. Their discovery allows the rapid, green manufacture of chemical building blocks, including some that had been commercially unavailable or environmentally unattractive.

"Coupling" reactions are one way to build valuable molecules, such as pharmaceuticals, pesticides, and similar complex substances. Coupling reactions connect two smaller molecules, usually through a new carbon–carbon (C–C) bond. A particularly powerful coupling reaction is the Suzuki coupling, which uses a molecule containing a carbon–boron bond to make a larger molecule through a new C–C bond. In fact, the Suzuki coupling is a well-established, mild, versatile method for constructing C–C bonds and has been reported to be the third most common C–C bond-forming reaction used to prepare drug candidates.

Chemical compounds with a carbon–boron bond are often prepared from the corresponding halides by Grignard or lithiate formation followed by reaction with trialkyl borate esters and hydrolytic workup. Miyaura improved this reaction with a palladium catalyst, but even this new reaction requires a halide precursor.

Several years ago, Professors Milton R. Smith, III and Robert E. Maleczka, Jr. began collaborating to find a "halogen-free" way to prepare the aryl and heteroaryl boronic esters that are the key building blocks for Suzuki couplings. Their collaboration builds upon Smith's invention of the first thermal, catalytic arene carbon–hydrogen bond (C–H) activation/borylation reaction. This led to transformations using iridium catalysts that are efficient, have high yields, and are tolerant of a variety of functional groups (alkyl, halo-, carboxy, alkoxy-, amino, etc.). Sterics, not electronics dictate the regiochemistry of the reactions. As a consequence, 1,3-substituted arenes give only 5-boryl (i.e., meta-substituted) products, even when both the 1- and 3-substituents are ortho/para directing. Just as significantly, the reactions are inherently clean as they can often be run without solvent, and they occur with hydrogen being the only coproduct. The success of these reactions has led Miyaura, Ishiyama, Hartwig, and others to use them as well.

In brief, catalytic C–H activation/borylation allows the direct construction of aryl boronic esters from hydrocarbon feedstocks in a single step, without aryl halide intermediates, without the limitations of the normal rules of aromatic substitution chemistry, and without many common functional group restrictions. Moreover, due to its mildness, the borylation chemistry combines readily in situ with subsequent chemical reactions.

This technology allows rapid, low-impact preparations of chemical building blocks that currently are commercially unavailable or only accessible by protracted, costly, and environmentally unattractive routes. Indeed, most recently, Michigan State University licensed the nominated technology to BoroPharm, Inc., which is using these catalytic borylations to produce much of the company's product line. Thus, the nominated technology is proving to be practical green chemistry beyond the laboratory bench.

Small Business Award

SiGNa Chemistry, Inc.

New Stabilized Alkali Metals for Safer, Sustainable Syntheses

Innovation and Benefits

Alkali metals, such as sodium and lithium, are powerful tools in synthetic chemistry because they are highly reactive. However, unless they are handled very carefully, their reactivity also makes them both flammable and explosive. SiGNa Chemistry developed a way to stabilize these metals by encapsulating them within porous, sand-like powders, while maintaining their usefulness in synthetic reactions. The stabilized metals are much safer to store, transport, and handle. They may also be useful for removing sulfur from fuels, storing hydrogen, and remediating a variety of hazardous wastes.

Alkali metals have a strong propensity for donating electrons, which makes these metals especially reactive. That reactivity has enormous potential for speeding chemical reactions throughout science and industry, possibly including new pathways to clean energy and environmental remediation. Unfortunately, that same reactivity also makes them highly unstable and dangerous to store and handle. In addition, increased risk of supply-chain interruption and the expense of handling these metals have made them unattractive to the chemical industry. Industries from pharmaceutical to petroleum have developed alternative synthetic routes to avoid using alkali metals, but these alternates require additional reactants and reaction steps that lead to inefficient, wasteful manufacturing processes.

SiGNa Chemistry addresses these problems with its technology for nanoscale absorption of reactive alkali metals in porous metal oxides. These new materials are sand-like powders. SiGNa's materials eliminate the danger and associated costs of using reactive metals directly but retain the utility of the alkali metals. Far from their hazardous precursors, SiGNa's materials react controllably with predictable activation that can be adapted to a variety of industry needs. By enabling practical chemical shortcuts and continuous flow processes, the encapsulated alkali metals create efficiencies in storage, supply chain, manpower, and waste disposal.

For the pharmaceutical, petrochemical, and general synthesis industries, SiGNa's breakthrough eliminates the additional steps that these industries usually take to avoid using the alkali metals and produces the desired reaction in 80–90 percent less time. For the pharmaceutical industry in particular, the materials can accelerate drug discovery and manufacturing while bolstering worker safety.

Beyond greening conventional chemical syntheses, SiGNa's materials enable the development of entirely new areas of chemistry. In clean-energy applications, the company's stabilized alkali metals safely produce record levels of pure hydrogen gas for the nascent fuel cell sector. With yield levels that already exceed the U.S. Department of Energy's targets for 2015, SiGNa's materials constitute the most effective means for processing water into hydrogen. SiGNa's materials also allow alkali metals to be safely applied to environmental remediation of oil contamination and the destruction of PCBs and CFCs.

SiGNa's success in increasing process efficiencies, health, and environmental safety and in enabling new chemical technologies has helped it attract more than 50 major global pharmaceutical, chemical, and energy companies as customers.

Greener Synthetic Pathways Award

Battelle

Development and Commercialization of Biobased Toners

Innovation and Benefits

Laser printers and copiers use over 400 million pounds of toner each year in the United States. Traditional toners fuse so tightly to paper that they are difficult to remove from waste paper for recycling. They are also made from petroleum-based starting materials. Battelle and its partners, Advanced Image Resources and the Ohio Soybean Council, have developed a soy-based toner that performs as well as traditional ones, but is much easier to remove. The new toner technology can save significant amounts of energy and allow more paper fiber to be recycled.

More than 400 million pounds of electrostatic dry toners based on petroleum-derived resins are used in the United States annually to make more than 3 trillion copies in photocopiers and printers. Conventional toners are based on synthetic resins such as styrene acrylates and styrene butadiene. These conventional resins make it difficult to remove the toner during recycling, a process called de-inking. This makes paper recycling more difficult. Although others have developed de-inkable toners, none of the competing technologies has become commercial due to high costs and inadequate de-inking performance.

With early-stage funding from the Ohio Soybean Council, Battelle and Advanced Image Resources (AIR) formed a team to develop and market biobased resins and toners for office copiers and printers. This novel technology uses soy oil and protein along with carbohydrates from corn as chemical feedstocks. Battelle developed bioderived polyester, polyamide, and polyurethane resins and toners from these feedstocks through innovative, cost-effective chemical modifications and processing, with the de-inking process in mind. By incorporating chemical groups that are susceptible to degradation during the standard de-inking process, Battelle created new inks that are significantly easier to remove from the paper fiber. AIR then scaled up the process with proprietary catalysts and conditions to make the new resins.

The new technology offers significant advantages in recycling waste office paper without sacrificing print quality. Improved de-inking of the fused ink from waste copy paper results in higher-quality recovered materials and streamlines the recycling process. Preliminary life-cycle analysis shows significant energy savings and reduced carbon dioxide (CO_2) emissions in the full value chain from resin manufacture using biobased feedstocks to toner production and, finally, to the recovery of secondary fibers from the office waste stream. At 25 percent market penetration in 2010, this technology could save 9.25 trillion British thermal units per year (Btu/yr) and eliminate over 360,000 tons of CO_2 emissions per year.

Overall, soy toner provides a cost-effective, systems-oriented, environmentally benign solution to the growing problem of waste paper generated from copiers and printers. In 2006, AIR, the licensee of the technology, successfully scaled up production of the resin and toners for use in HP LaserJet 4250 Laser Printer cartridges. Battelle and AIR coordinated to move from early-stage laboratory development to full-scale manufacturing and commercialization. Their efforts have resulted in a cost-competitive, highly marketable product that is compatible with current hardware. The new toner will be sold under trade names BioRez® and Rezilution®. Once commercial, it will provide users with seamless, environmentally friendly printing and copying.

Greener Reaction Conditions Award

Nalco Company

3D TRASAR® Technology

Innovation and Benefits

Cooling water touches many facets of human life, including cooling for comfort in commercial buildings and cooling industrial processes. Cooling systems require added chemicals to control microbial growth, mineral deposits, and corrosion. Nalco developed 3D TRASAR® technology to monitor the condition of cooling water continuously and add appropriate chemicals only when needed, rather than on a fixed schedule. The technique saves water and energy, minimizes the use of water-treatment chemicals, and decreases environmental damage from discharged water.

Most commercial buildings, including offices, universities, hospitals, and stores, as well as many industrial processes, use cooling systems based on water. These cooling systems can consume vast quantities of water. Also, unless mineral scale and microbes are well-controlled, several problems can arise leading to increased water and energy consumption and negative environmental impacts.

Mineral scale, which consists mostly of carbonates of calcium and magnesium, forms on heat-exchange surfaces; this makes heat transfer inefficient and increases energy use. Similarly, microbial growth can lead to the formation of biofilms on heat-exchange surfaces, decreasing exchange efficiency. Conversely, high levels of biocide intended to prevent biofilm cause several adverse effects including increased corrosion of system components. Gradually, the integrity of the system becomes compromised, increasing the risk of system leaks. The material from these leaks, along with metal-containing byproducts of corrosion and the additional biocide, are ultimately discharged with the cooling water. Every time water is discharged, called "blowdown", pollutants are released in the wastewater, and fresh water is used to replace the blowdown. Traditionally, antiscalants and antimicrobials are added at regular intervals or, at best, after manual or indirect measurements show scale or microbial buildup.

In 2004, Nalco commercialized its 3D TRASAR® Cooling System Chemistry and Control technology. By detecting scaling tendency early, cooling systems with Nalco's technology can operate efficiently; in addition, they can use less water or use poor-quality water.

3D Scale Control, part of the 3D TRASAR® system, prevents the formation of mineral scale on surfaces, maintaining efficient heat transfer. The system monitors antiscalant levels using a fluorescent-tagged, scale-dispersant polymer and responds quickly when conditions favor scale formation. In addition, 3D Bio-control, also part of the 3D TRASAR® system, is the only online, real-time test for measuring planktonic and sessile bacteria. It uses resazurin, another fluorescent molecule, which changes its fluorescent signature when it interacts with respiring microbes. By adding an oxidizing biocide in response to microbial activity, 3D Bio-control generally reduces the use of biocide and also prevents biofilm from building up on surfaces, maintaining efficient heat transfer.

A proprietary corrosion monitor and a novel corrosion inhibitor, phosphino succinic oligomer, provide improved corrosion protection. In 2006, the 2,500 installations using the 3D TRASAR® system saved approximately 21 billion gallons of water. These installations have also significantly reduced the discharge of water-treatment chemicals to water-treatment plants or natural waterways.

Designing Greener Chemicals Award

Dow AgroSciences LLC

Spinetoram: Enhancing a Natural Product for Insect Control

Innovation and Benefits

Spinosad biopesticide from Dow AgroSciences LLC controls many insect pests on vegetables, but is not particularly effective against certain key pests of tree fruits. To solve this problem, Dow AgroSciences LLC used an "artificial neural network" to identify analogous molecules that might be more effective against fruit-tree pests. They then developed a green chemical synthesis for the new insecticide, called spinetoram. Spinetoram retains the favorable environmental benefits of spinosad while replacing organophosphate pesticides for tree fruits, tree nuts, small fruits, and vegetables.

Spinosad biopesticide won the Presidential Green Chemistry Challenge Award for Designing Greener Chemicals in 1999. Spinosad, a combination of spinosyns A and D, is effective against insect pests on vegetables, but there have been few green chemistry alternatives for insect-pest control in tree fruits and tree nuts. Dow AgroSciences LLC has now developed spinetoram, a significant advancement over spinosad that extends the success of spinosad to new crops.

The discovery of spinetoram involved the novel application of an artificial neural network (ANN) to the molecular design of insecticides. Dow AgroSciences LLC researchers used an ANN to understand the quantitative structure-activity relationships of spinosyns and to predict analogues that would be more active. The result is spinetoram, a mixture of 3′-*O*-ethyl-5,6-dihydro spinosyn J and 3′-*O*-ethyl spinosyn L. Dow AgroSciences LLC makes spinetoram from naturally occurring fermentation products spinosyns J and L by modifying them with a low-impact synthesis in which catalysts and most reagents and solvents are recycled. The biology and chemistry of spinetoram have been extensively researched; the results have been published in peer-reviewed scientific journals and presented at scientific meetings globally.

Spinetoram provides significant and immediate benefits to human health and the environment over existing insecticides. Azinphos-methyl and phosmet, two organophosphate insecticides, are widely used in pome fruits (such as apples and pears), stone fruits (such as cherries and peaches), and tree nuts (such as walnuts and pecans). The mammalian acute oral toxicity of spinetoram is more than 1,000 times lower than that of azinphos-methyl and 44 times lower than that of phosmet. The low toxicity of spinetoram reduces the risk of exposures throughout the supply chain: in manufacturing, transportation, and application and to the public.

Spinetoram has a lower environmental impact than do many current insecticides because both its use rate and its toxicity to non-target species are low. Spinetoram is effective at much lower rates than many competing insecticides. It is effective at use rates that are 10–34 times lower than azinphos-methyl and phosmet. Spinetoram is also less persistent in the environment compared with other traditional insecticides. In the United States alone, Dow AgroSciences LLC expects spinetoram to eliminate about 1.8 million pounds of organophosphate insecticides applied to pome fruit, stone fruit, and tree nuts during its first five years of use. In 2007, EPA granted pesticide registrations to the spinetoram products Radiant™ and Delegate™, and Dow AgroSciences LLC began commercial sales.

2007 Winners

Academic Award

Professor Michael J. Krische
University of Texas at Austin

Hydrogen-Mediated Carbon—Carbon Bond Formation

Innovation and Benefits

A fundamental aspect of chemistry involves creating chemical bonds between carbon atoms. Chemical processes commonly used to make such bonds usually also generate significant amounts of waste. Professor Krische developed a broad new class of chemical reactions that make bonds between carbon atoms using hydrogen and metal catalysts. This new class of reactions can be used to convert simple chemicals into complex substances, such as pharmaceuticals, pesticides, and other important chemicals, with minimal waste.

Reductions mediated by hydrogen, termed "hydrogenations", rank among the most widely used catalytic methods employed industrially. They are generally used to form carbon–hydrogen (C–H) bonds. Professor Michael J. Krische and his coworkers at the University of Texas at Austin have developed a new class of hydrogenation reactions that form carbon–carbon (C–C) bonds. In these metal-catalyzed reactions, two or more organic molecules combine with hydrogen gas to create a single, more complex product. Because all atoms present in the starting building-block molecules appear in the final product, Professor Krische's reactions do not generate any byproducts or wastes. Hence, Professor Krische's C–C bond-forming hydrogenations eliminate pollution at its source.

Prior to Professor Krische's work, hydrogen-mediated C–C bond formations were limited almost exclusively to the use of carbon monoxide in reactions such as alkene hydroformylation (1938) and the Fischer-Tropsch reaction (1923). These prototypical hydrogen-mediated C–C bond formations are practiced industrially on an enormous scale. Yet, despite the importance of these reactions, no one had engaged in systematic research to develop related C–C bond-forming hydrogenations. Only a small fraction of hydrogenation's potential as a method of C–C coupling had been realized, and the field lay fallow for nearly 70 years.

Professor Krische's hydrogen-mediated couplings circumvent the use of preformed organometallic reagents, such as Grignard and Gilman reagents, in carbonyl and imine addition reactions. Such organometallic reagents are highly reactive, typically moisture-sensitive, and sometimes pyrophoric, meaning that they combust when exposed to air. Professor Krische's coupling reactions take advantage of catalysts that avoid the hazards of traditional organometallic reagents. Further, using chiral hydrogenation catalysts, Professor Krische's couplings generate C–C bonds in a highly enantioselective fashion.

Catalytic hydrogenation has been known for over a century and has stood the test of time due its efficiency, atom economy, and cost-effectiveness. By exploiting hydrogenation as a method of C–C bond formation, Professor Krische has added a broad, new dimension to one of chemistry's most fundamental catalytic processes. The C–C bond-forming hydrogenations developed by Professor Krische allow chemists to create complex organic molecules in a highly selective fashion, eliminating both hazardous starting materials and hazardous waste. Commercial application of this technology may eliminate vast quantities of hazardous chemicals. The resulting increases in plant and worker safety may enable industry to perform chemical transformations that were too dangerous using traditional reagents.

Small Business Award

NovaSterilis Inc.

Environmentally Benign Medical Sterilization Using Supercritical Carbon Dioxide

Innovation and Benefits

Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilization techniques use ethylene oxide or gamma radiation, which are toxic or have safety problems. NovaSterilis invented a technology that uses carbon dioxide and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor gamma radiation.

None of the common methods for medical sterilization is well-suited to sterilizing delicate biological materials. The sterility of these materials is critical. Distribution of contaminated donor tissues by tissue banks has resulted in serious infections and illnesses in transplant patients. The two most widely used sterilants (ethylene oxide and gamma radiation) also raise toxicity and safety concerns. Ethylene oxide is a mutagenic, carcinogenic, volatile, flammable, reactive gas. Residues of ethylene oxide remain in the sterilized material, increasing the risk of toxic side effects. Gamma radiation is highly penetrating and is lethal to all cells. Neither ethylene oxide nor gamma radiation can sterilize packaged biological products without eroding their physical integrity.

NovaSterilis, a privately held biotechnology company in Ithaca, NY, has successfully developed and commercialized a highly effective and environmentally benign technique for sterilizing delicate biological materials using supercritical carbon dioxide (CO_2). NovaSterilis licensed a patent for bacterial inactivation in biodegradable polymers that was issued to Professor Robert S. Langer and his team at the Massachusetts Institute of Technology. NovaSterilis then enhanced, expanded, and optimized the technology to kill bacterial endospores. Their supercritical CO_2 technology uses low temperature and cycles of moderate pressure along with a peroxide (peracetic acid) and small amounts of water. Their Nova 2200™ sterilizer consistently achieves rapid (less than one hour) and total inactivation of a wide range of microbes, including bacterial endospores. The mechanism of bacterial inactivation is not well-understood, but does not appear to involve bacterial cell lysis or wholesale degradation of bacterial proteins.

The new technology is compatible with sensitive biological materials and is effective for a wide range of important biomedical materials including: (a) musculoskeletal allograft tissue (e.g., human bone, tendons, dermis, and heart valves) for transplantation; (b) biodegradable polymers and related materials used in medical devices, instruments, and drugs; (c) drug delivery systems; and (d) whole-cell vaccines that retain high antigenicity. Besides being a green chemical technology, supercritical CO_2 sterilization achieves "terminal" sterilization, that is, sterilization of the final packaged product. Terminal sterilization provides greater assurance of sterility than traditional methods of aseptic processing. Sterilization of double-bagged tissue allows tissue banks to ship terminally sterilized musculoskeletal tissues in packages that can be opened in operating rooms by surgical teams immediately prior to use. NovaSterilis's patented technology addresses the market need in tissue banks as well as other needs in the biomedical, biologics, medical device, pharmaceutical, and vaccine industries. By the end of 2006, NovaSterilis had sold several units to tissue banks.

Greener Synthetic Pathways Award

Professor Kaichang Li, Oregon State University
Columbia Forest Products
Hercules Incorporated (now Ashland Inc.)

Development and Commercial Application of Environmentally Friendly Adhesives for Wood Composites

Innovation and Benefits

Adhesives used in manufacturing plywood and other wood composites often contain formaldehyde, which is toxic. Professor Kaichang Li of Oregon State University, Columbia Forest Products, and Hercules Incorporated developed an alternate adhesive made from soy flour. Their environmentally friendly adhesive is stronger than and cost-competitive with conventional adhesives. During 2006, Columbia used the new, soy-based adhesive to replace more than 47 million pounds of conventional formaldehyde-based adhesives.

Since the 1940s, the wood composites industry has been using synthetic adhesive resins to bind wood pieces into composites, such as plywood, particleboard, and fiberboard. The industry has been the predominate user of formaldehyde-based adhesives such as phenol–formaldehyde and urea–formaldehyde (UF) resins. Formaldehyde is a probable human carcinogen. The manufacture and use of wood composite panels bonded with formaldehyde-based resins release formaldehyde into the air, creating hazards for both workers and consumers.

Inspired by the superior properties of the protein that mussels use to adhere to rocks, Professor Li and his group at Oregon State University invented environmentally friendly wood adhesives based on abundant, renewable soy flour. Professor Li modified some of the amino acids in soy protein to resemble those of mussels' adhesive protein. Hercules Incorporated provided a critical curing agent and the expertise to apply it to commercial production of plywood.

Oregon State University, Columbia Forest Products (CFP), and Hercules have jointly commercialized soy-based adhesives to produce cost-competitive plywood and particleboard for interior uses. The soy-based adhesives do not contain formaldehyde or use formaldehyde as a raw material. They are environmentally friendly, cost-competitive with the UF resin in plywood, and superior to the UF resin in strength and water resistance. All CFP plywood plants now use soy-based adhesives, replacing more than 47 million pounds of the toxic UF resin in 2006 and reducing the emission of hazardous air pollutants (HAPs) from each CFP plant by 50 to 90 percent. This new CFP plywood is sold under the PureBond™ name. During 2007, CFP will replace UF at its particleboard plant; the company is also seeking arrangements with other manufacturers to further the adoption of this technology.

With this technology, those who make and use furniture, kitchen cabinetry, and other wood composite materials have a high-performing formaldehyde-free alternative. As a result, indoor air quality in homes and offices could improve significantly. This technology represents the first cost-competitive, environmentally friendly adhesive that can replace the toxic UF resin. The technology can greatly enhance the global competitiveness of U.S. wood composite companies. In addition, by creating a new market for soy flour, currently in over-supply, this technology provides economic benefits for soybean farmers.

Greener Reaction Conditions Award

Headwaters Technology Innovation

Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

Innovation and Benefits

Hydrogen peroxide is an environmentally friendly alternative to chlorine and chlorine-containing bleaches and oxidants. It is expensive, however, and its current manufacturing process involves the use of hazardous chemicals. Headwaters Technology Innovation (HTI) developed an advanced metal catalyst that makes hydrogen peroxide directly from hydrogen and oxygen, eliminates the use of hazardous chemicals, and produces water as the only byproduct. HTI has demonstrated their new technology and is partnering with Degussa AG to build plants to produce hydrogen peroxide.

Hydrogen peroxide (H_2O_2) is a clean, versatile, environmentally friendly oxidant that can substitute for environmentally harmful chlorinated oxidants in many manufacturing operations. However, the existing manufacturing process for H_2O_2 is complex, expensive, and energy-intensive. This process requires an anthraquinone working solution containing several toxic chemicals. The solution is reduced by hydrogen in the presence of a catalyst, forming anthrahydroquinone, which then reacts with oxygen to release H_2O_2. The H_2O_2 is removed from the solution with an energy-intensive stripping column and then concentrated by vacuum distillation. The bulk of the working solution is recycled, but the process generates a waste stream of undesirable quinone-derived byproducts that requires environmentally acceptable disposal.

Headwaters Technology Innovation (HTI) has produced a robust catalyst technology that enables the synthesis of H_2O_2 directly from hydrogen and oxygen. This breakthrough technology, called NxCat™, is a palladium-platinum catalyst that eliminates all the hazardous reaction conditions and chemicals of the existing process, along with its undesirable byproducts. It produces H_2O_2 more efficiently, cutting both energy use and costs. It uses innocuous, renewable feedstocks and generates no toxic waste.

NxCat™ catalysts work because of their precisely controlled surface morphology. HTI has engineered a set of molecular templates and substrates that maintain control of the catalyst's crystal structure, particle size, composition, dispersion, and stability. This catalyst has a uniform 4-nanometer feature size that safely enables a high rate of production with a hydrogen gas concentration below 4 percent in air (i.e., below the flammability limit of hydrogen). It also maximizes the selectivity for H_2O_2 up to 100 percent.

The NxCat™ technology enables a simple, commercially viable H_2O_2 manufacturing process. In partnership with Degussa AG (a major H_2O_2 manufacturer), HTI successfully demonstrated the NxCat™ technology and, in 2006, completed construction of a demonstration plant. This demonstration plant will allow the partners to collect the data necessary to design a full-scale plant and begin commercial production in 2009. The NxCat™ process has the potential to cut the cost of H_2O_2 significantly, generating a more competitively priced supply of H_2O_2 and increasing its market acceptance as an industrial oxidant. Except for its historically higher price, H_2O_2 is an excellent substitute for the more frequently used—and far more deleterious—chlorinated oxidants. The NxCat™ technology has the benefit of producing an effective, environmentally preferable oxidant (H_2O_2) without the waste or high cost associated with the traditional process.

Designing Greener Chemicals Award

Cargill, Incorporated

BiOH™ Polyols

Innovation and Benefits

Foam cushioning used in furniture or bedding is made from polyurethane, a man-made material. One of the two chemical building blocks used to make polyurethane is a "polyol." Polyols are conventionally manufactured from petroleum products. Cargill's BiOH™ polyols are manufactured from renewable, biological sources such as vegetable oils. Foams made with BiOH™ polyols are comparable to foams made from conventional polyols. As a result, each million pounds of BiOH™ polyols saves nearly 700,000 pounds of crude oil. In addition, Cargill's process reduces total energy use by 23 percent and carbon dioxide emissions by 36 percent.

Polyols are key ingredients in flexible polyurethane foams, which are used in furniture and bedding. Historically, polyurethane has been made from petrochemical polyols. The idea of replacing these polyols with biobased polyols is not new, but the poor performance, color, quality, consistency, and odor of previous biobased polyols restricted them to limited markets. Previous biobased polyols also suffer from poor chemical reactivity, resulting in foam with inferior properties.

Cargill has successfully developed biobased polyols for several polyurethane applications, including flexible foams, which are the most technically challenging. Cargill makes BiOH™ polyols by converting the carbon–carbon double bonds in unsaturated vegetable oils to epoxide derivatives and then further converting these derivatives to polyols using mild temperature and ambient pressure. BiOH™ polyols provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams. These foams set a new standard for consistent quality with low odor and color. Foams containing BiOH™ polyols retain their white color longer without ultraviolet stabilizers. They also are superior to foams containing only petroleum-based polyols in standard tests. In large slabstock foams, such as those used in furniture and bedding, BiOH 5000 polyol provides a wide processing window, improved comfort factor, and reduced variations in density and load-bearing capacity. In molded foams such as automotive seating and headrests, BiOH 2100 polyol can enhance load-bearing or hardness properties relative to conventional polyols.

Use of BiOH™ polyols reduces the environmental footprint relative to today's conventional polyols for polyurethane production. BiOH™ polyols "harvest" carbon that plants remove from the air during photosynthesis. All of the carbon in BiOH™ polyols is recently fixed. In conventional polyols, the carbon is petroleum-based. Replacing petroleum-based polyols with BiOH™ polyols cuts total energy use by 23 percent including a 61 percent reduction in nonrenewable energy use, leading to a 36 percent reduction in carbon dioxide emissions. For each million pounds of BiOH™ polyol used in place of petroleum-based polyols, about 700,000 pounds (2,200 barrels) of crude oil are saved, thereby reducing the dependence on petroleum. BiOH™ polyols diversify the industry's supply options and help mitigate the effects of uncertainty and volatility of petroleum supply and pricing. Cargill is the first company to commercialize biobased polyols on a large scale in the flexible foam market. Formulators can now use biobased polyols in flexible foam without compromising product performance. That the top North American polyol users choose BiOH™ polyols is validation of Cargill's accomplishment.

Academic Award

Professor Galen J. Suppes

University of Missouri-Columbia

Biobased Propylene Glycol and Monomers from Natural Glycerin

Innovation and Benefits

Professor Suppes developed an inexpensive method to convert waste glycerin, a byproduct of biodiesel fuel production, into propylene glycol, which can replace ethylene glycol in automotive antifreeze. This high-value use of the glycerin byproduct can keep production costs down and help biodiesel become a cost-effective, viable alternative fuel, thereby reducing emissions and conserving fossil fuels.

Glycerin is a coproduct of biodiesel production. The U.S. biodiesel industry is expected to introduce one billion pounds of additional glycerin into a market that is currently only 600 million pounds. The economics of biodiesel depend heavily on using its glycerin coproduct. A high-value use for glycerin could reduce the cost of biodiesel by as much as 40¢ per gallon. There is simply not enough demand for glycerin, however, to make use of all the waste glycerin expected.

One solution is to convert the glycerin to propylene glycol. Approximately 2.4 billion pounds of propylene glycol are currently made each year, almost exclusively from petroleum-based propylene oxide. Propylene glycol is a less toxic alternative to ethylene glycol in antifreeze, but is currently more expensive and, as a result, has a very small market share. Professor Galen J. Suppes has developed a catalytic process that efficiently converts crude glycerin to propylene glycol.

Professor Suppes's system couples a new copper-chromite catalyst with a reactive distillation. This system has a number of advantages over previous systems that perform this conversion. The new process uses a lower temperature and lower pressure than do previous systems (428 °F versus 500 °F and <145 psi versus >2,170 psi), converts glycerin to propylene glycol more efficiently, and produces less byproduct than do similar catalysts. Propylene glycol made from glycerin by Professor Suppes's method is also significantly cheaper than propylene glycol made from petroleum.

Another solution is to convert glycerin to acetol (i.e., 1-hydroxy-2-propanone or hydroxyacetone), a well-known intermediate and monomer used to make polyols. When made from petroleum, acetol costs approximately $5 per pound, prohibiting its wide use. Professor Suppes's technology can be used to make acetol from glycerin at a cost of approximately 50¢ per pound, opening up even more potential applications and markets for products made from glycerin.

Professor Suppes initiated this project in June 2003. The first commercial facility, with a capacity of 50 million pounds per year, is under construction and is expected to be in operation by October 2006.

Small Business Award

Arkon Consultants
NuPro Technologies, Inc. (now Eastman Kodak Company)

Environmentally Safe Solvents and Reclamation in the Flexographic Printing Industry

Innovation and Benefits

Flexographic printing is used in a wide array of print jobs such as food wrappers and boxes, but the process uses millions of gallons of solvents each year. Arkon and NuPro developed a safer chemical processing system that reduces the amounts of solvents needed for printing. The new system eliminates hazardous solvents, reduces explosion potential and emissions during solvent recycling, and increases worker safety in the flexographic printing industry.

Flexographic printing is used on everything from food wrappers to secondary containers such as cereal boxes to shipping cartons. The photopolymerizable material on a flexographic printing plate cross-links when exposed to light and captures an image. After exposure, flexographic printing plates are immersed in a solvent to remove the unpolymerized material. The developing, or washout, solvent is typically a mixture of chloro, saturated cyclic, or acyclic hydrocarbons. Xylene is the most common solvent. Most traditional washout solvents are hazardous air pollutants (HAPs) subject to stringent reporting requirements; they also raise worker safety issues and create problems with recycling and disposal. North America alone uses 2 million gallons of washout solvents each year with a market value of $20 million. Many small printing plants use these solvents.

Together, Arkon Consultants and NuPro Technologies have developed a safer chemical processing system, including washout solvents and reclamation/recycling machinery for the flexographic printing industry. NuPro/Arkon have developed several new classes of washout solvents with methyl esters, terpene derivatives, and highly substituted cyclic hydrocarbons. The advantages include higher flash points and lower toxicity, which reduce explosion potential, worker exposure, and regulatory reporting. The methyl esters and terpene derivatives are biodegradable and can be manufactured from renewable sources. All of their solvents are designed to be recycled in their Cold Reclaim System™. In contrast to traditional vacuum distillation, this combination of filtration and centrifugation lowers exposures, decreases maintenance, and reduces waste. The waste is a solid, nonhazardous polymeric material.

In the U.S. market, NuPro/Arkon are currently selling washout solvents that are terpene ether- and ester-based or made with low-hazard cyclics. They are marketing their methyl ester-based solvent in China and Japan. Their first filtration-based Cold Recovery System™ is currently in use in Menesha, WI and is being marketed to larger U.S. users. Their centrifugation reclamation system for smaller users is in the final stages of development.

Use of these solvents and systems benefits both human health and the environment by lowering exposure to hazardous materials, reducing explosion potential, reducing emissions, and, in the case of the terpene and methyl ester-based solvents, using renewable resources. These solvents and the reclamation equipment represent major innovations in the safety of handling, exposure, and recovery. The reduced explosion potential, reduced emissions, decreased worker exposure, and reduced transport and maintenance costs translate into decreased cost and improved safety in all aspects of flexographic printing processes.

Greener Synthetic Pathways Award

Merck & Co., Inc.

Novel Green Synthesis for β-Amino Acids Produces the Active Ingredient in Januvia™

Innovation and Benefits

Merck discovered a highly innovative and efficient catalytic synthesis for sitagliptin, which is the active ingredient in Januvia™, the company's new treatment for type 2 diabetes. This revolutionary synthesis creates 220 pounds less waste for each pound of sitagliptin manufactured and increases the overall yield by nearly 50 percent. Over the lifetime of Januvia™, Merck expects to eliminate the formation of at least 330 million pounds of waste, including nearly 110 million pounds of aqueous waste.

Januvia™ is a new treatment for type 2 diabetes; Merck filed for regulatory approval in December 2005. Sitagliptin, a chiral β-amino acid derivative, is the active ingredient in Januvia™. Merck used a first-generation synthesis of sitagliptin to prepare over 200 pounds for clinical trials. With modifications, this synthesis could have been a viable manufacturing process, but it required eight steps including a number of aqueous work-ups. It also required several high-molecular-weight reagents that were not incorporated into the final molecule and, therefore, ended up as waste.

While developing a highly efficient second-generation synthesis for sitagliptin, Merck researchers discovered a completely unprecedented transformation: the asymmetric catalytic hydrogenation of unprotected enamines. In collaboration with Solvias, a company with expertise in this area, Merck scientists discovered that hydrogenation of unprotected enamines using rhodium salts of a ferrocenyl-based ligand as the catalyst gives β-amino acid derivatives of high optical purity and yield. This new method provides a general synthesis of β-amino acids, a class of molecules well-known for interesting biological properties. Merck scientists and engineers applied this new method in a completely novel way: using it in the final synthetic step to maximize the yield in terms of the valuable chiral catalyst. The dehydro precursor to sitagliptin used in the asymmetric hydrogenation is prepared in an essentially one-pot procedure. Following the hydrogenation, Merck recovers and recycles over 95 percent of the valuable rhodium. The reactive amino group of sitagliptin is only revealed in the final step; as a result, there is no need for protecting groups. The new synthesis has only three steps and increases the overall yield by nearly 50 percent.

This strategy is broadly applicable to other pharmaceutical syntheses; Merck has used it to make several exploratory drug candidates. Implementing the new route on a manufacturing scale has reduced the amount of waste by over 80 percent and completely eliminated aqueous waste streams. This second-generation synthesis will create 220 pounds less waste for each pound of sitagliptin manufactured. Over the lifetime of the drug, Merck expects to eliminate the formation of 330 million pounds or more of waste, including nearly 110 million pounds of aqueous waste. Because Merck's new synthesis has reduced the amount of raw materials, processing time, energy, and waste, it is a more cost-effective option than the first-generation synthesis. The technology discovered, developed, and implemented by Merck for the manufacture of Januvia™ is an excellent example of scientific innovation resulting in benefits to the environment.

Greener Reaction Conditions Award

Codexis, Inc.

Directed Evolution of Three Biocatalysts to Produce the Key Chiral Building Block for Atorvastatin, the Active Ingredient in Lipitor®

Innovation and Benefits

Codexis developed cutting-edge genetic methods to create "designer enzymes". Codexis applied its methods to produce enzymes that greatly improve the manufacture of the key building block for Lipitor®, one of the world's best-selling drugs. The new enzymatic process reduces waste, uses less solvent, and requires less processing equipment—marked improvements over processes used in the past. The process also increases yield and improves worker safety.

Atorvastatin calcium is the active ingredient of Lipitor®, a drug that lowers cholesterol by blocking its synthesis in the liver. Lipitor® is the first drug in the world with annual sales exceeding $10 billion. The key chiral building block in the synthesis of atorvastatin is ethyl (*R*)-4-cyano-3-hydroxybutyrate, known as hydroxynitrile (HN). Annual demand for HN is estimated to be about 440,000 pounds. Traditional commercial processes for HN require a resolution step with 50 percent maximum yield or syntheses from chiral pool precursors; they also require hydrogen bromide to generate a bromohydrin for cyanation. All previous commercial HN processes ultimately substitute cyanide for halide under heated alkaline conditions, forming extensive byproducts. They require a difficult high-vacuum fractional distillation to purify the final product, which decreases the yield even further.

Codexis designed a green HN process around the exquisite selectivity of enzymes and their ability to catalyze reactions under mild, neutral conditions to yield high-quality products. Codexis developed three specific enzymes using state-of-the-art, recombinant-based, directed evolution technologies to provide the activity, selectivity, and stability required for a practical and economic process. The bioengineered enzymes are so active and stable that Codexis can recover high-quality product by extracting the reaction mixture. In the first step, two of the enzymes catalyze the enantioselective reduction of a prochiral chloroketone (ethyl 4-chloroacetoacetate) by glucose to form an enantiopure chlorohydrin. In the second step, a third enzyme catalyzes the novel biocatalytic cyanation of the chlorohydrin to the cyanohydrin under neutral conditions (aqueous, pH ~7, 77–104 °F, atmospheric pressure). On a biocatalyst basis, the three enzymes have improved the volumetric productivity of the reduction reaction by approximately 100-fold and that of the cyanation reaction by approximately 4,000-fold.

The process involves fewer unit operations than earlier processes, most notably obviating the fractional distillation of the product. The process provides environmental and human health benefits by increasing yield, reducing the formation of byproducts, reducing the generation of waste, avoiding hydrogen gas, reducing the need for solvents, reducing the use of purification equipment, and increasing worker safety. The Codexis process is operated by Lonza to manufacture HN for Pfizer's production of atorvastatin calcium.

Designing Greener Chemicals Award

S.C. Johnson & Son, Inc.

Greenlist™ Process to Reformulate Consumer Products

Innovation and Benefits

S.C. Johnson developed Greenlist™, a system that rates the environmental and health effects of the ingredients in its products. S.C. Johnson is now using Greenlist™ to reformulate many of its products. For example, S.C. Johnson eliminated the use of nearly 4 million pounds of polyvinylidene chloride (PVDC) annually after its "Greenlist" review of Saran Wrap® revealed opportunities for changes.

S.C. Johnson (SCJ) formulates and manufactures consumer products including a wide variety of products for home cleaning, air care, personal care, insect control, and home storage. For more than a century, SCJ has been guided by the belief that, because it is a family business, it must consider the next generation when it makes current product decisions, not merely the next fiscal quarter. The most recent initiative in SCJ's long history of commitment to environmentally preferable products is its Greenlist™ process, a system that rates the environmental footprint of the ingredients in its products. Through Greenlist™, SCJ chemists and product formulators around the globe have instant access to environmental ratings of potential product ingredients.

Starting in 2001, SCJ developed Greenlist™ according to the rigorous standards of scientific best practices. Greenlist™ uses four to seven specific criteria to rate ingredients within 17 functional categories. SCJ enlisted the help of suppliers, university scientists, government agencies, and nongovernmental organizations (NGOs) to ensure that the rating criteria were meaningful, objective, and valid. These criteria include vapor pressure, octanol/water partition coefficient, biodegradability, aquatic toxicity, human toxicity, European Union Classification, source/supply, and others, as appropriate. The Greenlist™ process assigns an environmental classification (EC) score to each ingredient by averaging its scores for the criteria in its category. EC scores range from Best (3) to Restricted Use Material (0). SCJ lowers the EC score for chemicals with other significant concerns including PBT (persistence, bioaccumulation, and toxicity), endocrine disruption, carcinogenicity, and reproductive toxicity. Today, Greenlist™ provides ratings for more than 90 percent of the raw materials SCJ uses, including solvents, surfactants, inorganic acids and bases, chelants, propellants, preservatives, insecticides, fragrances, waxes, resins, nonwoven fabrics, and packaging. Company scientists have also developed criteria for dyes, colorants, and thickeners and are working on additional categories as well.

During fiscal 2000-2001, the baseline year, SCJ's EC average was 1.12. Their goal was to reach an average EC of 1.40 during fiscal 2007–2008. The company reached this goal three years early, with an average EC of 1.41 covering almost 1.4 billion pounds of raw materials.

In recent years, SCJ has used Greenlist™ to reformulate multiple products to make them safer and more environmentally responsible. In one example, SCJ used the Greenlist™ process to replace polyvinylidene chloride (PVDC) with polyethylene in Saran Wrap®. In another example, SCJ applied Greenlist™ to remove a particular volatile organic compound (VOC) from Windex®. They developed a novel new formula containing amphoteric and anionic surfactants, a solvent system with fewer than 4 percent VOCs, and a polymer for superior wetting. Their formula cleans 30 percent better and eliminates over 1.8 million pounds of VOCs per year.

Academic Award

Professor Robin D. Rogers
The University of Alabama

A Platform Strategy Using Ionic Liquids to Dissolve and Process Cellulose for Advanced New Materials

Innovation and Benefits

Professor Rogers developed methods that allow cellulose from wood, cloth, or even paper to be chemically modified to make new biorenewable or biocompatible materials. His methods also allow cellulose to be mixed with other substances, such as dyes, or simply to be processed directly from solution into a formed shape. Together, these methods can potentially save resources, time, and energy.

Major chemical companies are currently making tremendous strides towards using renewable resources in biorefineries. In a typical biorefinery, the complexity of natural polymers, such as cellulose, is first broken down into simple building blocks (e.g., ethanol, lactic acid), then built up into complex polymers. If one could use the biocomplexity of natural polymers to form new materials directly, however, one could eliminate many destructive and constructive synthetic steps. Professor Robin D. Rogers and his group have successfully demonstrated a platform strategy to efficiently exploit the biocomplexity afforded by one of Nature's renewable polymers, cellulose, potentially reducing society's dependence on nonrenewable petroleum-based feedstocks for synthetic polymers. No one had exploited the full potential of cellulose previously, due in part to the shift towards petroleum-based polymers since the 1940s, difficulty in modifying the cellulose polymer properties, and the limited number of common solvents for cellulose.

Professor Rogers's technology combines two major principles of green chemistry: developing environmentally preferable solvents and using biorenewable feedstocks to form advanced materials. Professor Rogers has found that cellulose from virtually any source (fibrous, amorphous, pulp, cotton, bacterial, filter paper, etc.) can be dissolved readily and rapidly, without derivatization, in a low-melting ionic liquid (IL), 1-butyl-3-methylimidazolium chloride ([C4mim]Cl), by gentle heating (especially with microwaves). IL-dissolved cellulose can easily be reconstituted in water in controlled architectures (fibers, membranes, beads, flocs, etc.) using conventional extrusion spinning or forming techniques. By incorporating functional additives into the solution before reconstitution, Professor Rogers can prepare blended or composite materials. The incorporated functional additives can be either dissolved (e.g., dyes, complexants, other polymers) or dispersed (e.g., nanoparticles, clays, enzymes) in the IL before or after dissolution of the cellulose. With this simple, noncovalent approach, Professor Rogers can readily prepare encapsulated cellulose composites of tunable architecture, functionality, and rheology. The IL can be recycled by a novel salting-out step or by common cation exchange, both of which save energy compared to recycling by distillation. Professor Rogers's current work is aimed at improved, more efficient, and economical syntheses of [C4mim]Cl, studies of the IL toxicology, engineering process development, and commercialization.

Professor Rogers and his group are currently doing market research and business planning leading to the commercialization of targeted materials, either through joint development agreements with existing chemical companies or through the creation of small businesses. Green chemistry principles will guide the development work and product selection. For example, targeting polypropylene- and polyethylene-derived thermoplastic materials for the automotive industry could result in materials with lower cost, greater flexibility, lower weight, lower abrasion, lower toxicity, and improved biodegradability, as well as significant reductions in the use of petroleum-derived plastics.

Professor Rogers's work allows the novel use of ILs to dissolve and reconstitute cellulose and similar polymers. Using green chemistry principles to guide development and commercialization, he envisions that his platform strategy can lead to a variety of commercially viable advanced materials that will obviate or reduce the use of synthetic polymers.

Small Business Award

Metabolix, Inc.

Producing Nature's Plastics Using Biotechnology

Innovation and Benefits

Metabolix used new biotechnology methods to develop microorganisms that produce polyhydroxyalkanoates (PHAs) directly. PHAs are natural plastics with a range of environmental benefits, including reduced reliance on fossil carbon, reduced solid waste, and reduced greenhouse gas emissions. PHAs biodegrade to harmless products in the environment, reducing the burden of plastic waste on landfills and the environment. Metabolix hopes to develop plants that produce PHAs as well.

Metabolix is commercializing polyhydroxyalkanoates (PHAs), a broadly useful family of natural, environmentally friendly, high-performing, bio-based plastics. PHAs are based on a biocatalytic process that uses renewable feedstocks, such as cornstarch, cane sugar, cellulose hydrolysate, and vegetable oils. PHAs can provide a sustainable alternative to petrochemical plastics in a wide variety of applications.

Metabolix uses biotechnology to introduce entire enzyme-catalyzed reaction pathways into microbes, which then produce PHAs, in effect creating living biocatalysts. The performance of these engineered microbes has been fully validated in commercial equipment, demonstrating reliable production of a wide range of PHA copolymers at high yield and reproducibility. A highly efficient commercial process to recover PHAs has also been developed and demonstrated. The routine expression of exogenous, chromosomally integrated genes coding for the enzymes used in a non-native metabolic pathway is a tour de force in the application of biotechnology. These accomplishments have led Metabolix to form an alliance with Archer Daniels Midland Company, announced in November 2004, to produce PHAs commercially, starting with a 100-million-pound-per-year plant to be sited in the U.S. Midwest.

These new natural PHA plastics are highly versatile, have a broad range of physical properties, and are practical alternatives to synthetic petrochemical plastics. PHAs range from rigid to highly elastic, have very good barrier properties, and are resistant to hot water and greases. Metabolix has developed PHA formulations suitable for processing on existing equipment and demonstrated them in key end-use applications such as injection molding, thermoforming, blown film, and extrusion melt casting including film, sheet, and paper coating.

Metabolix's PHA natural plastics will bring a range of environmental benefits, including reduced reliance on fossil carbon and reduced greenhouse gas emissions. PHAs are now made from renewable raw materials, such as sugar and vegetable oils. In the future, they will be produced directly in plants. In addition, PHAs will reduce the burden of plastic waste on solid waste systems, municipal waste treatment systems, and marine and wetland ecosystems: they will biodegrade to harmless products in a wide variety of both aerobic and anaerobic environments, including soil, river and ocean water, septic systems, anaerobic digesters, and compost.

Metabolix's PHA technology is the first commercialization of plastics based on renewable resources that employs living biocatalysts in microbial fermentation to convert renewable raw materials all the way to the finished copolymer product. PHAs are also the first family of plastics that combine broadly useful properties with biodegradability in a wide range of environments, including marine and wetlands ecosystems. Replacement of petrochemical plastics with PHAs will also have significant economic benefits. Producing 50 billion pounds of PHA natural plastics to replace about half of the petrochemical plastics currently used in the United States would reduce oil imports by over 200–230 million barrels per year, improving the U.S. trade balance by \$6–9 billion per year, assuming oil at \$30–40 per barrel.

Archer Daniels Midland Company

Novozymes

NovaLipid™: Low *Trans* Fats and Oils Produced by Enzymatic Interesterification of Vegetable Oils Using Lipozyme®

Innovation and Benefits

Archer Daniels Midland Company and Novozymes developed a way to make edible fats and oils that contain no *trans* fatty acids. The improved "interesterification" process they developed uses less resources. Potential savings include hundreds of millions of pounds of soybean and other vegetable oils, processing chemicals, and water resources each year.

Two major challenges facing the food and ingredient industry are providing health-conscious products to the public and developing environmentally responsible production technology. Archer Daniels Midland Company (ADM) and Novozymes are commercializing enzymatic interesterification, a technology that not only has a tremendous positive impact on public health by reducing *trans* fatty acids in the American diet, but also offers great environmental benefits by eliminating the waste streams generated by the chemical interesterification process.

Triglycerides consist of one glycerol plus three fatty acids. Triglycerides that contain mostly unsaturated fatty acids are liquid at room temperature. Manufacturers partially hydrogenate these fatty acids to make them solids at room temperature. *Trans* fatty acids form during the hydrogenation process; they are found at high concentrations in a wide variety of processed foods. Unfortunately, consumption of *trans* fatty acids is also a strong risk factor for heart disease. To reduce *trans* fats in the American diet as much as possible, the FDA is requiring labeling of *trans* fats on all nutritional fact panels by January 1, 2006. In response, the U.S. food and ingredient industry has been investigating methods to reduce *trans* fats in food.

Of the available strategies, interesterification is the most effective way to decrease the *trans* fat content in foods without sacrificing the functionality of partially hydrogenated vegetable oils. During interesterification, triglycerides containing saturated fatty acids exchange one or two of their fatty acids with triglycerides containing unsaturated fatty acids, resulting in triglycerides that do not contain any *trans* fatty acids. Enzymatic interesterification processes have many benefits over chemical methods, but the high cost of the enzymatic process and poor enzyme stability had prevented its adoption in the bulk fat industry.

Extensive research and development work by both Novozymes and ADM has led to the commercialization of an enzymatic interesterification process. Novozymes developed a cost-effective immobilized enzyme, and ADM developed a process to stabilize the immobilized enzyme enough for successful commercial production. The interesterified oil provides food companies with broad options for zero and reduced *trans* fat food products. Since the first commercial production in 2002, ADM has produced more than 15 million pounds of interesterified oils. ADM is currently expanding the enzyme process at two of its U.S. production facilities.

Enzymatic interesterification positively affects both environmental and human health. Environmental benefits include eliminating the use of several harsh chemicals, eliminating byproducts and waste streams (solid and water), and improving the use of edible oil resources. As one example, margarines and shortenings currently consume 10 billion pounds of hydrogenated soybean oil each year. Compared to partial hydrogenation, the ADM/Novozymes process has the potential to save 400 million pounds of soybean oil and eliminate 20 million pounds of sodium methoxide, 116 million pounds of soaps, 50 million pounds of bleaching clay, and 60 million gallons of water each year. The enzymatic process also contributes to improved public health by replacing partially hydrogenated oils with interesterified oils that contain no *trans* fatty acids and have increased polyunsaturated fatty acids.

Greener Synthetic Pathways Award

Merck & Co., Inc.

A Redesigned, Efficient Synthesis of Aprepitant, the Active Ingredient in Emend®: A New Therapy for Chemotherapy-Induced Emesis

Innovation and Benefits

Emend® is a drug that combats the nausea and vomiting often resulting from chemotherapy treatment. Merck now makes Emend® using a new process that requires much less energy, raw materials, and water than the original process. With its new method, Merck eliminates approximately 41,000 gallons of waste per 1,000 pounds of the drug that it produces.

Emend® is a new therapy for chemotherapy-induced nausea and vomiting, the most common side effects associated with the chemotherapeutic treatment of cancer. Emend® has been clinically shown to reduce nausea and vomiting when used during and shortly after chemotherapy. Aprepitant is the active pharmaceutical ingredient in Emend®.

Aprepitant, which has two heterocyclic rings and three stereogenic centers, is a challenging synthetic target. Merck's first-generation commercial synthesis required six synthetic steps and was based on the discovery synthesis. The raw material and environmental costs of this route, however, along with operational safety issues compelled Merck to discover, develop, and implement a completely new route to aprepitant.

Merck's new route to aprepitant demonstrates several important green chemistry principles. This innovative and convergent synthesis assembles the complex target in three highly atom-economical steps using four fragments of comparable size and complexity. The first-generation synthesis required stoichiometric amounts of an expensive, complex chiral acid as a reagent to set the absolute stereochemistry of aprepitant. In contrast, the new synthesis incorporates a chiral alcohol as a feedstock; this alcohol is itself synthesized in a catalytic asymmetric reaction. Merck uses the stereochemistry of this alcohol feedstock in a practical crystallization-induced asymmetric transformation to set the remaining stereogenic centers of the molecule during two subsequent transformations. The new process nearly doubles the yield of the first-generation synthesis. Much of the chemistry developed for the new route is novel and has wider applications. In particular, the use of a stereogenic center that is an integral part of the final target molecule to set new stereocenters with high selectivity is applicable to the large-scale synthesis of other chiral molecules, especially drug substances.

Implementing the new route has drastically improved the environmental impact of aprepitant production. Merck's new route eliminates all of the operational hazards associated with the first-generation synthesis, including those of sodium cyanide, dimethyl titanocene, and gaseous ammonia. The shorter synthesis and milder reaction conditions have also reduced the energy requirements significantly. Most important, the new synthesis requires only 20 percent of the raw materials and water used by the original one. By adopting this new route, Merck has eliminated approximately 41,000 gallons of waste per 1,000 pounds of aprepitant that it produces.

The alternative synthetic pathway for the synthesis of aprepitant as discovered and implemented by Merck is an excellent example of minimizing environmental impact while greatly reducing production costs by employing the principles of green chemistry. Merck implemented the new synthesis during its first year of production of Emend®; as a result, Merck will realize the benefits of this route for virtually the entire lifetime of this product. The choice to implement the new route at the outset of production has led to a huge reduction in the cost to produce aprepitant, demonstrating quite clearly that green chemistry solutions can be aligned with cost-effective ones.

Greener Reaction Conditions Award

BASF Corporation

A UV-Curable, One-Component, Low-VOC Refinish Primer:
Driving Eco-Efficiency Improvements

Innovation and Benefits

BASF developed a new automobile paint primer that contains less than half the amount of volatile organic compounds (VOCs) used in conventional primers. The new primer is also free of diisocyanates, a major source of occupational asthma. Use in repair facilities has shown that only one-third as much of this primer is needed compared to conventional primer and that waste is reduced from 20 percent to nearly zero.

The market for automotive refinish coatings in North America exceeds $2 billion for both collision repairs and commercial vehicle applications. Over 50,000 body shops in North America use these products. For more than a decade, automotive refinishers and coating manufacturers have dealt with increasing regulation of emissions of volatile organic compounds (VOCs). At first, coating manufacturers were able to meet VOC maximums with high-performance products such as two-component reactive urethanes, which require solvents as carriers for their high-molecular-weight resins. As thresholds for VOCs became lower, however, manufacturers had to reformulate their reactive coatings, and the resulting reformulations were slow to set a film. Waterborne coatings are also available, but their utility has been limited by the time it takes the water to evaporate. Continuing market pressures demanded faster film setting without compromising either quality or emissions.

Through intense research and development, BASF has invented a new urethane acrylate oligomer primer system. The resin cross-links with monomer (added to reduce viscosity) into a film when the acrylate double bonds are broken by radical propagation. The oligomers and monomers react into the film's cross-linked structure, improving adhesion, water resistance, solvent resistance, hardness, flexibility, and cure speed. The primer cures in minutes by visible or near-ultraviolet (UV) light from inexpensive UV-A lamps or even sunlight. BASF's UV-cured primer eliminates the need for bake ovens that cure the current primers, greatly reducing energy consumption. BASF's primer performs better than the current conventional urethane technologies: it cures ten times faster, requires fewer preparation steps, has a lower application rate, is more durable, controls corrosion better, and has an unlimited shelf life. BASF is currently offering its UV-cured primers in its R-M® line as Flash Fill™ VP126 and in its Glasurit® line as 151-70.

BASF's primer contains only 1.7 pounds of VOCs per gallon, in contrast to 3.5–4.8 pounds of VOCs per gallon of conventional primers, a reduction of over 50 percent. The primer meets even the stringent requirements of South Coast California, whereas its superior properties ensure its acceptance throughout the U.S. market. The one-component nature of the product reduces hazardous waste and cleaning of equipment, which typically requires solvents. Applications in repair facilities over the past year have shown that only one-third as much primer is needed and that waste is reduced from 20 percent to nearly zero. The BASF acrylate-based technology requires less complex, less costly personal protective equipment (PPE) than the traditional isocyanate-based coatings; this, in turn, increases the probability that small body shops will purchase and use the PPE, increasing worker safety.

This eco-efficient product is the first step in an automobile refinishing coating system for which BASF plans to include the globally accepted waterborne basecoat from BASF (sold under the Glasurit® brand as line 90). In the near future, this system can be finished with the application of a one-component, UV-A-curable clearcoat. The system will deliver quality, energy efficiency, economy, and speed for the small businessperson operating a local body shop, while respecting the health and safety of the workers in this establishment and the environment in which these products are manufactured and used. To fully support these claims, BASF has conducted an eco-efficiency study with an independent evaluation.

Archer Daniels Midland Company

Archer RC™: A Nonvolatile, Reactive Coalescent for the Reduction of VOCs in Latex Paints

Innovation and Benefits

Latex paints require coalescents to help the paint particles flow together and cover surfaces well. Archer Daniels Midland developed Archer RC™, a new biobased coalescent to replace traditional coalescents that are volatile organic compounds (VOCs). This new coalescent has other performance advantages as well, such as lower odor, increased scrub resistance, and better opacity.

Since the 1980s, waterborne latex coatings have found increasingly broad acceptance in architectural and industrial applications. Traditional latex coatings are based on small-particle emulsions of a synthetic resin, such as acrylate- and styrene-based polymers. They require substantial quantities of a coalescent to facilitate the formation of a coating film as water evaporates after the coating is applied. The coalescent softens (plasticizes) the latex particles, allowing them to flow together to form a continuous film with optimal performance properties. After film formation, traditional coalescents slowly diffuse out of the film into the atmosphere. The glass transition temperature of the latex polymer increases as the coalescent molecules evaporate and the film hardens. Alcohol esters and ether alcohols, such as ethylene glycol monobutyl ether (EGBE) and Texanol® (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate), are commonly used as coalescents. They are also volatile organic compounds (VOCs). Both environmental concerns and economics continue to drive the trend to reduce the VOCs in coating formulations. Inventing new latex polymers that do not require a coalescent is another option, but these polymers often produce soft films and are expensive to synthesize, test, and commercialize. Without a coalescent, the latex coating may crack and may not adhere to the substrate surface when dry at ambient temperatures.

Archer RC™ provides the same function as traditional coalescing agents but eliminates the unwanted VOC emissions. Instead of evaporating into the air, the unsaturated fatty acid component of Archer RC™ oxidizes and even cross-links into the coating. Archer RC™ is produced by interesterifying vegetable oil fatty acid esters with propylene glycol to make the propylene glycol monoesters of the fatty acids. Corn and sunflower oils are preferred feedstocks for Archer RC™ because they have a high level of unsaturated fatty acids and tend to resist the yellowing associated with linolenic acid, found at higher levels in soybean and linseed oils. Because Archer RC™ remains in the coating after film formation, it adds to the overall solids of a latex paint, providing an economic advantage over volatile coalescents.

The largest commercial category for latex paint, the architectural market, was 618 million gallons in the United States in 2001. Typically, coalescing solvents constitute 2–3 percent of the finished paint by volume; this corresponds to an estimated 120 million pounds of coalescing solvents in the United States and perhaps three times that amount globally. Currently, nearly all of these solvents are lost into the atmosphere each year.

Archer Daniels Midland Company has developed and tested a number of paint formulations using Archer RC™ in place of conventional coalescing solvents. In these tests, Archer RC™ performed as well as commercial coalescents such as Texanol®. Archer RC™ often had other advantages as well, such as lower odor, increased scrub resistance, and better opacity. Paint companies and other raw material suppliers have demonstrated success formulating paints with Archer RC™ and their existing commercial polymers. Archer RC™ has been in commercial use since March 2004.

Academic Award

Professors Charles A. Eckert and Charles L. Liotta
Georgia Institute of Technology
Benign Tunable Solvents Coupling Reaction and Separation Processes

Innovation and Benefits

Professors Eckert and Liotta found ways to replace conventional organic solvents with benign solvents, such as supercritical carbon dioxide (CO_2) or water "tuned" by carefully selecting both temperature and pressure. These methods combine reactions and separations, improving efficiency and reducing waste in a variety of industrial applications.

For any chemical process, there must be both a reaction and a separation. Generally, the same solvent is used for both but is optimized only for the reaction. The separation typically involves 60–80 percent of the cost, however, and almost always has a large environmental impact. Conventional reactions and separations are often designed separately, but Professors Charles A. Eckert and Charles L. Liotta have combined them with a series of novel, benign, tunable solvents to create a paradigm for sustainable development: benign solvents and improved performance.

Supercritical carbon dioxide (CO_2), nearcritical water, and CO_2-expanded liquids are tunable benign solvents that offer exceptional opportunities as replacement solvents. They generally exhibit better solvent properties than gases and better transport properties than liquids. They offer substantial property changes with small variations in thermodynamic conditions, such as temperature, pressure, and composition. They also provide wide-ranging environmental advantages, from human health to pollution prevention and waste minimization. Professors Eckert, Liotta, and their team have combined reactions with separations in a synergistic manner to use benign solvents, minimize waste, and improve performance.

These researchers have used supercritical CO_2 to tune reaction equilibria and rates, improve selectivities, and eliminate waste. They were the first to use supercritical CO_2 with phase transfer catalysts to separate products cleanly and economically. Their method allows them to recycle their catalysts effectively. They have demonstrated the feasibility of a variety of phase transfer catalysts on reactions of importance in the chemical and pharmaceutical industries, including chiral syntheses. They have carried out a wide variety of synthetic reactions in nearcritical water, replacing conventional organic solvents. This includes acid- and base-catalysis using the enhanced dissociation of nearcritical water, negating the need for any added acid or base and eliminating subsequent neutralization and salt disposal. They have used CO_2 to expand organic fluids to make it easier to recycle homogeneous catalysts, including phase transfer catalysts, chiral catalysts, and enzymes. Finally, they have used tunable benign solvents to design syntheses that minimize waste by recycling and demonstrate commercial feasibility by process economics.

The team of Eckert and Liotta has combined state-of-the-art chemistry with engineering know-how, generating support from industrial sponsors to facilitate technology transfer. They have worked with a wide variety of government and industrial partners to identify the environmental and commercial opportunities available with these novel solvents; their interactions have facilitated the technology transfer necessary to implement their advances.

Small Business Award

Jeneil Biosurfactant Company

Rhamnolipid Biosurfactant: A Natural, Low-Toxicity Alternative to Synthetic Surfactants

Innovation and Benefits

Billions of pounds of surfactants are used each year to lubricate, clean, or reduce undesired foaming in industrial applications. Jeneil Biosurfactant Company developed biobased surfactants that are less toxic and more biodegradable than conventional surfactants. Jeneil makes its biosurfactants using a simple fermentation.

Surfactants are chemicals that reduce the surface tension of water. Surfactants are widely used in soaps, laundry detergents, dishwashing liquids, and many personal care products, such as shampoos. Other important uses are in lubricants, emulsion polymerization, textile processing, mining flocculates, petroleum recovery, and wastewater treatment. Most currently used surfactants are derived from petroleum feedstocks. The total worldwide chemical surfactant consumption in the year 2000 has been estimated to be approximately 36 billion pounds. Many of these chemical surfactants pose significant environmental risks because they form harmful compounds from incomplete biodegradation in water or soil.

Jeneil Biosurfactant Company has successfully produced a series of rhamnolipid biosurfactant products, making them commercially available and economical for the first time. These biosurfactant products provide good emulsification, wetting, detergency, and foaming properties, along with very low toxicity. They are readily biodegradable and leave no harmful or persistent degradation products. Their superior qualities make them suitable for many diverse applications.

Rhamnolipid biosurfactant is a naturally occurring extracellular glycolipid that is found in the soil and on plants. Jeneil produces this biosurfactant commercially in controlled, aerobic fermentations using particular strains of the soil bacterium, *Pseudomonas aeruginosa*. The biosurfactant is recovered from the fermentation broth after sterilization and centrifugation, then purified to various levels to fit intended applications.

Rhamnolipid biosurfactants are a much less toxic and more environmentally friendly alternative to traditional synthetic or petroleum-derived surfactants. Rhamnolipid biosurfactants are also "greener" throughout their life cycle. Biosurfactant production uses feedstocks that are innocuous and renewable compared to those used for synthetic or petroleum-derived surfactants. In addition, their production requires less resources, employs processes that are less complex and less capital- and energy-intensive, and does not require the use and disposal of hazardous substances.

Some current uses of rhamnolipid biosurfactant are in consumer cleaning products, in solutions to clean contact lenses, and in an agricultural fungicide as the active ingredient. These biosurfactants are also extremely effective in precluding harmful environmental impacts and remediating environmental pollution. For example, rhamnolipid biosurfactants can facilitate removal of hydrocarbons or heavy metals from soil, clean crude oil tanks, and remediate sludge; often they can facilitate recovery of a significant amount of the hydrocarbons. In many applications, these biosurfactants can replace less environmentally friendly synthetic or petroleum-derived surfactants. Further, these biosurfactants have excellent synergistic activity with many synthetic surfactants and, when formulated together in a cosurfactant system, can allow a substantial reduction in the synthetic surfactant component.

Although rhamnolipid biosurfactants have been the subject of considerable research, they had previously been produced only on a small scale in laboratories. Jeneil Biosurfactant Company, in conjunction with its associated company, Jeneil Biotech, Inc., has commercialized the rhamnolipid technology by developing efficient bacterial strains, as well as cost-effective processes and equipment for commercial-scale production. Jeneil's facility in Saukville, WI produces the surfactants.

Greener Synthetic Pathways Award

Bristol-Myers Squibb Company

Development of a Green Synthesis for Taxol® Manufacture via Plant Cell Fermentation and Extraction

Innovation and Benefits

Bristol-Myers Squibb manufactures paclitaxel, the active ingredient in the anticancer drug, Taxol®, using plant cell fermentation (PCF) technology. PCF replaces the conventional process that extracts a paclitaxel building block from leaves and twigs of the European yew. During the first five years of commercialization, PCF technology will eliminate an estimated 71,000 pounds of hazardous chemicals and materials, eliminate ten solvents and six drying steps, and save a significant amount of energy.

Paclitaxel, the active ingredient in the anticancer drug Taxol®, was first isolated and identified from the bark of the Pacific yew tree, *Taxus brevifolia*, in the late 1960s by Wall and Wani under the auspices of the National Cancer Institute (NCI). The utility of paclitaxel to treat ovarian cancer was demonstrated in clinical trials in the 1980s. The continuity of supply was not guaranteed, however, because yew bark contains only about 0.0004 percent paclitaxel. In addition, isolating paclitaxel required stripping the bark from the yew trees, killing them in the process. Yews take 200 years to mature and are part of a sensitive ecosystem.

The complexity of the paclitaxel molecule makes commercial production by chemical synthesis from simple compounds impractical. Published syntheses involve about 40 steps with an overall yield of approximately 2 percent. In 1991, NCI signed a Collaborative Research and Development Agreement with Bristol-Myers Squibb (BMS) in which BMS agreed to ensure supply of paclitaxel from yew bark while it developed a semisynthetic route (semisynthesis) to paclitaxel from the naturally occurring compound 10-deacetylbaccatin III (10-DAB).

10-DAB contains most of the structural complexity (8 chiral centers) of the paclitaxel molecule. It is present in the leaves and twigs of the European yew, *Taxus baccata*, at approximately 0.1 percent by dry weight and can be isolated without harm to the trees. *Taxus baccata* is cultivated throughout Europe, providing a renewable supply that does not adversely impact any sensitive ecosystem. The semisynthetic process is complex, however, requiring 11 chemical transformations and seven isolations. The semisynthetic process also presents environmental concerns, requiring 13 solvents along with 13 organic reagents and other materials.

BMS developed a more sustainable process using the latest plant cell fermentation (PCF) technology. In the cell fermentation stage of the process, calluses of a specific taxus cell line are propagated in a wholly aqueous medium in large fermentation tanks under controlled conditions at ambient temperature and pressure. The feedstock for the cell growth consists of renewable nutrients: sugars, amino acids, vitamins, and trace elements. BMS extracts paclitaxel directly from plant cell cultures, then purifies it by chromatography and isolates it by crystallization. By replacing leaves and twigs with plant cell cultures, BMS improves the sustainability of the paclitaxel supply, allows year-round harvest, and eliminates solid biomass waste. Compared to the semisynthesis from 10-DAB, the PCF process has no chemical transformations, thereby eliminating six intermediates. During its first five years, the PCF process will eliminate an estimated 71,000 pounds of hazardous chemicals and other materials. In addition, the PCF process eliminates ten solvents and six drying steps, saving a considerable amount of energy. BMS is now manufacturing paclitaxel using only plant cell cultures.

Greener Reaction Conditions Award

Buckman Laboratories International, Inc.

Optimyze®: A New Enzyme Technology to Improve Paper Recycling

Innovation and Benefits

Paper mills traditionally use hazardous solvents, such as mineral spirits, to remove sticky contaminants (stickies) from machinery. Optimyze® technology uses a novel enzyme to remove stickies from paper products prior to recycling, increasing the percentage of paper that can be recycled. Each paper mill that switches to Optimyze® can reduce its hazardous solvent use by 200 gallons daily, reduce its chemical use by approximately 600,000 pounds yearly, increase its production by more than 6 percent, and save up to $1 million per year.

Recycling paper products is an important part of maintaining our environment. Although produced from renewable resources, paper is a major contributor to landfilled waste. Paper can be recycled numerous times, and much progress has been made: about one-half of the paper and paperboard currently used in the United States is collected and reused. Some papers, however, contain adhesives, coatings, plastics, and other materials that form sticky contaminants, creating serious problems during the paper recycling process. These contaminants, called "stickies" by the paper industry, can produce spots and holes in paper goods made from recycled materials, ruining their appearance and lowering their quality.

Stickies also waste significant manufacturing resources when production must stop to clean the equipment. One source estimates the cost to the industry from production downtime alone to be more than $500 million annually. Further, this cleaning is traditionally done with chemical solvents, typically mineral spirits, which can have health and safety problems, are obtained from nonrenewable, petroleum resources, and are not readily recycled. These solvents are volatile organic compounds (VOCs) that contribute to air pollution. As a result, some paper grades cannot be recycled into reusable products.

Optimyze® technology from Buckman Laboratories is a completely new way to control the problems associated with stickies. It uses a novel enzyme to eliminate common problems in the manufacture of paper from recycled papers. A major component of the sticky contaminants in paper is poly(vinyl acetate) and similar materials. Optimyze® contains an esterase enzyme that catalyzes the hydrolysis of this type of polymer to poly(vinyl alcohol), which is not sticky and is water-soluble. A bacterial species produces large amounts of the Optimyze® enzyme by fermentation. As a protein, the enzyme is completely biodegradable, much less toxic than alternatives, and much safer. Only renewable resources are required to manufacture Optimyze®.

Optimyze® has been commercially available since May 2002. In that short time, more than 40 paper mills have converted to Optimyze® for manufacturing paper goods from recycled papers. In one U.S. mill, conversion to Optimyze® reduced solvent use by 200 gallons per day and chemical use by about 600,000 pounds per year. Production increased by more than 6 percent, which amounted to a $1 million benefit per year for this mill alone.

This new enzyme technology has improved production of a broad range of paper products, including tissue, paper toweling, corrugated cartons, and many other materials. It improves the quality and efficiency of papermaking, dramatically reducing downtime to clean equipment. As a result, more paper is being recycled and grades of paper that were not recyclable earlier are now being recycled. Paper mills adopting Optimyze® have been able to greatly reduce the use of hazardous solvents.

In summary, Optimyze® makes it possible to recycle more grades of paper, allows more efficient processing of recycled papers, and produces higher-quality paper goods from recycled materials. The Optimyze® technology comes from renewable resources, is safe to use, and is itself completely recyclable.

Designing Greener Chemicals Award

Engelhard Corporation (now BASF Corporation)

Engelhard Rightfit™ Organic Pigments: Environmental Impact, Performance, and Value

Innovation and Benefits

Rightfit™ azo pigments contain calcium, strontium, or barium; they replace conventional heavy-metal-based pigments containing lead, hexavalent chromium, or cadmium. Because of their low potential toxicity and very low migration, most of the Rightfit™ azo pigments have received U.S. Food and Drug Administration (FDA) and Canadian Health Protection Branch (HPB) approval for indirect food contact applications. By 2004, Engelhard expects to have replaced all 6.5 million pounds of its heavy-metal-based pigments with Rightfit™ pigments.

Historically, pigments based on lead, chromium(VI), and cadmium have served the red, orange, and yellow color market. When EPA began regulating heavy metals, however, color formulators typically turned to high-performance organic pigments to replace heavy-metal-based pigments. Although high-performance pigments meet performance requirements, they do so at the expense of the following: (1) their higher cost often acts as a deterrent to reformulation; (2) their production uses large volumes of organic solvents; (3) some require large quantities of polyphosphoric acid, resulting in phosphates in the effluent; and (4) some are based on dichlorobenzidine or polychlorinated phenyls.

Engelhard has developed a wide range of environmentally friendly Rightfit™ azo pigments that contain calcium, strontium, or sometimes barium instead of heavy metals. True to their name, the Rightfit™ pigments have the right environmental impact, right color space, right performance characteristics, and right cost-to-performance value. Since 1995, when Engelhard produced 6.5 million pounds of pigments containing heavy metals, it has been transitioning to Rightfit™ azo pigments. In 2002, Engelhard produced only 1.2 million pounds of heavy-metal pigments; they expect to phase them out completely in 2004.

Rightfit™ pigments eliminate the risk to human health and the environment from exposure to heavy metals such as cadmium, chromium(VI), and lead used in the manufacture of cadmium and chrome yellow pigments. They are expected to have very low potential toxicity based on toxicity studies, physical properties, and structural similarities to many widely used food colorants. Because they have low potential toxicity and very low migration, most of the Rightfit™ pigments have been approved both by the U.S. Food and Drug Administration (FDA) and the Canadian Health Protection Branch (HPB) for indirect food contact applications. In addition, these pigments are manufactured in aqueous medium, eliminating exposure to the polychlorinated intermediates and organic solvents associated with the manufacture of traditional high-performance pigments.

Rightfit™ pigments have additional benefits, such as good dispersibility, improved dimensional stability, improved heat stability, and improved color strength. Their higher color strength achieves the same color values using less pigment. Rightfit™ pigments also cover a wide color range from purple to green-shade yellow color. Being closely related chemically, these pigments are mutually compatible, so two or more can combine to achieve any desired intermediate color shade.

Rightfit™ pigments meet the essential performance characteristics at significantly lower cost than high-performance organic pigments. Thus, formulators get the right performance properties at the right cost, resulting in a steadily increasing market for these pigments. Rightfit™ pigments provide environmentally friendly, value-added color to packaging used in the food, beverage, petroleum product, detergent, and other household durable goods markets.

Academic Award

Professor Richard A. Gross

Polytechnic University

New Options for Mild and Selective Polymerizations Using Lipases

Innovation and Benefits

Professor Gross developed a highly selective, more efficient way to make polyesters using enzymes. This technique requires less energy and toxic substances than conventional methods that typically use heavy metal catalysts and hazardous solvents. This innovation also makes it possible to manufacture new types of polyesters.

Isolated lipases, harvested from living organisms, have been used as catalysts for polymer synthesis in vitro. Professor Richard A. Gross's developments on lipase-catalyzed polymer synthesis have relied on the ability of enzymes to reduce the activation energy of polymerizations and, thus, to decrease process energy consumption. Further, the regioselectivity of lipases has been used to polymerize polyols directly. Alternative synthetic pathways for such polymerizations require protection-deprotection chemical steps. The mild reaction conditions allow polymerization of chemically and thermally sensitive molecules. Current alternative chemical routes require coupling agents (e.g., carbodiimides) that would be consumed in stoichiometric quantities relative to the reactants. Fundamental studies of these polymerizations have uncovered remarkable capabilities of lipases for polymerization chemistry. Selected examples include: (1) lipases catalyze transesterification reactions between high-molecular-weight chains in melt conditions; (2) lipases will use non-natural nucleophiles such as carbohydrates and monohydroxyl polybutadiene (M_n 19,000) in place of water; (3) the catalysis of ring-opening polymerization occurs in a controlled manner without termination reactions and with predictable molecular weights; and (4) the selectivity of lipase-catalyzed step-condensation polymerizations leads to nonstatistical molecular weight distributions (polydispersities well below 2.0). These accomplishments are elaborated on the next page.

A series of polyol-containing polyesters was synthesized via a one-pot lipase-catalyzed condensation polymerization. By using various mixtures of polyols (e.g., glycerol, sorbitol) with other diacid and diol building blocks, the polyols are partially or completely solubilized, resulting in highly reactive condensation polymerizations. By this method, organic solvents and activated acids (e.g., divinyl esters) are not needed. The polymerization reactions give high-molecular-weight products (M_w up to 200,000) with narrow polydispersities (as low as 1.3). Further, the condensation reactions with glycerol and sorbitol building blocks proceed with high regioselectivity. Although the polyols used have three or more hydroxyl groups, only two of these hydroxyl groups are highly reactive in the polymerization. Thus, instead of obtaining highly cross-linked products, the regioselectivity provided by the lipase leads to lightly branched polymers where the degree of branching varies with the reaction time and monomer stoichiometry. By using lipase as the catalyst, highly versatile polymerizations result that can simultaneously polymerize lactones, hydroxyacids, cyclic carbonates, cyclic anhydrides, amino alcohols, and hydroxylthiols. The method developed offers simplicity, mild reaction conditions, and the ability to incorporate carbohydrates, such as sugars, into polyesters without protection-deprotection steps.

Professor Gross's laboratory discovered that certain lipases catalyze transesterification reactions between high-molecular-weight chains that contain intrachain esters or have functional end-groups. Thus, lipases, such as Lipase B from *Candida antarctica*, catalyze intrachain exchange reactions between polymer chains as well as transesterification reactions between a monomer and a polymer. For polymers that have melting points below 100 °C, the reactions can be conducted in bulk. Transacylation reactions occur because the lipase has the ability to accommodate large-molecular-weight substrates and to catalyze the breaking of ester bonds within chains. Immobilized *Candida antarctica* Lipase B (Novozyme-435) catalyzed transesterification reactions between aliphatic polyesters that had M_n values in excess of 40,000 grams per mole. In addition to catalyzing metal-free transesterifications at remarkably low temperatures, lipases endow transesterification reactions with remarkable selectivity. This feature allows the preparation of block copolymers that have selected block lengths.

Small Business Award

AgraQuest, Inc.

Serenade®: An Effective, Environmentally Friendly Biofungicide

Innovation and Benefits

Serenade® is a new biofungicide for fruits and vegetables based on a naturally occurring strain of bacteria. Serenade® is nontoxic to beneficial and other nontarget organisms, does not generate any hazardous chemical residues, and is safe for workers and groundwater. It is well-suited for use in integrated pest management (IPM) programs and is listed with the Organic Materials Review Institute (OMRI) for use in organic agriculture.

Serenade® biofungicide is based on a naturally occurring strain of *Bacillus subtilis* QST-713, discovered in a California orchard by AgraQuest scientists. Serenade® has been registered for sale as a microbial pesticide in the United States since July 2000. It is also registered for use in Chile, Mexico, Costa Rica, and New Zealand. Registration is pending in the Philippines, Europe, Japan, and several other countries. The product is formulated as a wettable powder, wettable granule, and liquid aqueous suspension. Serenade® has been tested on 30 crops in 20 countries and is registered for use in the United States on blueberries, cherries, cucurbits, grape vines, greenhouse vegetables, green beans, hops, leafy vegetables, mint, peanuts, peppers, pome fruit, potatoes, tomatoes, and walnuts. It is also registered for home and garden use. AgraQuest has been issued four U.S. patents; several international patents are pending on the QST-713 strain, associated antifungal lipopeptides, formulations, and combinations with other pesticides.

Serenade® works through a complex mode of action that is manifested both by the physiology of the bacteria and through the action of secondary metabolites produced by the bacteria. Serenade® prevents plant diseases first by covering the leaf surface and physically preventing attachment and penetration of the pathogens. In addition, Serenade® produces three groups of lipopeptides (iturins, agrastatins/plipastatins, and surfactins) that act in concert to destroy germ tubes and mycelium. The iturins and plipastatins have been reported to have antifungal properties. Strain QST-713 is the first strain reported to produce iturins, plipastatins, and surfactins, as well as two new compounds with a novel cyclic peptide moiety, the agrastatins. The surfactins have no activity on their own, but low levels (25 ppm or less) in combination with the iturins or the agrastatin/plipastatin group cause significant inhibition of spores and germ tubes. In addition, the agrastatins and iturins have synergistic activities towards inhibition of plant pathogen spores.

The Serenade® formulation is available as a wettable powder, wettable granule, and aqueous suspension that is applied just like any other foliar fungicide. It can be applied alone or tank mixed; it can also be alternated with traditional chemical pesticides. Serenade® is not toxic to beneficial and nontarget organisms, such as trout, quail, lady beetles, lacewings, parasitic wasps, earthworms, and honey bees. Serenade® is exempt from tolerance because there are no synthetic chemical residues and it is safe to workers and ground water.

Serenade®'s wettable granule formulation is listed with the Organic Materials Review Institute (OMRI) for use in organic agriculture and will continue to be listed under the National Organic Standards, which were enacted in the United States in October 2002.

Serenade®'s novel, complex mode of action, environmental friendliness, and broad spectrum control make it well-suited for use in integrated pest management (IPM) programs that utilize many tools, such as cultural practices, classical biological control, and other fungicides. Serenade® can be applied right up until harvest, providing needed pre- and post-harvest protection when there is weather conducive to disease development around harvest time.

Greener Synthetic Pathways Award

Süd-Chemie Inc.

A Wastewater-Free Process for Synthesis of Solid Oxide Catalysts

Innovation and Benefits

Süd-Chemie's new process to synthesize solid oxide catalysts used in producing hydrogen and clean fuel has virtually zero wastewater discharge, zero nitrate discharge, and no or little NO_X emissions. Each 10 million pounds of oxide catalyst produced by the new pathway eliminates approximately 760 million pounds of wastewater discharges, 29 million pounds of nitrate discharges, and 7.6 million pounds of NO_X emissions. The process also saves water and energy.

Some major achievements in pollution reduction have been made recently through advancement of catalytic technologies. One such effort is in the area of hydrogen and clean fuel production. However, the synthesis of catalysts for such reactions is often accompanied by the discharge of large amounts of wastewater and other pollutants, such as NO_X, SO_X, and halogens.

As a result of their commitment to continuously develop and invest in new and improved catalyst synthesis technologies, Süd-Chemie successfully developed and demonstrated a new synthetic pathway that is able to achieve virtually zero wastewater discharge, zero nitrate discharge, and no or little NO_X emissions. Meantime, it substantially reduces the consumption of water and energy. For example, it is estimated that about 760 million pounds of wastewater discharges, about 29 million pounds of nitrate discharges, and about 7.6 million pounds of NO_X emissions can be eliminated for every 10 million pounds of oxide catalyst produced.

The new synthetic pathway is based on very simple chemistry. Instead of acid-base precipitation typically using metal nitrate as raw material, the new process starts with a clean metal that is readily and economically available in commercial quantities. The synthesis proceeds by reaction of the metal with a mild organic acid in the presence of an oxidation agent. The function of the acid is to activate the metal and extract electrons to form the oxide precursor. With assistance of the oxidation agent (typically air), a porous solid oxide is synthesized in one step at ambient temperature without any wastewater discharge. The other active ingredients of the catalyst can be incorporated using the concept of wet-agglomeration. In contrast, the precipitation process requires intensive washing and filtration to remove nitrate and the other salts. Further, the new process substantially reduces the consumption of water and energy for production of solid oxide catalysts over conventional methods. The emission in the entire process is only pure water vapor and a small amount of CO_2 that is generated during spray-drying and afterburning of hydrogen.

This wastewater-free process for making solid oxide catalysts has been demonstrated, and more than 300 kilograms of the metal oxide catalysts have been produced. Patent protection is being sought for the development. The catalysts made by the green process give superior performance in the synthesis of clean fuels and chemicals. The market for such solid oxide catalysts is estimated to be approximately $100 million. Süd-Chemie is the first in the industry to use the green process for making a catalyst for the synthesis of "green" fuels and chemicals.

Greener Reaction Conditions Award

DuPont

Microbial Production of 1,3-Propanediol

Innovation and Benefits

DuPont and Genencor International jointly developed a genetically engineered microorganism to manufacture the key building block for DuPont's Sorona® polyester. The process uses renewable cornstarch instead of petroleum to make environmentally friendly, cost-competitive textiles.

DuPont is integrating biology in the manufacture of its newest polymer platform, DuPont Sorona® polymer. Combining metabolic engineering with polymer science, researchers are introducing a microbial process in a business that, historically, has relied solely on traditional chemistry and petrochemical feedstocks. This achievement, comprising biocatalytic production of 1,3-propanediol from renewable resources, offers economic as well as environmental advantages. The key to the novel biological process is an engineered microorganism that incorporates several enzyme reactions, obtained from naturally occurring bacteria and yeast, into an industrial host cell line. For the first time, a highly engineered microorganism will be used to convert a renewable resource into a chemical at high volume.

The catalytic efficiency of the engineered microorganism allows replacement of a petroleum feedstock, reducing the amount of energy needed in manufacturing steps and improving process safety. The microbial process is environmentally green, less expensive, and more productive than the chemical operations it replaces. 1,3-Propanediol, a key ingredient in the Sorona® polymers, provides advantageous attributes for apparel, upholstery, resins, and nonwoven applications.

Scientists and engineers from DuPont and Genencor International, Inc. redesigned a living microbe to produce 1,3-propanediol. Inserting biosynthetic pathways from several microorganisms into an industrial host cell line allows the direct conversion of glucose to 1,3-propanediol, a route not previously available in a single microorganism. Genes from a yeast strain with the ability to convert glucose, derived from cornstarch, to glycerol were inserted into the host. Genes from a bacterium with the ability to transform glycerol to 1,3-propanediol were also incorporated. Additionally, the reactions present naturally in the host were altered to optimize product formation. The modifications maximize the ability of the organism to convert glucose to 1,3-propanediol while minimizing its ability to produce biomass and unwanted byproducts. Coalescing enzyme reactions from multiple organisms expands the range of materials that can be economically produced by biological means.

For more than 50 years, scientists have recognized the performance benefits of polyesters produced with 1,3-propanediol; however, the high cost of manufacturing the ingredient using petroleum feedstock and traditional chemistry kept it from the marketplace. The biological process using glucose as starting material will enable cost-effective manufacture of Sorona® polymer, which will offer consumer fabrics with softness, stretch and recovery, easy care, stain resistance, and colorfastness. A unique kink in the structure of the polymer containing 1,3-propanediol allows recovery at a high rate when it is stretched. As a result, Sorona® improves fit and comfort because the fabric quickly recovers its original shape when stretched, for example, in knees or elbows. The resilience of Sorona® also adds beneficial features to automotive upholstery and home textiles. In resin applications, Sorona®'s barrier characteristics protect moisture, taste, and odor.

Biology offers chemical manufacturers attractive options for the production of chemicals while adhering to the principles of green chemistry. This microbial production of a key polymer ingredient from renewable sources is one example. By integrating biology with chemistry, physics, and engineering, DuPont develops new solutions that enhance the environment and improve upon existing materials.

Shaw Industries, Inc.

EcoWorx™ Carpet Tile: A Cradle-to-Cradle Product

Innovation and Benefits

Conventional backings for carpet tiles contain bitumen, polyvinyl chloride (PVC), or polyurethane. EcoWorx™ carpet tiles have a novel backing that uses less toxic materials and has superior adhesion and dimensional stability. Because EcoWorx™ carpet tiles can be readily separated into carpet fiber and backing, each component can be easily recycled.

Historically, carpet tile backings have been manufactured using bitumen, polyvinyl chloride (PVC), or polyurethane (PU). While these backing systems have performed satisfactorily, there are several inherently negative attributes due to their feedstocks or their ability to be recycled. Although PVC has, to date, held the largest market share of carpet tile backing systems, it was Shaw's intent to design around PVC due to the health and environmental concerns around vinyl chloride monomer, chlorine-based products, plasticized PVC-containing phthalate esters, and toxic byproducts of combustion of PVC, such as dioxin and hydrochloric acid. While some claims are accepted by the Agency for Toxic Substances and Disease Registry (ATSDR) and the EPA, those resulting from publicly debated consumer perceptions provide ample justification for finding a PVC alternative.

Due to the thermoset cross-linking of polyurethanes, they are extremely difficult to recycle and are typically downcycled or landfilled at the end of their useful life. Bitumen provides some advantages in recycling, but the modified bitumen backings offered in Europe have failed to gain market acceptance in the United States and are unlikely to do so.

Shaw selected a combination of polyolefin resins from Dow Chemical as the base polymer of choice for EcoWorx™ due to the low toxicity of its feedstocks, superior adhesion properties, dimensional stability, and its ability to be recycled. The EcoWorx™ compound also had to be designed to be compatible with nylon carpet fiber. Although EcoWorx™ may be recovered from any fiber type, nylon-6 provides a significant advantage. Polyolefins are compatible with known nylon-6 depolymerization methods. PVC interferes with those processes. Nylon-6 chemistry is well-known and not addressed in first-generation production.

From its inception, EcoWorx™ met all of the design criteria necessary to satisfy the needs of the marketplace from a performance, health, and environmental standpoint. Research indicated that separation of the fiber and backing through elutriation, grinding, and air separation proved to be the best way to recover the face and backing components, but an infrastructure for returning postconsumer EcoWorx™ to the elutriation process was necessary. Research also indicated that the postconsumer carpet tile had a positive economic value at the end of its useful life. The cost of collection, transportation, elutriation, and return to the respective nylon and EcoWorx™ manufacturing processes is less than the cost of using virgin raw materials.

With introduction in 1999 and an anticipated lifetime of ten to fifteen years on the floor, significant quantities of EcoWorx™ will not flow back to Shaw until 2006 to 2007. An expandable elutriation unit is now operating at Shaw, typically dealing with industrial EcoWorx™ waste. Recovered EcoWorx™ is flowing back to the backing extrusion unit. Caprolactam recovered from the elutriated nylon-6 is flowing back into nylon compounding. EcoWorx™ will soon displace all PVC at Shaw.

Academic Award

Professor Eric J. Beckman

University of Pittsburgh

Design of Non-Fluorous, Highly CO_2-Soluble Materials

Innovation and Benefits

Carbon dioxide (CO_2) is a nontoxic chemical that can be used as a solvent in many industrial processes. Professor Beckman developed new detergents that allow a broad range of substances to dissolve in CO_2. Any process that can now use CO_2 may reduce or eliminate the use of hazardous solvents.

Carbon dioxide (CO_2), an environmentally benign and nonflammable solvent, has been investigated extensively in both academic and industrial settings. Solubility studies performed during the 1980s had suggested that CO_2's solvent power was similar to that of n-alkanes, leading to hopes that the chemical industry could use CO_2 as a "drop-in" replacement for a wide variety of organic solvents. It was learned that these solubility studies inflated the solvent power value by as much as 20 percent due to the strong quadrupole moment of CO_2 and that CO_2 is actually a rather feeble solvent compared to alkanes. As the 1980s drew to a close, a number of research groups began to explore the design of CO_2-philic materials, that is, compounds that dissolve in CO_2 at significantly lower pressures than do their alkyl analogs. These new CO_2-philes, primarily fluoropolymers, opened up a host of new applications for CO_2 including heterogeneous polymerization, protein extraction, and homogeneous catalysis.

Although fluorinated amphiphiles allow new applications for CO_2, their cost (approximately $1 per gram) reduces the economic viability of CO_2 processes, particularly given that the use of CO_2 requires high-pressure equipment. Furthermore, data have recently shown that fluoroalkyl materials persist in the environment, leading to the withdrawal of certain consumer products from the market. The drawbacks inherent to the use of fluorinated precursors, therefore, have inhibited the commercialization of many new applications for CO_2, and the full promise of CO_2-based technologies has yet to be realized. To address this need, Professor Eric J. Beckman and his group at the University of Pittsburgh have developed materials that work well, exhibiting miscibility pressures in CO_2 that are comparable or lower than fluorinated analogs and yet contain no fluorine.

Drawing from recent studies of the thermodynamics of CO_2 mixtures, Professor Beckman hypothesized that CO_2-philic materials should contain three primary features: (1) a relatively low glass transition temperature; (2) a relatively low cohesive energy density; and (3) a number of Lewis base groups. Low glass transition temperature correlates to high free volume and high molecular flexibility, which imparts a high entropy of mixing with CO_2 (or any solvent). A low cohesive energy density is primarily a result of weak solute–solute interactions, a necessary feature given that CO_2 is a rather feeble solvent. Finally, because CO_2 is a Lewis acid, the presence of Lewis base groups should create sites for specific favorable interactions with CO_2.

Professor Beckman's simple heuristic model was demonstrated on three sets of materials: functional silicones; poly(ether-carbonates); and acetate-functional polyethers. Poly(ether-carbonates) were found to exhibit lower miscibility pressures in CO_2 than perfluoropolyethers, yet are biodegradable and 100 times less expensive to prepare. Other families of non-fluorous CO_2-philes will inevitably be discovered using this model, further broadening the applicability of CO_2 as a greener process solvent.

Small Business Award

SC Fluids, Inc.

SCORR—Supercritical CO_2 Resist Remover

Innovation and Benefits

SCORR (Supercritical CO_2 Resist Remover) technology cleans residues from semiconductor wafers during their manufacture. SCORR improves on conventional techniques: it minimizes hazardous solvents and waste, is safer for workers, costs less, and uses less water and energy. SCORR also eliminates rinsing with ultrapure water and subsequent drying.

The semiconductor industry is the most successful growth industry in history, with sales totaling over $170 billion in the year 2000. The fabrication of integrated circuits (ICs) relies heavily on photolithography to define the shape and pattern of individual components. Current manufacturing practices use hazardous chemicals and enormous amounts of purified water during this intermediate step, which may be repeated up to 30 times for a single wafer. It is estimated that a typical chip-fabrication plant generates 4 million gallons of wastewater and consumes thousands of gallons of corrosive chemicals and hazardous solvents each day.

SC Fluids, in partnership with Los Alamos National Laboratory, has developed a new process, SCORR, that removes photoresist and post-ash, -etch, and -CMP (particulate) residue from semiconductor wafers. The SCORR technology outperforms conventional photoresist removal techniques in the areas of waste minimization, water use, energy consumption, worker safety, feature size compatibility, material compatibility, and cost. The key to the effectiveness of SCORR is the use of supercritical CO_2 in place of hazardous solvents and corrosive chemicals. Neat CO_2 is also utilized for the rinse step, thereby eliminating the need for a deionized water rinse and an isopropyl alcohol drying step. In the closed-loop SCORR process, CO_2 returns to a gaseous phase upon depressurization, leaving the silicon wafer dry and free of residue.

SCORR is cost-effective for five principal reasons. It minimizes the use of hazardous solvents, thereby minimizing costs required for disposal and discharge permits. It thoroughly strips photoresists from the wafer surface in less than half the time required for wet-stripping and far outperforms plasma, resulting in increased throughput. It eliminates rinsing and drying steps during the fabrication process, thereby simplifying and streamlining the manufacturing process. It eliminates the need for ultrapure deionized water, thus reducing time, energy, and cost. Supercritical CO_2 costs less than traditional solvents and is recyclable.

SCORR will meet future, as well as current technology demands. To continue its astounding growth, the semiconductor industry must develop ICs that are smaller, faster, and cheaper. Due to their high viscosity, traditional wet chemistries cannot clean small feature sizes. Vapor cleaning technologies are available, but viable methods for particle removal in the gas phase have not yet been developed. Using SCORR, the smallest features present no barriers because supercritical fluids have zero surface tension and a "gaslike" viscosity and, therefore, can clean features less than 100 nm. The low viscosity of super-critical fluids also allows particles less than 100 nm to be removed. The end result is a technically enabling "green" process that has been accepted by leading semiconductor manufacturers and equipment and material suppliers.

SCORR technology is being driven by industry in pursuit of its own accelerated technical and manufacturing goals. SCORR was initially developed through a technical request from Hewlett Packard (now Agilent). A joint Cooperative Research and Development Agreement between Los Alamos National Laboratory and SC Fluids has led to the development of commercial units (SC Fluids's Arroyo™ System). Other industry leaders, such as IBM, ATMI, and Shipley, are participating in the development of this innovative technology.

Greener Synthetic Pathways Award

Pfizer, Inc.

Green Chemistry in the Redesign of the Sertraline Process

Innovation and Benefits

Pfizer dramatically improved its manufacturing process for sertraline, the active ingredient in its popular drug, Zoloft®. The new process doubles overall product yield, reduces raw material use by 20–60 percent, eliminates the use or generation of approximately 1.8 million pounds of hazardous materials, reduces energy and water use, and increases worker safety.

Sertraline is the active ingredient in the important pharmaceutical, Zoloft®. Zoloft® is the most prescribed agent of its kind and is used to treat an illness (depression) that each year strikes 20 million adults in the United States, and that costs society $43.7 billion (1990 dollars). As of February 2000, more than 115 million Zoloft® prescriptions had been written in the United States.

Applying the principles of green chemistry, Pfizer has dramatically improved the commercial manufacturing process of sertraline. After meticulously investigating each of the chemical steps, Pfizer implemented a substantive green chemistry technology for a complex commercial process requiring extremely pure product. As a result, Pfizer significantly improved both worker and environmental safety. The new commercial process (referred to as the "combined" process) offers substantial pollution prevention benefits including improved safety and material handling, reduced energy and water use, and doubled overall product yield.

Specifically, a three-step sequence in the original manufacturing process was streamlined to a single step in the new sertraline process. The new process consists of imine formation of monomethylamine with a tetralone, followed by reduction of the imine function and in situ resolution of the diastereomeric salts of mandelic acid to provide chirally pure sertraline in much higher yield and with greater selectivity. A more selective palladium catalyst was implemented in the reduction step, which reduced the formation of impurities and the need for reprocessing. Raw material use was cut by 60 percent, 45 percent, and 20 percent for monomethylamine, tetralone, and mandelic acid, respectively.

Pfizer also optimized its process using the more benign solvent ethanol for the combined process. This change eliminated the need to use, distill, and recover four solvents (methylene chloride, tetrahydrofuran, toluene, and hexane) from the original synthesis. Pfizer's innovative use of solubility differences to drive the equilibrium toward imine formation in the first reaction of the combined steps eliminated approximately 310,000 pounds per year of the problematic reagent titanium tetrachloride. This process change eliminates 220,000 pounds of 50 percent sodium hydroxide, 330,000 pounds of 35 percent hydrochloric acid waste, and 970,000 pounds of solid titanium dioxide waste per year.

By eliminating waste, reducing solvents, and maximizing the yield of key intermediates, Pfizer has demonstrated significant green chemistry innovation in the manufacture of an important pharmaceutical agent.

Greener Reaction Conditions Award

Cargill Dow LLC (now NatureWorks LLC)

NatureWorks™ PLA Process

Innovation and Benefits

The NatureWorks™ process makes biobased, compostable, and recyclable polylactic acid (PLA) polymers using 20–50 percent less fossil fuel resources than comparable petroleum-based polymers. The synthesis of PLA polymers eliminates organic solvents and other hazardous materials, completely recycles product and byproduct streams, and efficiently uses catalysts to reduce energy consumption and improve yield.

NatureWorks™ polylactic acid (PLA) is the first family of polymers derived entirely from annually renewable resources that can compete head-to-head with traditional fibers and plastic packaging materials on a cost and performance basis. For fiber consumers, this will mean a new option for apparel and carpeting applications: a material that bridges the gap in performance between conventional synthetic fibers and natural fibers such as silk, wool, and cotton. Clothing made with NatureWorks™ fibers features a unique combination of desirable attributes such as superior hand, touch, and drape, wrinkle resistance, excellent moisture management, and resilience. In packaging applications, consumers will have the opportunity to use a material that is natural, compostable, and recyclable without experiencing any tradeoffs in product performance.

The NatureWorks™ PLA process offers significant environmental benefits in addition to the outstanding performance attributes of the polymer. NatureWorks™ PLA products are made in a revolutionary new process developed by Cargill Dow LLC that incorporates all 12 green chemistry principles. The process consists of three separate and distinct steps that lead to the production of lactic acid, lactide, and PLA high polymer. Each of the process steps is free of organic solvent: water is used in the fermentation while molten lactide and polymer serve as the reaction media in monomer and polymer production. Each step not only has exceptionally high yields (over 95 percent) but also utilizes internal recycle streams to eliminate waste. Small (ppm) amounts of catalyst are used in both the lactide synthesis and polymerization to further enhance efficiency and reduce energy consumption. Additionally, the lactic acid is derived from annually renewable resources, PLA requires 20–50 percent less fossil resources than comparable petroleum-based plastics, and PLA is fully biodegradable or readily hydrolyzed into lactic acid for recycling back into the process.

While the technology to create PLA in the laboratory has been known for many years, previous attempts at large-scale production were targeted solely at niche biodegradable applications and were not commercially viable. Only now has Cargill Dow been able to perfect the NatureWorks™ process and enhance the physical properties of PLA resins to compete successfully with commodity petroleum-based plastics. Cargill Dow is currently producing approximately 8.8 million pounds of PLA per year to meet immediate market development needs. Production in the first world-scale 310-million-pound-per-year plant began November 1, 2001.

The NatureWorks™ process embodies the well-known principles of green chemistry by preventing pollution at the source through the use of a natural fermentation process to produce lactic acid, substituting annually renewable materials for petroleum-based feedstock, eliminating the use of solvents and other hazardous materials, completely recycling product and byproduct streams, and efficiently using catalysts to reduce energy consumption and improve yield. In addition, NatureWorks™ PLA products can be either recycled or composted after use.

Designing Greener Chemicals Award

Chemical Specialties, Inc. (CSI) (now Viance)

ACQ Preserve®: The Environmentally Advanced Wood Preservative

Innovation and Benefits

ACQ Preserve® is an environmentally advanced wood preservative designed to replace chromated copper arsenate (CCA) wood preservatives, which have been phased out because of their toxicity. ACQ Preserve® will eliminate the use of 40 million pounds of arsenic and 64 million pounds of hexavalent chromium each year. It also avoids the potential risks associated with producing, transporting, using, and disposing of CCA wood preservatives and CCA-treated wood.

The pressure-treated wood industry is a $4 billion industry, producing approximately 7 billion board feet of preserved wood per year. More than 95 percent of the pressure-treated wood used in the United States is currently preserved with chromated copper arsenate (CCA). Approximately 150 million pounds of CCA wood preservatives were used in the production of pressure-treated wood in 2001, enough wood to build 435,000 homes. About 40 million pounds of arsenic and 64 million pounds of chromium(VI) were used to manufacture these CCA wood preservatives.

Over the past few years, scientists, environmentalists, and regulators have raised concerns regarding the risks posed by the arsenic that is either dislodged or leached from CCA-treated wood. A principal concern is the risk to children from contact with CCA-treated wood in playground equipment, picnic tables, and decks. This concern has led to increased demand for and use of alternatives to CCA.

Chemical Specialties, Inc. (CSI) developed its alkaline copper quaternary (ACQ) wood preservative as an environmentally advanced formula designed to replace the CCA industry standard. ACQ formulations combine a bivalent copper complex and a quaternary ammonium compound in a 2:1 ratio. The copper complex may be dissolved in either ethanolamine or ammonia. Carbon dioxide (CO_2) is added to the formulation to improve stability and to aid in solubilization of the copper.

Replacing CCA with ACQ is one of the most dramatic pollution prevention advancements in recent history. Because more than 90 percent of the 44 million pounds of arsenic used in the United States each year is used to make CCA, replacing CCA with ACQ will virtually eliminate the use of arsenic in the United States. In addition, ACQ Preserve® will eliminate the use of 64 million pounds of chromium(VI). Further, ACQ avoids the potential risks associated with the production, transportation, use, and disposal of the arsenic and chromium(VI) contained in CCA wood preservatives and CCA-treated wood. In fact, ACQ does not generate any RCRA (i.e., Resource Conservation and Recovery Act) hazardous waste from production and treating facilities. The disposal issues associated with CCA-treated wood and ash residues associated with the burning of treated wood will also be avoided.

In 1996, CSI commercialized ACQ Preserve® in the United States. More than one million active pounds of ACQ wood preservatives were sold in the United States in 2001 for use by 13 wood treaters to produce over 100 million board feet of ACQ-preserved wood. In 2002, CSI plans to spend approximately $20 million to increase its production capacity for ACQ to over 50 million active pounds. By investing in ACQ technology, CSI has positioned itself and the wood preservation industry to transition away from arsenic-based wood preservatives to a new generation of preservative systems.

Academic Award

Professor Chao-Jun Li
Tulane University

Quasi-Nature Catalysis: Developing Transition Metal Catalysis in Air and Water

Innovation and Benefits

Professor Li developed a novel method to carry out a variety of important chemical reactions that had previously required both an oxygen-free atmosphere and hazardous organic solvents. His reactions use metal catalysts and run in open containers of water. His method is inherently safer, requires fewer process steps, operates at lower temperatures, and generates less waste.

The use of transition metals for catalyzing reactions is of growing importance in modern organic chemistry. These catalyses are widely used in the synthesis of pharmaceuticals, fine chemicals, petrochemicals, agricultural chemicals, polymers, and plastics. Of particular importance is the formation of C–C, C–O, C–N, and C–H bonds. Traditionally, the use of an inert gas atmosphere and the exclusion of moisture have been essential in both organometallic chemistry and transition-metal catalysis. The catalytic actions of transition metals in ambient atmosphere have played key roles in various enzymatic reactions including biocatalysis, biodegradation, photosynthesis, nitrogen fixation, and digestions, as well as the evolution of bioorganisms. Unlike traditionally used transition-metal catalysts, these "natural" catalytic reactions occur under aqueous conditions in an air atmosphere.

The research of Professor Chao-Jun Li has focused on the development of numerous transition-metal-catalyzed reactions both in air and water. Specifically, Professor Li has developed a novel [3+2] cycloaddition reaction to generate 5-membered carbocycles in water; a synthesis of β-hydroxyl esters in water; a chemoselective alkylation and pinacol coupling reaction mediated by manganese in water; and a novel alkylation of 1,3-dicarbonyl-type compounds in water. His work has enabled rhodium-catalyzed carbonyl addition and rhodium-catalyzed conjugate addition reactions to be carried out in air and water for the first time. A highly efficient, zinc-mediated Ullman-type coupling reaction catalyzed by palladium in water has also been designed. This reaction is conducted at room temperature under an atmosphere of air. In addition, a number of Barbier-Grignard-type reactions in water have been developed; these novel synthetic methodologies are applicable to the synthesis of a variety of useful chemicals and compounds. Some of these reactions demonstrate unprecedented chemoselectivity that eliminates byproduct formation and product separation. Application of these new methodologies to natural product synthesis, including polyhydroxylated natural products, medium-sized rings, and macrocyclic compounds, yields shorter reaction sequences.

Transition-metal-catalyzed reactions in water and air offer many advantages. Water is readily available and inexpensive; it is not flammable, explosive, or toxic. Consequently, aqueous-based production processes are inherently safer with regard to accident potential. Using water as a reaction solvent can save synthetic steps by avoiding protection and deprotection processes that affect overall synthetic efficiency and contribute to solvent emission. Product isolation may be facilitated by simple phase separation rather than energy-intensive and organic-emitting processes involving distillation of organic solvent. The temperature of reactions performed in aqueous media is also easier to control since water has such a high heat capacity. The open-air feature offers convenience in operations of chemical synthesis involving small-scale combinatorial synthesis, large-scale manufacturing, and catalyst recycling. As such, Professor Li's work in developing transition-metal-mediated and -catalyzed reactions in air and water offers an attractive alternative to the inert atmosphere and organic solvents traditionally used in synthesis.

Small Business Award

EDEN Bioscience Corporation (technology acquired by Plant Health Care, Inc.)

Messenger®: A Green Chemistry Revolution in Plant Production and Food Safety

Innovation and Benefits

EDEN Bioscience Corporation discovered and commercialized harpins, a new class of nontoxic, naturally occurring, biodegradable proteins, as an alternative to traditional pesticides. Harpins activate a plant's defense and growth mechanisms, thereby increasing crop yield and quality, and minimizing crop losses. EDEN manufactures Messenger®, its commercially available, harpin-containing, EPA-approved product, using a water-based fermentation system.

In today's competitive agricultural environment, growers must maximize crop productivity by enhancing yield and minimizing crop losses. The Food and Agriculture Organization of the United Nations estimates that annual losses to growers from pests reach $300 billion worldwide. In addition to basic agronomic practices, growers generally have two alternatives to limit these economic losses and increase yields: (1) use traditional chemical pesticides; or (2) grow crops that are genetically engineered for pest resistance. Each of these approaches has come under increasing criticism from a variety of sources worldwide including environmental groups, government regulators, consumers, and labor advocacy groups. Harpin technology, developed by EDEN Bioscience Corporation, provides growers with a highly effective alternative approach to crop production that addresses these concerns.

EDEN's harpin technology is based on a new class of nontoxic, naturally occurring proteins called harpins, which were first discovered by Dr. Zhongmin Wei, EDEN's Vice President of Research, and his colleagues during his tenure at Cornell University. Harpin proteins trigger a plant's natural defense systems to protect against disease and pests and simultaneously activate certain plant growth systems without altering the plant's DNA. When applied to crops, harpins increase plant biomass, photosynthesis, nutrient uptake, and root development, and, ultimately, lead to greater crop yield and quality.

Unlike most agricultural chemicals, harpin-based products are produced in a water-based fermentation system that uses no harsh solvents or reagents, requires only modest energy inputs, and generates no hazardous chemical wastes. Fermentation byproducts are fully biodegradable and safely disposable. In addition, EDEN uses low-risk ingredients to formulate the harpin protein-based end product. Approximately 70 percent of the dried finished product consists of an innocuous, food-grade substance that is used as a carrier for harpin protein.

The result of this technology is an EPA-approved product called Messenger® that has been demonstrated on more than 40 crops to effectively stimulate plants to defend themselves against a broad spectrum of viral, fungal, and bacterial diseases, including some for which there currently is no effective treatment. In addition, Messenger® has been shown through an extensive safety evaluation to have virtually no adverse effect on any of the organisms tested, including mammals, birds, honey bees, plants, fish, aquatic invertebrates, and algae. Only 0.004–0.14 pounds of harpin protein per acre per season is necessary to protect crops and enhance yields. As with most proteins, harpin is a fragile molecule that is degraded rapidly by UV and natural microorganisms and has no potential to bioaccumulate or to contaminate surface or groundwater resources.

Deployment of harpin technology conserves resources and protects the environment by reducing total agricultural inputs and partially replacing many higher-risk products. Using environmentally benign harpin protein technology, growers for the first time in the history of modern agriculture will be able to harness the innate defense and growth systems of crops to substantially enhance yields, improve crop quality, and reduce reliance on conventional agricultural chemicals.

Greener Synthetic Pathways Award

Bayer Corporation
Bayer AG
(technology acquired by LANXESS)

Baypure™ CX (Sodium Iminodisuccinate): An Environmentally Friendly and Readily Biodegradable Chelating Agent

Innovation and Benefits

Chelating agents are ingredients in a variety of products, such as detergents, fertilizers, and household and industrial cleaners. Most traditional chelating agents do not break down readily in the environment. Bayer Corporation and Bayer AG developed a waste-free, environmentally friendly manufacturing process for a new, biodegradable, nontoxic chelating agent. This new process eliminates the use of formaldehyde and hydrogen cyanide.

Chelating agents are used in a variety of applications, including detergents, agricultural nutrients, and household and industrial cleaners. Most traditional chelating agents, however, are poorly biodegradable. Some are actually quite persistent and do not adsorb at the surface of soils in the environment or at activated sludge in wastewater treatment plants. Because of this poor biodegradability combined with high water solubility, traditional chelators are readily released into the environment and have been detected in the surface waters of rivers and lakes and in make-up water processed for drinking water.

As part of its commitment to Responsible Care®, Bayer Corporation manufactures a readily biodegradable and environmentally friendly chelating agent, D,L-aspartic-*N*-(1,2-dicarboxyethyl) tetrasodium salt, also known as sodium iminodisuccinate. This agent is characterized by excellent chelation capabilities, especially for iron(III), copper(II), and calcium, and is both readily biodegradable and benign from a toxicological and ecotoxicological standpoint. Sodium iminodisuccinate is also an innovation in the design of chemicals that favorably impact the environment. This accomplishment was realized not by "simple" modification of molecular structures of currently used chelating agents, but instead by the development of a wholly new molecule. Sodium iminodisuccinate is produced by a 100 percent waste-free and environmentally friendly manufacturing process. Bayer AG was the first to establish an environmentally friendly, patented manufacturing process to provide this innovative chelant commercially.

Sodium iminodisuccinate belongs to the aminocarboxylate class of chelating agents. Nearly all aminocarboxylates in use today are acetic acid derivatives produced from amines, formaldehyde, sodium hydroxide, and hydrogen cyanide. The industrial use of thousands of tons of hydrogen cyanide is an extreme toxicity hazard. In contrast, Bayer's sodium iminodisuccinate is produced from maleic anhydride (a raw material also produced by Bayer), water, sodium hydroxide, and ammonia. The only solvent used in the production process is water, and the only side product formed, ammonia dissolved in water, is recycled back into sodium iminodisuccinate production or used in other Bayer processes.

Because sodium iminodisuccinate is a readily biodegradable, nontoxic, and nonpolluting alternative to other chelating agents, it can be used in a variety of applications that employ chelating agents. For example, it can be used as a builder and bleach stabilizer in laundry and dishwashing detergents to extend and improve the cleaning properties of the eight billion pounds of these products that are used annually. Specifically, sodium iminodisuccinate chelates calcium to soften water and improve the cleaning function of the surfactant. In photographic film processing, sodium iminodisuccinate complexes metal ions and helps to eliminate precipitation onto the film surface. In agriculture, chelated metal ions help to prevent, correct, and minimize crop mineral deficiencies. Using sodium iminodisuccinate as the chelating agent in agricultural applications eliminates the problem of environmental persistence common with other synthetic chelating agents. In summary, Bayer's sodium iminodisuccinate chelating agent offers the dual benefits of producing a biodegradable, environmentally friendly chelating agent that is also manufactured in a waste-free process.

Greener Reaction Conditions Award

Novozymes North America, Inc.

BioPreparation™ of Cotton Textiles: A Cost-Effective, Environmentally Compatible Preparation Process

Innovation and Benefits

Novozymes North America developed BioPreparation™, a technology to separate natural waxes, oils, and contaminants from cotton before it is made into fabric. This technology uses enzymes instead of corrosive chemicals and could save 7–12 billion gallons of water each year.

In textiles, the source of one of the most negative impacts on the environment originates from traditional processes used to prepare cotton fiber, yarn, and fabric. Fabric preparation consists of a series of various treatments and rinsing steps critical to obtaining good results in subsequent textile finishing processes. These water-intensive, wet processing steps generate large volumes of wastes, particularly from alkaline scouring and continuous/batch dyeing. These wastes include large amounts of salts, acids, and alkali. In view of the 40 billion pounds of cotton fiber that are prepared annually on a global scale, it becomes clear that the preparation process is a major source of environmentally harsh chemical contribution to the environment.

Cotton wax, a natural component in the outer layer of cotton fibers, is a major obstacle in processing textiles; it must be removed to prepare the textile for dyeing and finishing. Conventional chemical preparation processes involve treatment of the cotton substrate with hot solutions of sodium hydroxide, chelating agents, and surface active agents, often followed by a neutralization step with acetic acid. The scouring process is designed to break down or release natural waxes, oils, and contaminants and emulsify or suspend these impurities in the scouring bath. Typically, scouring wastes contribute high biological oxygen demand (BOD) loads during cotton textile preparation (as much as 50 percent).

Novozymes's BioPreparation™ technology is an alternative to sodium hydroxide that offers many advantages for textile wet processing, including reduced biological and chemical oxygen demand (BOD/COD) and decreased water use. BioPreparation™ is an enzymatic process for treating cotton textiles that meets the performance characteristics of alkaline scour systems while reducing chemical and effluent load. Pectate lyase is the main scouring agent that degrades pectin to release the entangled waxes and other components from the cotton surface. The enzyme is also compatible with other enzymatic preparations (amylases, cellulases) used to improve the performance properties of cotton fabrics.

The practical implications that BioPreparation™ technology has on the textile industry are realized in terms of conservation of chemicals, water, energy, and time. Based on field trials, textile mills may save as much as 30–50 percent in water costs by replacing caustic scours or by combining the usually separate scouring and dyeing steps into one. This water savings results because BioPreparation™ uses fewer rinsing steps than required during a traditional caustic scour. Significant time savings were also demonstrated by combining treatment steps. A recent statistical survey determined that 162 knitting mills typically use 24 billion gallons per year of water in processing goods from scouring to finishing; the BioPreparation™ approach would save from 7–12 billion gallons per year of water. In addition, field trials established that BOD and COD loads are decreased by 25 and 40 percent, respectively, when compared to conventional sodium hydroxide treatments. Furthermore, these conservation measures translate directly into cost savings of 30 percent or more. As such, this patented process provides an economical and environmentally friendly alternative to alkaline scour systems currently used in the textile industry.

Designing Greener Chemicals Award

PPG Industries

Yttrium as a Lead Substitute in Cationic Electrodeposition Coatings

Innovation and Benefits

PPG Industries developed a novel metal primer that uses yttrium instead of lead to resist corrosion in automobiles. The metal yttrium is far less toxic to human health and the environment than is lead and is more effective in preventing corrosion. PPG's primer should eliminate one million pounds of lead from automobile manufacture over the next few years. In addition, this primer does not require chromium- or nickel-based pretreatments, potentially eliminating the use of 25,000 pounds of chromium and 50,000 pounds of nickel each year.

PPG Industries introduced the first cationic electrodeposition primer to the automotive industry in 1976. During the succeeding years, this coating technology became very widely used in the industry such that today essentially all automobiles are given a primer coat using the chemistry and processing methods developed by PPG. The major benefits of this technology are corrosion resistance, high transfer efficiency (low waste), reliable automated application, and very low organic emissions. Unfortunately, the high corrosion resistance property of electrocoat has always been dependent on the presence of small amounts of lead salts or lead pigments in the product. As regulatory pressure on lead increased and consumer demand for improved corrosion resistance grew, lead was regularly exempted from regulation in electrocoat because there were no cost-effective substitutes. This is especially important in moderately priced cars and trucks where the high cost of using 100 percent zinc-coated (galvanized) steel could not be tolerated. Lead is very effective for protecting cold-rolled steel, which is still a common material of construction in automobiles.

For more than 20 years, PPG and other paint companies have sought a substitute for lead in this application. This search led to PPG's discovery that yttrium can replace lead in cationic electrocoat without any sacrifice in corrosion performance. Yttrium is a common element in the environment, being widely distributed in low concentrations throughout the earth's crust and more plentiful in the earth's crust than lead and silver. Although yttrium is much less studied than lead, the available data on yttrium indicate orders of magnitude lower hazard. As a dust hazard, yttrium is 100 times safer than lead at typical levels of use.

Numerous other benefits are realized when yttrium is used in electrocoat applications. Yttrium is twice as effective as lead on a weight basis, allowing the formulation of commercial coatings that contain half the yttrium by weight relative to lead in comparably performing lead-containing products. In addition, it has been found that as yttrium is deposited in an electrocoat film, it deposits as the hydroxide. The hydroxide is converted to yttrium oxide during normal baking of the electrocoat. The oxide is extraordinarily nontoxic by ingestion as indicated by the LD_{50} of over 10 grams per kilogram in rats, which is in stark contrast to lead. The ubiquitous nature of yttrium in the environment and the insoluble ceramic-like nature of the oxide combine to make it an unlikely cause of future environmental or health problems.

An environmental side benefit of yttrium is its performance over low-nickel and chrome-free metal pretreatments. In automotive production, a metal pretreatment is always applied to the body prior to electrocoat, which is designed to assist in adhesion and corrosion performance. This process generates significant quantities of chromium- and nickel-containing waste and, like lead, is also a concern to recyclers of the finished vehicle. By using yttrium in the electrocoat step, chrome can be completely eliminated using standard chrome-free rinses and low-nickel or possibly nickel-free pretreatments, both of which are commercially available today. This should be possible without concern of compromising long-term vehicle corrosion performance. For PPG pretreatment customers, this should result in the elimination of up to 25,000 pounds of chrome and 50,000 pounds of nickel annually from PPG products. As PPG customers implement yttrium over the next several years, approximately one million pounds of lead (as lead metal) will be removed from the electrocoat applications of PPG automotive customers.

Academic Award

Professor Chi-Huey Wong
The Scripps Research Institute

Enzymes in Large-Scale Organic Synthesis

Innovation and Benefits

Professor Wong developed methods to replace traditional reactions requiring toxic metals and hazardous solvents. His methods use enzymes, environmentally acceptable solvents, and mild reaction conditions. His methods also enable novel reactions that were otherwise impossible or impractical on an industrial scale. Professor Wong's methods hold promise for applications in a wide variety of chemical industries.

Organic synthesis has been one of the most successful of scientific disciplines and has contributed significantly to the development of the pharmaceutical and chemical industries. New synthetic reagents, catalysts, and processes have made possible the synthesis of molecules with varying degrees of complexity. The types of problems at which nonbiological organic synthesis has excelled, ranging from stoichiometric reactions to catalysis with acids, bases, and metals, will continue to be very important. New synthetic and catalytic methods are, however, necessary to deal with the new classes of compounds that are becoming the key targets of molecular research and development.

Compounds with polyfunctional groups such as carbohydrates and related structures pose particular challenges to nonbiological synthetic methods but are natural targets for biological methods. In addition, biological methods are necessary to deal with increasing environmental concerns. Transition metals, heavy elements, and toxic organic solvents are often used in nonbiological processes. When these materials are used with great care and efficiency, they may still be environmentally acceptable, but their handling and disposal pose problems. The ability to use recombinant and engineered enzymes to carry out environmentally acceptable synthetic transformations that are otherwise impossible or impractical offers one of the best opportunities now available to chemistry and the pharmaceutical industry.

Professor Chi-Huey Wong at the Scripps Research Institute has pioneered work on the development of effective enzymes and the design of novel substrates and processes for large-scale organic synthesis. The methods and strategies that Professor Wong has developed have made possible synthetic transformations that are otherwise impossible or impractical, especially in areas vitally important in biology and medicine, and have pointed the way toward new green methodologies for use in large-scale chemistry. A recent study by the Institute for Scientific Information ranked Professor Wong in the top 15 of the most-cited chemists in the world for the period 1994 to 1996. According to this study, he is also the most-cited chemist worldwide working in the area of enzymes.

Some of the strategies and methods developed by Professor Wong are breakthrough achievements that laid the framework for much of the current use of enzymes as catalysts in large-scale organic synthesis. The techniques and reagents developed in this body of pioneering work are used widely today for research and development. The scope of contributions ranges from relatively simple enzymatic processes (e.g., chiral resolutions and stereoselective syntheses) to complex, multistep enzymatic reactions (e.g., oligosaccharide synthesis). For example, the irreversible enzymatic transesterification reaction using enol esters in environmentally acceptable organic solvents invented by Professor Wong represents the most widely used method for enantioselective transformation of alcohols in pharmaceutical development. The multi-enzyme system based on genetically engineered glycosyltransferases coupled with in situ regeneration of sugar nucleotides developed by Professor Wong has revolutionized the field of carbohydrate chemistry and enabled the large-scale synthesis of complex oligosaccharides for clinical evaluation. All of these new enzymatic reactions are carried out in environmentally acceptable solvents, under mild reaction conditions, at ambient temperature, and with minimum protection of functional groups. The work of Professor Wong represents a new field of green chemistry suitable for large-scale synthesis that is impossible or impractical to achieve by nonenzymatic means.

Small Business Award

RevTech, Inc.

Envirogluv™: A Technology for Decorating Glass and Ceramicware with Radiation-Curable, Environmentally Compliant Inks

Innovation and Benefits

RevTech developed the Envirogluv™ process to print top-quality labels directly on glass, replacing paper labels, decals, or applied ceramic labeling. Envirogluv™ inks do not contain heavy metals, contain little to no volatile organic compounds (VOCs), and are biodegradable. This technology saves energy by replacing high-temperature ovens with ultraviolet light, saves raw materials, wastes no ink, and produces decorated glass that is completely recyclable.

Billions of products are sold in glass containers in the United States every year. Most, if not all, of these glass containers are labeled in some fashion. Typically, decorative indicia are applied to glass using paper labels, decals, or a process known as applied ceramic labeling (ACL). ACL involves first printing the glass with an ink composition that contains various heavy metals such as lead, cadmium, and chromium, then bonding the ink to the glass by baking in an oven known as a lehr at temperatures of 1,000 °F or more for several hours.

All of these processes have disadvantages. Paper labels are inexpensive but can be easily removed if the container is exposed to water or abrasion. In addition, paper labels do not provide the aesthetics desired by decorators who want rich, expensive-looking containers. Decals are expensive and difficult to apply at the high line speeds that are required in the decoration of most commercial containers. More important, decals are made from materials that are not biodegradable, which causes serious problems in the recycling of glass containers that are decorated by this method. The use and disposal of the heavy metals required in ACL presents serious environmental concerns. Moreover, the high-temperature lehr ovens required in ACL decorating utilize substantial amounts of energy and raise safety issues with respect to workers and plant facilities that use this equipment. The inks used in ACL decorating also tend to contain high levels of volatile organic compounds (VOCs) that can lead to undesirable emissions.

Clearly, there has been a need in the glass decorating industry for a decorated glass container that is aesthetically pleasing, durable, and obtained in a cost-effective, environmentally friendly, and energy-efficient manner. Envirogluv™ technology fills that need. Envirogluv™ is a glass decorating technology that directly silk-screens radiation-curable inks onto glass, then cures the ink almost instantly by exposure to UV light. The result is a crisp, clean label that is environmentally sound, with a unit cost that is about half that of traditional labeling.

Envirogluv™ technology offers many human health and environmental benefits. The ink compositions used in the Envirogluv™ process do not contain any heavy metals and contain little to no VOCs. All Envirogluv™ pigments are biodegradable. The Envirogluv™ inks are cured directly on the glass by exposure to UV radiation, eliminating the high-temperature baking in a lehr oven that is associated with the ACL process. This provides additional safety and environmental benefits, such as reduced energy consumption and reduced chance of worker injury. In addition, the process uses less raw materials and does not generate any waste ink. Furthermore, Envirogluv™ decorated glass containers eliminate the need for extra packaging and are completely recyclable. Applications suitable for the Envirogluv™ process include tableware, cosmetics containers, and plate glass.

Greener Synthetic Pathways Award

Roche Colorado Corporation

An Efficient Process for the Production of Cytovene®, a Potent Antiviral Agent

Innovation and Benefits

Roche Colorado developed an environmentally friendly way to synthesize Cytovene®, a potent antiviral drug. Their process eliminates nearly 2.5 million pounds of hazardous liquid waste and over 55,000 pounds of hazardous solid waste each year. This process also increases the overall yield more than 25 percent and doubles the production throughput.

The design, development, and implementation of environmentally friendly processes for the large-scale production of pharmaceutical products is one of the most technically challenging aspects of business operations in the pharmaceutical industry. Roche Colorado Corporation (RCC), in establishing management and operational systems for the continuous improvement of environmental quality in its business activities, has, in essence, adopted the Presidential Green Chemistry Challenge Program's basic principles of green chemistry: the development of environmentally friendly processes for the manufacture of pharmaceutical products. In particular, RCC has successfully applied these principles to the manufacture of ganciclovir, the active ingredient in Cytovene®, a potent antiviral agent. Cytovene® is used in the treatment of cytomegalovirus (CMV) retinitis infections in immunocompromised patients, including patients with AIDS, and also used for the prevention of CMV disease in transplant recipients at risk for CMV.

In the early 1990s, Roche Colorado Corporation developed the first commercially viable process for the production of Cytovene®. By 1993, chemists at RCC's Boulder Technology Center designed a new and expedient process for the production of Cytovene®, which at the time had an estimated commercial demand of approximately 110,000 pounds per year. Leveraging the basic principles of green chemistry and molecular conservation into the design process, significant improvements were demonstrated in the second-generation Guanine Triester (GTE) Process. Compared to the first-generation commercial manufacturing process, the GTE Process reduced the number of chemical reagents and intermediates from 22 to 11, eliminated the (only) two hazardous solid waste streams, eliminated 11 different chemicals from the hazardous liquid waste streams, and efficiently recycled and reused four of the five ingredients not incorporated into the final product. Inherent within the process improvements demonstrated was the complete elimination of the need for operating and monitoring three different potentially hazardous chemical reactions. Overall, the GTE Process provided an expedient method for the production of Cytovene®, demonstrating a procedure that provided an overall yield increase of more than 25 percent and a production throughput increase of 100 percent.

In summary, the new GTE Process for the commercial production of Cytovene® clearly demonstrates the successful implementation of the general principles of green chemistry: the development of environmentally friendly syntheses, including the development of alternative syntheses utilizing nonhazardous and nontoxic feedstocks, reagents, and solvents; elimination of waste at the source (liquid waste: 2.5 million pounds per year and solid waste: 56,000 pounds per year); and elimination of the production of toxic wastes and byproducts. The process establishes new and innovative technology for a general and efficient method for the preparation of Cytovene® and other potent antiviral agents. It is registered with the U.S. Food and Drug Administration (FDA) as the current manufacturing process for the world's supply of Cytovene®.

Greener Reaction Conditions Award

Bayer Corporation

Bayer AG

Two-Component Waterborne Polyurethane Coatings

Innovation and Benefits

Bayer developed a series of high-performance, water-based, two-component polyurethane coatings that eliminate most or all of the organic solvents used in conventional polyurethane coatings. Bayer's water-based polyurethane coatings reduce volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions by 50–90 percent.

Two-component (2K) waterborne polyurethane coatings are an outstanding example of the use of alternative reaction conditions for green chemistry. This technology is achieved by replacing most or all of the volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) used in conventional 2K solventborne polyurethane coatings with water as the carrier, without significant reduction in performance of the resulting coatings. This may seem an obvious substitution, but, due to the particular chemistry of the reactive components of polyurethane, it is not that straightforward.

Two-component solventborne polyurethane coatings have long been considered in many application areas to be the benchmark for high-performance coatings systems. The attributes that make these systems so attractive are fast cure under ambient or bake conditions, high-gloss and mirror-like finishes, hardness or flexibility as desired, chemical and solvent resistance, and excellent weathering. The traditional carrier, however, has been organic solvent that, upon cure, is freed to the atmosphere as VOC and HAP material. High-solids systems and aqueous polyurethane dispersions ameliorate this problem but do not go far enough.

An obvious solution to the deficiencies of 2K solventborne polyurethanes and aqueous polyurethane dispersions is a reactive 2K polyurethane system with water as the carrier. In order to bring 2K waterborne polyurethane coatings to the U.S. market, new waterborne and water-reducible resins had to be developed. To overcome some application difficulties, new mixing/spraying equipment was also developed. For the technology to be commercially viable, an undesired reaction of a polyisocyanate cross-linker with water had to be addressed, as well as problems with the chemical and film appearance resulting from this side reaction. The work done on the 2K waterborne polyurethanes over the past several years has resulted in a technology that will provide several health and environmental benefits. VOCs will be reduced by 50–90 percent and HAPs by 50–99 percent. The amount of chemical byproducts evolved from films in interior applications will also be reduced, and rugged interior coatings with no solvent smell will now be available.

Today, 2K waterborne polyurethane is being applied on industrial lines where good properties and fast cure rates are required for such varied products as metal containers and shelving, sporting equipment, metal- and fiberglass-reinforced utility poles, agricultural equipment, and paper products. In flooring coatings applications where the market-driving force is elimination of solvent odor, 2K waterborne polyurethane floor coatings provide a quick dry, high abrasion resistance, and lack of solvent smell (<0.1 pound organic solvent per gallon). In wood applications, 2K waterborne polyurethane coatings meet the high-performance wood finishes requirements for kitchen cabinet, office, and laboratory furniture manufacturers while releasing minimal organic solvents in the workplace or to the atmosphere. In the United States, the greatest market acceptance of 2K waterborne polyurethane is in the area of special-effect coatings in automotive applications. These coatings provide the soft, luxurious look and feel of leather to hard plastic interior automobile surfaces, such as instrument panels and air bag covers. Finally, in military applications, 2K waterborne polyurethane coatings are being selected because they meet the demanding military performance criteria that include flat coatings with camouflage requirements, corrosion protection, chemical and chemical agent protection, flexibility, and exterior durability, along with VOC reductions of approximately 50 percent.

Designing Greener Chemicals Award

Dow AgroSciences LLC

SentriconTM Termite Colony Elimination System, A New Paradigm for Termite Control

Innovation and Benefits

Dow's SentriconTM System eliminates termite colonies with highly specific bait applied only where termites are active; it replaces widespread applications of pesticide in the soil around houses and other structures. EPA has registered SentriconTM as a reduced-risk pesticide. Dow's system reduces the use of hazardous materials and reduces potential impacts on human health and the environment. By late1999, SentriconTM was used for over 300,000 structures in the United States.

The annual cost of termite treatments to the U.S. consumer is about $1.5 billion, and each year as many as 1.5 million homeowners will experience a termite problem and seek a control option. From the 1940s until 1995, the nearly universal treatment approach for subterranean termite control involved the placement of large volumes of insecticide dilutions into the soil surrounding a structure to create a chemical barrier through which termites could not penetrate. Problems with this approach include difficulty in establishing an uninterrupted barrier in the vast array of soil and structural conditions, use of large volumes of insecticide dilution, and potential hazards associated with accidental misapplications, spills, off-target applications, and worker exposure. These inherent problems associated with the use of chemical barrier approaches for subterranean termite control created a need for a better method. The search for a baiting alternative was the focus of a research program established by Dr. Nan-Yao Su of the University of Florida who, in the 1980s, had identified the characteristics needed for a successful termite bait toxicant.

The unique properties of hexaflumuron made it an excellent choice for use in controlling subterranean termite colonies. The SentriconTM Termite Colony Elimination System, developed by Dow AgroSciences in collaboration with Dr. Su, was launched commercially in 1995 after receiving EPA registration as a reduced-risk pesticide. SentriconTM represents truly novel technology employing an Integrated Pest Management approach using monitoring and targeted delivery of a highly specific bait. Because it eliminates termite colonies threatening structures using a targeted approach, SentriconTM delivers unmatched technical performance, environmental compatibility, and reduced human risk. The properties of hexaflumuron as a termite control agent are attractive from an environmental and human risk perspective, but more important, the potential for adverse effects is dramatically reduced because it is present only in very small quantities in stations with termite activity. The comparisons to barrier methods show significant reduction in the use of hazardous materials and substantial reduction in potential impacts on human health and the environment.

The discovery of hexaflumuron's activity with its unique fit and applicability for use as a termite bait was a key milestone for the structural pest control industry and Dow AgroSciences. The development and commercial launch of SentriconTM changed the paradigm for protecting structures from damage caused by subterranean termites. The development of novel research methodologies, new delivery systems, and the establishment of an approach that integrates monitoring and baiting typify the innovation that has been a hallmark of the project. More than 300,000 structures across the United States are now being safeguarded through application of this revolutionary technology, and adoption is growing rapidly.

Academic Award

Professor Terry Collins
Carnegie Mellon University

TAML™ Oxidant Activators: General Activation of Hydrogen Peroxide for Green Oxidation Technologies

Innovation and Benefits

Professor Collins developed a series of activator chemicals that work with hydrogen peroxide to replace chlorine bleaches. His TAML™ activators have many potential uses that include preparing wood pulp for papermaking and removing stains from laundry. This novel, environmentally benign technology eliminates chlorinated byproducts from wastewater streams and saves both energy and water.

In nature, selectivity is achieved through complex mechanisms using a limited set of elements available in the environment. In the laboratory, chemists prefer a simpler design that utilizes the full range of the periodic table. The problem of persistent pollutants in the environment can be minimized by employing reagents and processes that mimic those found in nature. By developing a series of activators effective with the natural oxidant, hydrogen peroxide, Professor Terry Collins has devised an environmentally benign oxidation technique with widespread applications. TAML™ activators (tetraamido-macrocyclic ligand activators) are iron-based and contain no toxic functional groups. These activators offer significant technology breakthroughs in the pulp and paper industry and the laundry field.

The key to quality papermaking is the selective removal of lignin from the white fibrous polysaccharides, cellulose and hemicellulose. Wood pulp delignification has traditionally relied on chlorine-based processes that produce chlorinated pollutants. Professor Collins has demonstrated that TAML™ activators effectively catalyze hydrogen peroxide in the selective delignification of wood pulp. This is the first low-temperature peroxide oxidation technique for treating wood pulp, which translates to energy savings for the industry. Environmental compliance costs may be expected to decrease with this new approach because chlorinated organics are not generated in this totally chlorine-free process.

TAML™ activators may also be applied to the laundry field, where most bleaches are based on peroxide. When bound to fabric, most commercial dyes are unaffected by the TAML™-activated peroxide. However, random dye molecules that "escape" the fabric during laundering are intercepted and destroyed by the activated peroxide before they have a chance to transfer to other articles of clothing. This technology prevents dye-transfer accidents while offering improved stain-removal capabilities. Washing machines that require less water will be practical when the possibility of dye-transfer is eliminated.

An active area of investigation is the use of TAML™ peroxide activators for water disinfection. Ideally, the activators would first kill pathogens in the water sample, then destroy themselves in the presence of a small excess of peroxide. This protocol could have global applications, from developing nations to individual households.

The versatility of the TAML™ activators in catalyzing peroxide has been demonstrated in the pulp and paper and laundry industries. Environmental benefits include decreased energy requirements, elimination of chlorinated organics from the waste stream, and decreased water use. The development of new activators and new technologies will provide environmental advantages in future applications.

Small Business Award

Biofine, Inc. (now DPS Biometics, Inc.)

Conversion of Low-Cost Biomass Wastes to Levulinic Acid and Derivatives

Innovation and Benefits

Biofine developed a process to convert the waste cellulose in paper mill sludge, municipal solid waste, unrecyclable waste paper, waste wood, and agricultural residues into levulinic acid (LA). LA can be used as a building block for many other useful chemicals. LA made from waste cellulose reduces the use of fossil fuels and reduces the overall cost of LA from $4–6 per pound to as little as $0.32 per pound.

Replacing petroleum-based feedstocks with renewable ones is a crucial step toward achieving sustainability. When considering alternatives to traditional feedstocks, attention often focuses on plant-based materials. Renewable biomass conserves our dwindling supplies of fossil fuels and contributes no net CO_2 to the atmosphere. Biofine has developed a high-temperature, dilute-acid hydrolysis process that converts cellulosic biomass to levulinic acid (LA) and derivatives. Cellulose is initially converted to soluble sugars, which are then transformed to levulinic acid. Byproducts in the process include furfural, formic acid, and condensed tar, all of which have commercial value as commodities or fuel. Feedstocks used include paper mill sludge, municipal solid waste, unrecyclable waste paper, waste wood, and agricultural residues.

Levulinic acid serves as a building block in the synthesis of useful chemical products. Markets already exist for tetrahydrofuran, succinic acid, and diphenolic acid, all of which are levulinic acid derivatives. The use of diphenolic acid (DPA) as a monomer for polycarbonates and epoxy resins is currently under investigation. An industry/government consortium has conducted research on two additional derivatives with commercial value: methyltetrahydrofuran (MTHF), a fuel additive, and δ-amino levulinic acid (DALA), a pesticide.

The conversion of levulinic acid to MTHF is accomplished at elevated temperature and pressure using a catalytic hydrogenation process. MTHF is a fuel additive that is miscible with gasoline and hydrophobic, allowing it to be blended at the refinery rather than later in the distribution process. Using MTHF as a fuel additive increases the oxygenate level in gasoline without adversely affecting engine performance. MTHF also boasts a high octane rating (87) and a lower vapor pressure, thereby reducing fuel evaporation and improving air quality.

DALA can be obtained from levulinic acid in high yield using a three-step process. DALA is a broad-spectrum pesticide that is nontoxic and biodegradable. Its activity is triggered by light, selectively killing weeds while leaving most major crops unaffected. DALA also shows potential as an insecticide.

Diphenolic acid is synthesized by reacting levulinic acid with phenol. DPA has the potential to displace bisphenol-A, a possible endocrine disruptor, in polymer applications. Brominated DPA shows promise as an environmentally-acceptable marine coating, while dibrominated DPA may find use as a fire retardant.

Currently, levulinic acid has a worldwide market of about one million pounds per year at a price of $4–6 per pound. Large-scale commercialization of the Biofine process could produce levulinic acid for as little as $0.32 per pound, spurring increased demand for LA and its derivatives. Using the Biofine process, waste biomass can be transformed into valuable chemical products. The ability to produce levulinic acid economically from waste biomass and renewable feedstocks is the key to increased commercialization of LA and its derivatives.

Greener Synthetic Pathways Award

Lilly Research Laboratories

Practical Application of a Biocatalyst in Pharmaceutical Manufacturing

Innovation and Benefits

Lilly Research Laboratories developed a novel, low-waste process for drug synthesis. One key aspect uses yeast to replace a chemical reaction. Applying its process, Lilly eliminates approximately 41 gallons of solvent and 3 pounds of chromium waste for every pound of a drug candidate that it manufactures. Lilly's process also improves worker safety and increases product yield from 16 to 55 percent.

The synthesis of a pharmaceutical agent is frequently accompanied by the generation of a large amount of waste. This should not be surprising, as numerous steps are commonly necessary, each of which may require feedstocks, reagents, solvents, and separation agents. Lilly Research Laboratories has redesigned its synthesis of an anticonvulsant drug candidate, LY300164. This pharmaceutical agent is being developed for the treatment of epilepsy and neurodegenerative disorders.

The synthesis used to support clinical development of the drug candidate proved to be an economically viable process, although several steps proved problematic. A large amount of chromium waste was generated, an additional activation step was required, and the overall process required a large volume of solvent. Significant environmental improvements were realized upon implementing the new synthetic strategy. Roughly 9,000 gallons of solvent and 660 pounds of chromium waste were eliminated for every 220 pounds of LY300164 produced. Only three of the six intermediates generated were isolated, limiting worker exposure and decreasing processing costs. The synthetic scheme proved more efficient as well, with percent yield climbing from 16 to 55 percent.

The new synthesis begins with the biocatalytic reduction of a ketone to an optically pure alcohol. The yeast *Zygosaccharomyces rouxii* demonstrated good reductase activity but was sensitive to high product concentrations. To circumvent this problem, a novel three-phase reaction design was employed. The starting ketone was charged to an aqueous slurry containing a polymeric resin, buffer, and glucose, with most of the ketone adsorbed on the surface of the resin. The yeast reacted with the equilibrium concentration of ketone remaining in the aqueous phase. The resulting product was adsorbed onto the surface of the resin, simplifying product recovery. All of the organic reaction components were removed from the aqueous waste stream, permitting the use of conventional wastewater treatments.

A second key step in the synthesis was selective oxidation to eliminate the unproductive redox cycle present in the original route. The reaction was carried out using dimethylsulfoxide, sodium hydroxide, and compressed air, eliminating the use of chromium oxide, a possible carcinogen, and preventing the generation of chromium waste. The new protocol was developed by combining innovations from chemistry, microbiology, and engineering. Minimizing the number of changes to the oxidation state improved the efficiency of the process while reducing the amount of waste generated. The alternative synthesis presents a novel strategy for producing 5*H*-2,3-benzodiazepines. The approach is general and has been applied to the production of other anticonvulsant drug candidates. The technology is low-cost and easily implemented; it should have broad applications within the manufacturing sector.

Greener Reaction Conditions Award

Nalco Chemical Company

The Development and Commercialization of ULTIMER®: The First of a New Family of Water-Soluble Polymer Dispersions

Innovation and Benefits

The Nalco Chemical Company developed a novel way to synthesize the polymers used to treat water in a variety of industrial and municipal operations. Nalco now manufactures these polymers in water, replacing the traditional water-in-oil mixtures and preventing the release of organic solvents and other chemicals into the environment.

High-molecular-weight polyacrylamides are commonly used as process aids and water treatment agents in various industrial and municipal operations. Annually, at least 200 million pounds of water-soluble, acrylamide-based polymers are used to condition and purify water. These water-soluble polymers assist in removing suspended solids and contaminants and effecting separations. Traditionally, these polymers are produced as water-in-oil emulsions. Emulsions are prepared by combining the monomer, water, and a hydrocarbon oil–surfactant mixture in approximately equal parts. Although the oil and surfactant are required for processing, they do not contribute to the performance of the polymer. Consequently, approximately 90 million pounds of oil and surfactant are released to the environment each year. Nalco has developed a new technology that permits production of the polymers as stable colloids in water, eliminating the introduction of oil and surfactants into the environment.

The Nalco process uses a homogeneous dispersion polymerization technique. The water-soluble monomers are dissolved in an aqueous salt solution of ammonium sulfate then polymerized using a water-soluble, free-radical initiator. A low-molecular-weight dispersant polymer is added to prevent aggregation of the growing polymer chains. For end-use applications, the dispersion is simply added to water, thereby diluting the salt and allowing the polymer to dissolve into a clear, homogeneous, polymer solution. This technology has been successfully demonstrated with cationic copolymers of acrylamide, anionic copolymers of acrylamide, and non-ionic polymers.

Development of water-based dispersion polymers provides three important environmental benefits. First, the new process eliminates the use of hydrocarbon solvents and surfactants required in the manufacture of emulsion polymers. Dispersion polymers produce no VOCs and exhibit lower biological oxygen demand (BOD) and chemical oxygen demand (COD) than do emulsion polymers. Second, the salt used, ammonium sulfate, is a waste byproduct from another industrial process, the production of caprolactam. Caprolactam is the precursor in the manufacture of nylon; 2.5–4.5 million pounds of ammonium sulfate are produced for every million pounds of caprolactam, providing a ready supply of feedstock. Finally, dispersion polymers eliminate the need for costly equipment and inverter surfactants needed for mixing emulsion polymers. This technological advantage will make wastewater treatment more affordable for small- and medium-sized operations.

Nalco's dispersion polymers contain the same active polymer component as traditional emulsion polymers without employing oil and surfactant carrier systems. The polymers are produced as stable colloids in water, retaining ease and safety of handling while eliminating the release of oil and surfactants into the environment. By adopting this new technology, Nalco has conserved over one million pounds of hydrocarbon solvent and surfactants since 1997 on two polymers alone. In 1998, the water-based dispersions used 3.2 million pounds of ammonium sulfate, a by-product from caprolactam synthesis that would otherwise be treated as waste. Additional environmental benefits will be realized as the dispersion polymerization process is extended to the manufacture of other polymers.

Designing Greener Chemicals Award

Dow AgroSciences LLC

Spinosad: A New Natural Product for Insect Control

Innovation and Benefits

Dow developed spinosad, a highly selective, environmentally friendly insecticide made by a soil microorganism. It controls many chewing insect pests in cotton, trees, fruits, vegetables, turf, and ornamentals. Unlike traditional pesticides, it does not persist in the environment; it also has low toxicity to mammals and birds.

Controlling insect pests is essential to maintaining high agricultural productivity and minimizing monetary losses. Synthetic organic pesticides, from a relatively small number of chemical classes, play a leading role in pest control. The development of new and improved pesticides is necessitated by increased pest resistance to existing products, along with stricter environmental and toxicological regulations. To meet this need, Dow AgroSciences has designed spinosad, a highly selective, environmentally friendly insecticide.

High-volume testing of fermentation isolates in agricultural screens produced numerous leads, including the extracts of a Caribbean soil sample found to be active on mosquito larvae. The microorganism, *Saccharopolyspora spinosa*, was isolated from the soil sample, and the insecticidal activity of the spinosyns was identified. Spinosyns are unique macrocyclic lactones, containing a tetracyclic core to which two sugars are attached. Most of the insecticidal activity is due to a mixture of spinosyns A and D, commonly referred to as spinosad. Products such as Tracer® Naturalyte® Insect Control and Precise® contain spinosad as the active ingredient.

Insects exposed to spinosad exhibit classical symptoms of neurotoxicity: lack of coordination, prostration, tremors, and other involuntary muscle contractions leading to paralysis and death. Although the mode of action of spinosad is not fully understood, it appears to affect nicotinic and γ-aminobutyric acid receptor function through a novel mechanism.

Spinosad presents a favorable environmental profile. It does not leach, bioaccumulate, volatilize, or persist in the environment. Spinosad will degrade photochemically when exposed to light after application. Because spinosad strongly adsorbs to most soils, it does not leach through soil to groundwater. Spinosad demonstrates low mammalian and avian toxicity. No long-term health problems were noted in mammals, and a low potential for acute toxicity exists due to low oral, dermal, and inhalation toxicity. This is advantageous, because low mammalian toxicity imparts reduced risk to those who handle, mix, and apply the product. Although spinosad is moderately toxic to fish, this toxicity represents a reduced risk to fish when compared with many synthetic insecticides currently in use.

Spinosad has proven effective in controlling many chewing insect pests in cotton, trees, fruits, vegetables, turf, and ornamentals. High selectivity is also observed: 70–90 percent of beneficial insects and predatory wasps are left unharmed. Spinosad features a novel molecular structure and mode of action that provide the excellent crop protection associated with synthetic products coupled with the low human and environmental risk found in biological products. The selectivity and low toxicity of spinosad make it a promising tool for integrated pest management.

Academic Award

Professor Barry M. Trost
Stanford University

The Development of the Concept of Atom Economy

Innovation and Benefits

Professor Trost developed the concept of atom economy: chemical reactions that do not waste atoms. Professor Trost's concept of atom economy includes reducing the use of nonrenewable resources, minimizing the amount of waste, and reducing the number of steps used to synthesize chemicals. Atom economy is one of the fundamental cornerstones of green chemistry. This concept is widely used by those who are working to improve the efficiency of chemical reactions.

The general area of chemical synthesis covers virtually all segments of the chemical industry—oil refining, bulk or commodity chemicals, and fine chemicals, including agrochemicals, flavors, fragrances, pharmaceuticals, etc. Economics generally dictates the feasibility of processes that are "practical". A criterion that traditionally has not been explicitly recognized relates to the total quantity of raw materials required for the process compared to the quantity of product produced or, simply put, "how much of what you put into your pot ends up in your product." In considering the question of what constitutes synthetic efficiency, Professor Barry M. Trost has explicitly enunciated a new set of criteria by which chemical processes should be evaluated. They fall under two categories—selectivity and atom economy.

Selectivity and atom economy evolve from two basic considerations. First, the vast majority of the synthetic organic chemicals in production derive from nonrenewable resources. It is self-evident that such resources should be used as sparingly as possible. Second, all waste streams should be minimized. This requires employment of reactions that produce minimal byproducts, either through the intrinsic stoichiometry of a reaction or as a result of minimizing competing undesirable reactions (i.e., making reactions more selective).

The issues of selectivity can be categorized under four headings—chemoselectivity (differentiation among various functional groups in a molecule), regioselectivity (locational), diastereoselectivity (relative stereochemistry), and enantioselectivity (absolute stereochemistry). The chemical community at large has readily accepted these considerations. In too many cases, however, efforts to achieve the goal of selectivity led to reactions requiring multiple components in stoichiometric quantities that are not incorporated into the product, thus creating significant amounts of waste. How much of the reactants end up in the product (i.e., atom economy) traditionally has been ignored. When Professor Trost's first paper on atom economy appeared in the literature, the idea generally was not adopted by either academia or industry. Many in industry, however, were practicing this concept without explicitly enunciating it. Others in industry did not consider the concept because it did not appear to have any economic consequence. Today, all of the chemical industry explicitly acknowledges the importance of atom economy.

Achieving the objectives of selectivity and atom economy encompasses the entire spectrum of chemical activities—from basic research to commercial processes. In enunciating these principles, Professor Trost has set a challenge for those involved in basic research to create new chemical processes that meet the objectives. Professor Trost's efforts to meet this challenge involve the rational invention of new chemical reactions that are either simple additions or, at most, produce low-molecular-weight innocuous byproducts. A major application of these reactions is in the synthesis of fine chemicals and pharmaceuticals, which, in general, utilize very atom-uneconomical reactions. Professor Trost's research involves catalysis, largely focused on transition metal catalysis but also main group catalysis. The major purpose of his research is to increase the toolbox of available reactions to serve these industries for problems they encounter in the future. However, even today, there are applications for which such methodology may offer more efficient syntheses.

Academic Award

Dr. Karen M. Draths and Professor John W. Frost
Michigan State University

Use of Microbes as Environmentally Benign Synthetic Catalysts

Innovation and Benefits

Adipic acid, a building block for nylon, and catechol, a building block for pharmaceuticals and pesticides, are two chemicals of major industrial importance. Using environmentally benign, genetically engineered microbes, Dr. Draths and Professor Frost synthesized adipic acid and catechol from sugars. These two chemicals are traditionally made from benzene, a petroleum product; they can now be made with less risk to human health and the environment.

Fundamental change in chemical synthesis can be achieved by elaboration of new, environmentally benign routes to existing chemicals. Alternatively, fundamental change can follow from characterization and environmentally benign synthesis of chemicals that can replace those chemicals currently manufactured by environmentally problematic routes. Examples of these design principles are illustrated by the syntheses of adipic acid and catechol developed by Dr. Karen M. Draths and Professor John W. Frost. The Draths-Frost syntheses of adipic acid and catechol use biocatalysis and renewable feedstocks to create alternative synthetic routes to chemicals of major industrial importance. These syntheses rely on the use of genetically manipulated microbes as synthetic catalysts. Nontoxic glucose is employed as a starting material, which, in turn, is derived from renewable carbohydrate feedstocks, such as starch, hemicellulose, and cellulose. In addition, water is the primary reaction solvent, and the generation of toxic intermediates and environment-damaging byproducts is avoided.

In excess of 4.2 billion pounds of adipic acid are produced annually and used in the manufacture of nylon 6,6. Most commercial syntheses of adipic acid use benzene, derived from the benzene–toluene–xylene (BTX) fraction of petroleum refining, as the starting material. In addition, the last step in the current manufacture of adipic acid employs a nitric acid oxidation resulting in the formation of nitrous oxide as a byproduct. Due to the massive scale on which it is industrially synthesized, adipic acid manufacture has been estimated to account for some 10 percent of the annual increase in atmospheric nitrous oxide levels. The Draths-Frost synthesis of adipic acid begins with the conversion of glucose into *cis,cis*-muconic acid using a single, genetically engineered microbe expressing a biosynthetic pathway that does not exist in nature. This novel biosynthetic pathway was assembled by isolating and amplifying the expression of genes from different microbes including *Klebsiella pneumoniae*, *Acinetobacter calcoaceticus*, and *Escherichia coli*. The *cis,cis*-muconic acid, which accumulates extracellularly, is hydrogenated to afford adipic acid.

Yet another example of the Draths-Frost strategy for synthesizing industrial chemicals using biocatalysis and renewable feedstocks is their synthesis of catechol. Approximately 46 million pounds of catechol are produced globally each year. Catechol is an important chemical building block used to synthesize flavors (e.g., vanillin, eugenol, isoeugenol), pharmaceuticals (e.g., L-DOPA, adrenaline, papaverine), agrochemicals (e.g., carbofuran, propoxur), and polymerization inhibitors and antioxidants (e.g., 4-*t*-butylcatechol, veratrol). Although some catechol is distilled from coal tar, petroleum-derived benzene is the starting material for most catechol production. The Draths-Frost synthesis of catechol uses a single, genetically engineered microbe to catalyze the conversion of glucose into catechol, which accumulates extracellularly. As mentioned previously, plant-derived starch, hemicellulose, and cellulose can serve as the renewable feedstocks from which the glucose starting material is derived.

In contrast to the traditional syntheses of adipic acid and catechol, the Draths-Frost syntheses are based on renewable feedstocks, carbohydrate starting materials, and microbial biocatalysis. As the world moves to national limits on carbon dioxide (CO_2) emissions, each molecule of a chemical made from a carbohydrate may well be counted as a credit due to the CO_2 that is fixed by plants to form the carbohydrate. Biocatalysis using intact microbes also allows the Draths-Frost syntheses to use water as a reaction solvent, near-ambient pressures, and temperatures that typically do not exceed human body temperature.

Small Business Award

PYROCOOL Technologies, Inc.

Technology for the Third Millennium: The Development and Commercial Introduction of an Environmentally Responsible Fire Extinguishment and Cooling Agent

Innovation and Benefits

PYROCOOL Technologies developed PYROCOOL F.E.F., a fire extinguishing foam that is nontoxic and highly biodegradable. PYROCOOL F.E.F. replaces ozone-depleting gases and aqueous foams that release toxic and persistent chemicals to the environment during use. PYROCOOL F.E.F. is effective at approximately one-tenth the concentration of conventional fire extinguishing chemicals.

Advances in chemical technology have greatly benefited firefighting in this century. From the limitation of having only local water supplies at their disposal, firefighters have been presented over the years with a wide variety of chemical agents, as additives or alternatives to water, to assist them. These advances in chemical extinguishment agents, however, have themselves created, in actual use, potential long-term environmental and health problems that tend to outweigh their firefighting benefits. PYROCOOL Technologies, Inc. developed PYROCOOL F.E.F. (Fire Extinguishing Foam) as an alternative formulation of highly biodegradable surfactants designed for use in very small quantities as a universal fire extinguishment and cooling agent.

Halon gases, hailed as a tremendous advance when introduced, have since proven to be particularly destructive to the ozone layer, having an ozone depletion potential (ODP) value of 10–16 times that of common refrigerants. Aqueous film-forming foams (AFFFs) developed by the U.S. Navy in the 1960s to combat pooled-surface, volatile, hydrocarbon fires release both toxic hydrofluoric acid and fluorocarbons when used. The fluorosurfactant compounds that make these agents so effective against certain types of fires render them resistant to microbial degradation, often leading to contamination of groundwater supplies and failure of wastewater treatment systems.

In 1993, PYROCOOL Technologies initiated a project to create a fire extinguishment and cooling agent that would be effective in extinguishing fires and that would greatly reduce the potential long-term environmental and health problems associated with traditional products. To achieve this objective, PYROCOOL Technologies first determined that the product (when finally developed) would contain no glycol ethers or fluorosurfactants. In addition, it decided that the ultimate formulation must be an effective fire extinguishment and cooling agent at very low mixing ratios. PYROCOOL F.E.F. is a formulation of highly biodegradable nonionic surfactants, anionic surfactants, and amphoteric surfactants with a mixing ratio (with water) of 0.4 percent. In initial fire tests at the world's largest fire-testing facility in the Netherlands, PYROCOOL F.E.F. was demonstrated to be effective against a broad range of combustibles.

Since its development in 1993, PYROCOOL F.E.F. has been employed successfully against numerous fires both in America and abroad. PYROCOOL F.E.F. carries the distinction of extinguishing the last large oil tanker fire at sea (a fire estimated by Lloyd's of London to require 10 days to extinguish) on board the *Nassia* tanker in the Bosphorous Straits in just 12.5 minutes, saving 80 percent of the ship's cargo and preventing 160 million pounds of crude oil from spilling into the sea.

As demonstrated by the PYROCOOL F.E.F. technology, selective employment of rapidly biodegradable substances dramatically enhances the effectiveness of simple water, while eliminating the environmental and toxic impact of other traditional fire extinguishment agents. Because PYROCOOL F.E.F. is mixed with water at only 0.4 percent, an 87–93 percent reduction in product use is realized compared to conventional extinguishment agents typically used at 3–6 percent. Fire affects all elements of industry and society, and no one is immune from its dangers. PYROCOOL F.E.F. provides an innovative, highly effective, and green alternative for firefighters.

Greener Synthetic Pathways Award

Flexsys America L.P.

Elimination of Chlorine in the Synthesis of 4-Aminodiphenylamine:
A New Process That Utilizes Nucleophilic Aromatic Substitution
for Hydrogen

Innovation and Benefits

Flexsys developed a new method to eliminate waste from a critically important reaction used to manufacture a wide range of chemical products. They are using this method to manufacture 4-ADPA, a key, high-volume building block for a rubber preservative. Converting just 30 percent of the world's production capacity of this key building block to the Flexsys process would reduce chemical waste by 74 million pounds per year and wastewater by 1.4 billion pounds per year.

The development of new environmentally favorable routes for the production of chemical intermediates and products is an area of considerable interest to the chemical processing industry. Recently, the use of chlorine in large-scale chemical syntheses has come under intense scrutiny. Solutia, Inc. (formerly Monsanto Chemical Company), one of the world's largest producers of chlorinated aromatics, has funded research over the years to explore alternative synthetic reactions for manufacturing processes that do not require the use of chlorine. It was clear that replacing chlorine in a process would require the discovery of new atom-efficient chemical reactions. Ultimately, it was Monsanto's goal to incorporate fundamentally new chemical reactions into innovative processes that would focus on the elimination of waste at the source. In view of these emerging requirements, Monsanto's Rubber Chemicals Division (now Flexsys), in collaboration with Monsanto Corporate Research, began to explore new routes to a variety of aromatic amines that would not rely on the use of halogenated intermediates or reagents. Of particular interest was the identification of novel synthetic strategies to 4-aminodiphenylamine (4-ADPA), a key intermediate in the Rubber Chemicals family of antidegradants. The total world volume of antidegradants based on 4-ADPA and related materials is approximately 300 million pounds per year, of which Flexsys is the world's largest producer. (Flexsys is a joint venture of the rubber chemicals operations of Monsanto and Akzo Nobel.)

Flexsys's current process to 4-ADPA is based on the chlorination of benzene. Since none of the chlorine used in the process ultimately resides in the final product, the pounds of waste generated in the process per pound of product produced from the process are highly unfavorable. A significant portion of the waste is in the form of an aqueous stream that contains high levels of inorganic salts contaminated with organics that are difficult and expensive to treat. Furthermore, the process also requires the storage and handling of large quantities of chlorine gas. Flexsys found a solution to this problem in a class of reactions known as nucleophilic aromatic substitution of hydrogen (NASH). Through a series of experiments designed to probe the mechanism of NASH reactions, Flexsys realized a breakthrough in understanding this chemistry that has led to the development of a new process to 4-ADPA that utilizes the base-promoted, direct coupling of aniline and nitrobenzene.

The environmental benefits of this process are significant and include a dramatic reduction in waste generated. In comparison to the process traditionally used to synthesize 4-ADPA, the Flexsys process generates 74 percent less organic waste, 99 percent less inorganic waste, and 97 percent less wastewater. In global terms, if just 30 percent of the world's capacity to produce 4-ADPA and related materials were converted to the Flexsys process, 74 million pounds less chemical waste would be generated per year and 1.4 billion pounds less wastewater would be generated per year. The discovery of the new route to 4-ADPA and the elucidation of the mechanism of the reaction between aniline and nitrobenzene have been recognized throughout the scientific community as a breakthrough in the area of nucleophilic aromatic substitution chemistry.

This new process for the production of 4-ADPA has achieved the goal for which all green chemistry endeavors strive: the elimination of waste at the source via the discovery of new chemical reactions that can be implemented into innovative and environmentally safe chemical processes.

Greener Reaction Conditions Award

Argonne National Laboratory

Novel Membrane-Based Process for Producing Lactate Esters—
Nontoxic Replacements for Halogenated and Toxic Solvents

Innovation and Benefits

Argonne developed a novel process to synthesize organic solvents from sugars. These solvents can replace a wide variety of more hazardous solvents, such as methylene chloride. Argonne's process requires little energy, is highly efficient, eliminates large volumes of salt waste, and reduces pollution and emissions. These solvents can potentially replace 7.6 billion pounds of toxic solvents used annually by industry, commerce, and households.

Argonne National Laboratory (ANL) has developed a process based on selective membranes that permits low-cost synthesis of high-purity ethyl lactate and other lactate esters from carbohydrate feedstock. The process requires little energy input, is highly efficient and selective, and eliminates the large volumes of salt waste produced by conventional processes. ANL's novel process uses pervaporation membranes and catalysts. In the process, ammonium lactate is thermally and catalytically cracked to produce the acid, which, with the addition of alcohol, is converted to the ester. The selective membranes pass the ammonia and water with high efficiency while retaining the alcohol, acid, and ester. The ammonia is recovered and reused in the fermentation to make ammonium lactate, eliminating the formation of waste salt. The innovation overcomes major technical hurdles that had made current production processes for lactate esters technically and economically noncompetitive. The innovation will enable the replacement of toxic solvents widely used by industry and consumers, expand the use of renewable carbohydrate feedstocks, and reduce pollution and emissions.

Ethyl lactate has a good temperature performance range (boiling point: 309 °F, melting point: 104 °F), is compatible with both aqueous and organic systems, is easily biodegradable, and has been approved for food by the U.S. Food and Drug Administration (FDA). Lactate esters (primarily ethyl lactate) can replace most halogenated solvents (including ozone-depleting chlorofluorocarbons (CFCs), carcinogenic methylene chloride, toxic ethylene glycol ethers, perchloroethylene, and chloroform) on a 1:1 basis. At 1998 prices ($1.60–2.00 per pound), the market for ethyl lactate is about 20 million pounds per year for a wide variety of specialty applications. The novel and efficient ANL membrane process will reduce the selling price of ethyl lactate to $0.85–1.00 per pound and enable ethyl lactate to compete directly with the petroleum-derived toxic solvents currently in use. The favorable economics of the ANL membrane process, therefore, can lead to the widespread substitution of petroleum-derived toxic solvents by ethyl lactate in electronics manufacturing, paints and coatings, textiles, cleaners and degreasers, adhesives, printing, de-inking, and many other industrial, commercial, and household applications. More than 80 percent of the applications requiring the use of more than 7.6 billion pounds of solvents in the United States each year are suitable for reformulation with environmentally friendly lactate esters.

The ANL process has been patented for producing esters from all fermentation-derived organic acids and their salts. Organic acids and their esters, at the purity achieved by this process, offer great potential as intermediates for synthesizing polymers, biodegradable plastics, oxygenated chemicals (e.g., propylene glycol and acrylic acid), and specialty products. By improving purity and lowering costs, the ANL process promises to make fermentation-derived organic acids an economically viable alternative to many chemicals and products derived from petroleum feedstocks.

A U.S. patent on this technology has been allowed, and international patents have been filed. NTEC, Inc. has licensed the technology for lactate esters and provided the resources for a pilot-scale demonstration of the integrated process at ANL. The pilot-scale demonstration has produced a high-purity ethyl lactate product that meets or exceeds all the process performance objectives. A 10-million-pound-per-year demonstration plant is being planned for early 1999, followed by a 100-million-pound-per-year, full-scale plant.

Designing Greener Chemicals Award

Rohm and Haas Company (now a subsidiary of The Dow Chemical Company)

Invention and Commercialization of a New Chemical Family of Insecticides Exemplified by CONFIRM™ Selective Caterpillar Control Agent and the Related Selective Insect Control Agents MACH 2™ and INTREPID™

Innovation and Benefits

Rohm and Haas developed CONFIRM™, a novel insecticide for controlling caterpillar pests in turf and a variety of crops. CONFIRM™ is less toxic than other insecticides to a wide range of nontarget organisms, poses no significant hazard to farm workers or the food chain, and does not present a significant spill hazard. EPA has classified CONFIRM™ as a reduced-risk pesticide.

The value of crops destroyed worldwide by insects exceeds tens of billions of dollars. Over the past fifty years, only a handful of classes of insecticides have been discovered to combat this destruction. Rohm and Haas Company has discovered a new class of chemistry, the diacylhydrazines, that offers farmers, consumers, and society a safer, effective technology for insect control in turf and a variety of agronomic crops. One member of this family, CONFIRM™, is a breakthrough in caterpillar control. It is chemically, biologically, and mechanistically novel. It effectively and selectively controls important caterpillar pests in agriculture without posing significant risk to the applicator, the consumer, or the ecosystem. It will replace many older, less effective, more hazardous insecticides and has been classified by EPA as a reduced-risk pesticide.

CONFIRM™ controls target insects through an entirely new mode of action that is inherently safer than current insecticides. The product acts by strongly mimicking a natural substance found within the insect's body called 20-hydroxy ecdysone, which is the natural "trigger" that induces molting and regulates development in insects. Because of this "ecdysonoid" mode of action, CONFIRM™ powerfully disrupts the molting process in target insects, causing them to stop feeding shortly after exposure and to die soon thereafter.

Since 20-hydroxy ecdysone neither occurs nor has any biological function in most nonarthropods, CONFIRM™ is inherently safer than other insecticides to a wide range of nontarget organisms such as mammals, birds, earthworms, plants, and various aquatic organisms. CONFIRM™ is also remarkably safe to a wide range of key beneficial, predatory, and parasitic insects such as honeybees, lady beetles, parasitic wasps, predatory bugs, beetles, flies, and lacewings, as well as other predatory arthropods such as spiders and predatory mites. Because of this unusual level of safety, the use of these products will not create an outbreak of target or secondary pests due to destruction of key natural predators or parasites in the local ecosystem. This should reduce the need for repeat applications of additional insecticides and reduce the overall chemical load on both the target crop and the local environment.

CONFIRM™ has low toxicity to mammals by ingestion, inhalation, and topical application and has been shown to be completely non-oncogenic, nonmutagenic, and without adverse reproductive effects. Because of its high apparent safety and relatively low use rates, CONFIRM™ poses no significant hazard to the applicator or the food chain and does not present a significant spill hazard. CONFIRM™ has proven to be an outstanding tool for control of caterpillar pests in many integrated pest management (IPM) and resistance management situations. All of these attributes make CONFIRM™ among the safest, most selective, and most useful insect control agents ever discovered.

Academic Award

Professor Joseph M. DeSimone
University of North Carolina at Chapel Hill (UNC)
and North Carolina State University (NCSU)

Design and Application of Surfactants for Carbon Dioxide

Innovation and Benefits

Professor DeSimone developed new detergents that allow carbon dioxide (CO_2), a nontoxic gas, to be used as a solvent in many industrial applications. Using CO_2 as a solvent allows manufacturers to replace traditional, often hazardous chemical solvents and processes, conserve energy, and reduce worker exposure to hazardous substances.

It has been a dilemma of modern industrial technology that the solvents required to dissolve the environment's worst contaminants themselves have a contaminating effect. Now, new technologies for the design and application of surfactants for carbon dioxide (CO_2), developed at UNC, promise to resolve this dilemma.

Over 30 billion pounds of organic and halogenated solvents are used worldwide each year as solvents, processing aids, cleaning agents, and dispersants. Solvent-intensive industries are considering alternatives that can reduce or eliminate the negative impact that solvent emissions can have in the workplace and in the environment. CO_2 in a solution state has long been recognized as an ideal solvent, extractant, and separation aid. CO_2 solutions are nontoxic, nonflammable, energy-efficient, cost-effective, waste-minimizing, reusable, and safe to work with. Historically, the prime factor inhibiting the use of this solvent replacement has been the low solubility of most materials in CO_2, in both its liquid and supercritical states. With the discovery of CO_2 surfactant systems, Professor Joseph M. DeSimone and his students have dramatically advanced the solubility performance characteristics of CO_2 systems for several industries.

The design of broadly applicable surfactants for CO_2 relies on the identification of "CO_2-philic" materials from which to build amphiphiles. Although CO_2 in both its liquid and supercritical states dissolves many small molecules readily, it is a very poor solvent for many substances at easily accessible conditions ($T < 212$ °F and $P < 4{,}350$ psi). As an offshoot of Professor DeSimone's research program on polymer synthesis in CO_2, he and his researchers exploited the high solubility of a select few CO_2-philic polymeric segments to develop nonionic surfactants capable of dispersing high-solids polymer latexes in both liquid and supercritical CO_2 phases. The design criteria they developed for surfactants, which were capable of stabilizing heterogeneous polymerizations in CO_2, have been expanded to include CO_2-insoluble compounds in general.

This development lays the foundation by which surfactant-modified CO_2 can be used to replace conventional (halogenated) organic solvent systems currently used in manufacturing and service industries such as precision cleaning, medical device fabrication, and garment care, as well as in the chemical manufacturing and coating industries.

Small Business Award

Legacy Systems, Inc.

Coldstrip™, A Revolutionary Organic Removal and Wet Cleaning Technology

Innovation and Benefits

During manufacture, silicon-based semiconductors and flat-panel displays require cleaning to remove manufacturing residues, usually with corrosive acid solutions. Legacy Systems developed the Coldstrip™ process, which uses only water and oxygen to clean silicon semiconductors. Coldstrip™ has the potential to cut the use of corrosive solutions by hundreds of thousands of gallons and also save millions of gallons of water each year.

For over 30 years, the removal of photoresists with Piranha solutions (sulfuric acid, hydrogen peroxide, or ashers) has been the standard in the semiconductor, flat panel display, and micromachining industries. Use of Piranha solutions has been associated with atmospheric, ground, and water pollution. Legacy Systems, Inc. (LSI) has developed a revolutionary wet processing technology, Coldstrip™, which removes photoresist and organic contaminants for the semiconductor, flat panel display, and micromachining industries.

LSI's Coldstrip™ process is a chilled-ozone process that uses only oxygen and water as raw materials. The active product is ozone, which safely decomposes to oxygen in the presence of photoresist. Carbon dioxide, carbon monoxide, oxygen, and water are formed. There are no high temperatures, no hydrogen peroxide, and no nitric acid, all of which cause environmental issues.

The equipment required for the chilled-ozone process consists of a gas diffuser, an ozone generator, a recirculating pump, a water chiller, and a process vessel. The water solution remains clear and colorless throughout the entire process sequence. There are no particles or resist flakes shed from the wafer into the water; therefore, there are no requirements for particle filtration.

Using oxygen and water as raw materials replacing the Piranha solutions significantly benefits the environment. One benefit is the elimination of over 8,400 gallons of Piranha solutions used per year per silicon wet station and over 25,200 gallons used per year per flat panel display station. Additionally, the overall water consumption is reduced by over 3,355,800 gallons per year per silicon wafer wet station and over 5,033,700 gallons per year per flat panel display station. The corresponding water consumption in LSI's process is 4,200 gallons per year and there is no Piranha use.

In 1995, the U.S. Patent Office granted LSI Patent 5,464,480 covering this technology. The system has the lowest environmental impact of any wet-resist-strip process, eliminating the need for thousands of gallons of Piranha chemicals and millions of gallons of water a year.

Greener Synthetic Pathways Award

BHC Company (now BASF Corporation)

BHC Company Ibuprofen Process

Innovation and Benefits

BHC Company developed an efficient method to make ibuprofen, a commonly used painkiller, using only three steps instead of six. BHC recovers and recycles the waste byproduct from the manufacturing process and has virtually eliminated large volumes of aqueous salt wastes. BASF Corporation, one of the BHC partners, uses this process in one of the largest ibuprofen production plants in the world.

BHC Company has developed a new synthetic process to manufacture ibuprofen, a well-known nonsteroidal anti-inflammatory painkiller marketed under brand names such as Advil™ and Motrin™. Commercialized since 1992 in BHC's 7.7-million-pound-per-year facility in Bishop, TX, the new process has been cited as an industry model of environmental excellence in chemical processing technology. For its innovation, BHC was the recipient of the Kirkpatrick Achievement Award for "outstanding advances in chemical engineering technology" in 1993.

The new technology involves only three catalytic steps with approximately 80 percent atom utilization (virtually 99 percent including the recovered byproduct acetic acid) and replaces technology with six stoichiometric steps and less than 40 percent atom utilization. The use of anhydrous hydrogen fluoride as both catalyst and solvent offers important advantages in reaction selectivity and waste reduction. As such, this chemistry is a model of source reduction, the method of waste minimization that tops EPA's waste management hierarchy. Virtually all starting materials are either converted to product or reclaimed byproduct or are completely recovered and recycled in the process. The generation of waste is practically eliminated.

The BHC ibuprofen process is an innovative, efficient technology that has revolutionized bulk pharmaceutical manufacturing. The process provides an elegant solution to a prevalent problem encountered in bulk pharmaceutical synthesis (i.e., how to avoid the large quantities of solvents and wastes associated with the traditional stoichiometric use of auxiliary chemicals for chemical conversions). Large volumes of aqueous wastes (salts) normally associated with such manufacturing are virtually eliminated. The anhydrous hydrogen fluoride catalyst/solvent is recovered and recycled with greater than 99.9 percent efficiency. No other solvent is needed in the process, simplifying product recovery and minimizing fugitive emissions. The nearly complete atom utilization of this streamlined process truly makes it a waste-minimizing, environmentally friendly technology.

Greener Reaction Conditions Award

Imation (technology acquired by Eastman Kodak Company)

DryView™ Imaging Systems

Innovation and Benefits

Imation's DryView™ Imaging Systems use a new type of photographic film for medical imaging that uses heat instead of hazardous developer chemicals. During 1996, Imation delivered more than 1,500 DryView™ Imaging Systems worldwide. These units alone eliminate the annual disposal of over half a million gallons of developer chemicals and 54.5 million gallons of contaminated water and reduce workers' exposure to chemicals.

Photothermography is an imaging technology whereby a latent image, created by exposing a sensitized emulsion to appropriate light energy, is processed by the application of thermal energy. Photothermographic films are easily imaged by laser diode imaging systems, with the resultant exposed film processed by passing it over a heat roll. A heat roll operating at 250 °F in contact with the film will produce diagnostic-quality images in approximately 15 seconds. Based on photothermography technology, Imation's DryView™ Imaging Systems use no wet chemistry, create no effluent, and require no additional postprocess steps such as drying.

In contrast, silver halide photographic films are processed by being bathed in a chemical developer, soaked in a fix solution, washed with clean water, and finally dried. The developer and fix solutions contain toxic chemicals such as hydroquinone, silver, and acetic acid. In the wash cycle, these chemicals, along with silver compounds, are flushed from the film and become part of the waste stream. The resulting effluent amounts to billions of gallons of liquid waste each year.

Significant developments in photothermographic image quality have been achieved that allow it to compete successfully with silver halide technology. During 1996, Imation placed more than 1,500 DryView™ medical laser imagers, which represent 6 percent of the world's installed base. These units alone have eliminated the annual disposal of 192,000 gallons of developer, 330,000 gallons of fixer, and 54.5 million gallons of contaminated water into the waste stream. As future systems are placed, the reductions will be even more dramatic.

DryView™ technology is applicable to all industries that process panchromatic film products. The largest of these industries are medical radiography, printing, industrial radiography, and military reconnaissance. DryView™ is valued by these industries because it supports pollution prevention through source reduction.

Designing Greener Chemicals Award

Albright & Wilson Americas (now Rhodia)

THPS Biocides: A New Class of Antimicrobial Chemistry

Innovation and Benefits

Albright & Wilson discovered the antimicrobial properties of THPS and developed it into a safer biocide that can be used to control the growth of bacteria and algae in industrial water systems. THPS, or tetrakis(hydroxymethyl) phosphonium sulfate, offers many advantages over other, traditional biocides because, for example, it is significantly less toxic to nontarget organisms, is effective at much lower concentrations, and is more biodegradable than other biocides.

Conventional biocides used to control the growth of bacteria, algae, and fungi in industrial cooling systems, oil fields, and process applications are highly toxic to humans and aquatic life and often persist in the environment, leading to long-term damage. To address this problem, a new and relatively benign class of biocides, tetrakis (hydroxymethyl)phosphonium sulfate (THPS), has been discovered by Albright & Wilson Americas. THPS biocides represent a completely new class of antimicrobial chemistry that combines superior antimicrobial activity with a relatively benign toxicology profile. THPS's benefits include low toxicity, low recommended treatment level, rapid breakdown in the environment, and no bioaccumulation. When substituted for more toxic biocides, THPS biocides provide reduced risks to both human health and the environment.

THPS is so effective as a biocide that, in most cases, the recommended treatment level is below that which would be toxic to fish. In addition, THPS rapidly breaks down in the environment through hydrolysis, oxidation, photodegradation, and biodegradation. In many cases, it has already substantially broken down before the treated water enters the environment. The degradation products have been shown to possess a relatively benign toxicology profile. Furthermore, THPS does not bioaccumulate and, therefore, offers a much-reduced risk to higher life forms.

THPS biocides are aqueous solutions and do not contain volatile organic compounds (VOCs). Because THPS is halogen-free, it does not contribute to the formation of dioxin or absorbable organic halides (AOX). Because of its low overall toxicity and easier handling compared to alternative products, THPS provides an opportunity to reduce the risk of health and safety incidents.

THPS has been applied to a range of industrial water systems for the successful control of microorganisms. The U.S. industrial water treatment market for nonoxidizing biocides alone is 42 million pounds per year and growing at 6–8 percent annually. There are over 500,000 individual user sites in this industry category. Because of its excellent environmental profile, THPS has already been approved for use in environmentally sensitive areas around the world and is being used as a replacement for higher risk alternatives.

1996 Winners

Academic Award

Professor Mark Holtzapple
Texas A&M University
Conversion of Waste Biomass to Animal Feed, Chemicals, and Fuels

Innovation and Benefits

Professor Holtzapple developed a family of technologies that convert waste biomass, such as sewage sludge and agricultural wastes, into animal feed products, industrial chemicals, or fuels, depending on the technology used. Because these technologies convert waste biomass into useful products, other types of basic resources, such as petroleum, can be conserved. Also, the technologies can reduce the amount of biomass waste going to landfills or incinerators.

A family of technologies has been developed by Professor Mark Holzapple at Texas A&M University that converts waste biomass into animal feed, industrial chemicals, and fuels. Waste biomass includes such resources as municipal solid waste, sewage sludge, manure, and agricultural residues. Waste biomass is treated with lime to improve digestibility. Lime-treated agricultural residues (e.g., straw, stover, and bagasse) may be used as ruminant animal feeds. Alternatively, the lime-treated biomass can be fed into a large anaerobic fermentor in which rumen microorganisms convert the biomass into volatile fatty acid (VFA) salts, such as calcium acetate, propionate, and butyrate. The VFA salts are concentrated and may be converted into chemicals or fuels via three routes. In one route, the VFA salts are acidified, releasing acetic, propionic, and butyric acids. In a second route, the VFA salts are thermally converted to ketones, such as acetone, methyl ethyl ketone, and diethyl ketone. In a third route, the ketones are hydrogenated to their corresponding alcohols such as isopropanol, isobutanol, and isopentanol.

The technologies above offer many benefits for human health and the environment. Lime-treated animal feed can replace feed corn, which is approximately 88 percent of corn production. Growing corn exacerbates soil erosion and requires intensive inputs of fertilizers, herbicides, and pesticides, all of which contaminate ground water.

Chemicals (e.g., organic acids and ketones) may be produced economically from waste biomass. Typically, waste biomass is landfilled or incinerated, which incurs a disposal cost and contributes to land or air pollution. Through the production of chemicals from biomass, non-renewable resources, such as petroleum and natural gas, are conserved for later generations. Because 50 percent of U.S. petroleum consumption is now imported, displacing foreign oil will help reduce the U.S. trade deficit.

Fuels (e.g., alcohols) produced from waste biomass have the benefits cited above (i.e., reduced environmental impact from waste disposal and reduced trade deficit). In addition, oxygenated fuels derived from biomass are cleaner-burning and do not add net carbon dioxide to the environment, thereby reducing factors that contribute to global warming.

Donlar Corporation (now NanoChem Solutions, Inc.)

Production and Use of Thermal Polyaspartic Acid

Innovation and Benefits

Donlar developed TPA, a nontoxic, environmentally safe, biodegradable polymer for use in agriculture, water treatment, and other industries. Donlar manufactures TPA using a highly efficient process that eliminates use of organic solvents, cuts waste, and uses less energy. TPA has been used successfully in a variety of applications, such as improving fertilizer uptake in plants, and improving the efficiency of oil and gas production.

Millions of pounds of anionic polymers are used each year in many industrial applications. Polyacrylic acid (PAC) is one important class of such polymers, but the disposal of PAC is problematic because it is not biodegradable. An economically viable, effective, and biodegradable alternative to PAC is thermal polyaspartate (TPA).

Donlar Corporation invented two highly efficient processes to manufacture TPA for which patents have either been granted or allowed. The first process involves a dry and solid polymerization converting aspartic acid to polysuccinimide. No organic solvents are involved during the conversion and the only byproduct is water. The process is extremely efficient—a yield of more than 97 percent of polysuccinimide is routinely achieved. The second step in this process, the base hydrolysis of polysuccinimide to polyaspartate, is also extremely efficient and waste-free.

The second TPA production process involves using a catalyst during the polymerization, which allows a lower heating temperature to be used. The resulting product has improvements in performance characteristics, lower color, and biodegradability. The catalyst can be recovered from the process, thus minimizing waste.

Independent toxicity studies of commercially produced TPA have been conducted using mammalian and environmental models. Results indicate that TPA is nontoxic and environmentally safe. TPA biodegradability has also been tested by an independent lab using established Organization for Economic Cooperation and Development (OECD) methodology. Results indicate that TPA meets OECD guidelines for Intrinsic Biodegradability. PAC cannot be classified as biodegradable when tested under these same conditions.

Many end-uses of TPA have been discovered, such as in agriculture to improve fertilizer or nutrient management. TPA increases the efficiency of plant nutrient uptake, thereby increasing crop yields while protecting the ecology of agricultural lands. TPA can also be used for water treatment, as well as in the detergent, oil, and gas industries.

Greener Synthetic Pathways Award

Monsanto Company

Catalytic Dehydrogenation of Diethanolamine

Innovation and Benefits

DSIDA is a key building block for the herbicide RoundUp®. Monsanto's novel synthesis of DSIDA eliminates most of the manufacturing hazards associated with the previous synthesis; it uses no ammonia, cyanide, or formaldehyde. This synthesis is safer to operate, has a higher overall yield, and has fewer process steps.

Disodium iminodiacetate (DSIDA) is a key intermediate in the production of Monsanto's Roundup® herbicide, an environmentally friendly, nonselective herbicide. Traditionally, Monsanto and others have manufactured DSIDA using the Strecker process requiring ammonia, formaldehyde, hydrochloric acid, and hydrogen cyanide. Hydrogen cyanide is acutely toxic and requires special handling to minimize risk to workers, the community, and the environment. Furthermore, the chemistry involves the exothermic generation of potentially unstable intermediates, and special care must be taken to preclude the possibility of a runaway reaction. The overall process also generates up to 1 pound of waste for every 7 pounds of product, and this waste must be treated prior to safe disposal.

Monsanto has developed and implemented an alternative DSIDA process that relies on the copper-catalyzed dehydrogenation of diethanolamine. The raw materials have low volatility and are less toxic. Process operation is inherently safer, because the dehydrogenation reaction is endothermic and, therefore, does not present the danger of a runaway reaction. Moreover, this zero-waste route to DSIDA produces a product stream that, after filtration of the catalyst, is of such high quality that no purification or waste cut is necessary for subsequent use in the manufacture of Roundup®. The new technology represents a major breakthrough in the production of DSIDA because it avoids the use of cyanide and formaldehyde, is safer to operate, produces higher overall yield, and has fewer process steps.

The metal-catalyzed conversion of amino-alcohols to amino acid salts has been known since 1945. Commercial application, however, was not known until Monsanto developed a series of proprietary catalysts that made the chemistry commercially feasible. Monsanto's patented improvements on metallic copper catalysts afford an active, easily recoverable, highly selective, and physically durable catalyst that has proven itself in large-scale use.

This catalysis technology also can be used in the production of other amino acids, such as glycine. Moreover, it is a general method for conversion of primary alcohols to carboxylic acid salts; it is potentially applicable to the preparation of many other agricultural, commodity, specialty, and pharmaceutical chemicals.

Greener Reaction Conditions Award

The Dow Chemical Company

100 Percent Carbon Dioxide as a Blowing Agent for the Polystyrene Foam Sheet Packaging Market

Innovation and Benefits

Dow developed a process for manufacturing polystyrene foam sheets that uses carbon dioxide (CO_2) as a blowing agent, eliminating 3.5 million pounds per year of traditional blowing agents. Traditional blowing agents deplete the ozone layer or contribute to ground-level smog. In addition, Dow will obtain CO_2 only from existing commercial and natural sources that generate it as a byproduct, so this process will not contribute to global CO_2 levels.

In recent years the chlorofluorocarbon (CFC) blowing agents used to manufacture polystyrene foam sheet have been associated with environmental concerns such as ozone depletion, global warming, and ground-level smog. Due to these environmental concerns, The Dow Chemical Company has developed a novel process for the use of 100 percent carbon dioxide (CO_2). Polystyrene foam sheet is a useful packaging material offering a high stiffness-to-weight ratio, good thermal insulation value, moisture resistance, and recyclability. This combination of desirable properties has resulted in the growth of the polystyrene foam sheet market in the United States to over 700 million pounds in 1995. Current applications for polystyrene foam include thermoformed meat, poultry, and produce trays; fast food containers; egg cartons; and serviceware.

The use of 100 percent CO_2 offers optimal environmental performance because CO_2 does not deplete the ozone layer, does not contribute to ground-level smog, and will not contribute to global warming because CO_2 will be used from existing byproduct commercial and natural sources. The use of CO_2 byproduct from existing commercial and natural sources, such as ammonia plants and natural gas wells, will ensure that no net increase in global CO_2 results from the use of this technology. CO_2 is also nonflammable, providing increased worker safety. It is cost-effective and readily available in food-grade quality. CO_2 also is used in such common applications as soft drink carbonation and food chilling and freezing.

The Dow 100 percent CO_2 technology eliminates the use of 3.5 million pounds per year of hard CFC-12 and soft HCFC-22. This technology has been scaled from pilot-line to full-scale commercial facilities. Dow has made the technology available through a commercial license covering both patented and know-how technology. The U.S. Patent Office granted Dow two patents for this technology (5,250,577 and 5,266,605).

Designing Greener Chemicals Award

Rohm and Haas Company (now a subsidiary of The Dow Chemical Company)

Designing an Environmentally Safe Marine Antifoulant

Innovation and Benefits

Rohm and Haas developed Sea-Nine™, a novel antifoulant to control the growth of plants and animals on the hulls of ships. In 1995, fouling cost the shipping industry approximately $3 billion a year in increased fuel consumption. Sea-Nine™ replaces environmentally persistent and toxic tin-containing antifoulants.

Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry approximately $3 billion a year, largely due to increased fuel consumption to overcome hydrodynamic drag. Increased fuel consumption contributes to pollution, global warming, and acid rain.

The main compounds used worldwide to control fouling are the organotin antifoulants, such as tributyltin oxide (TBTO). While effective, they persist in the environment and cause toxic effects, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish. These harmful effects led to an EPA special review and to the Organotin Antifoulant Paint Control Act of 1988. This act mandated restrictions on the use of tin in the United States, and charged EPA and the U.S. Navy with conducting research on alternatives to organotins.

Rohm and Haas Company searched for an environmentally safe alternative to organotin compounds. Compounds from the 3-isothiazolone class were chosen as likely candidates and over 140 were screened for antifouling activity. The 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine™ antifoulant) was chosen as the candidate for commercial development.

Extensive environmental testing compared Sea-Nine™ antifoulant to TBTO, the current industry standard. Sea-Nine™ antifoulant degraded extremely rapidly with a half-life of one day in seawater and one hour in sediment. Tin had bioaccumulation factors as high as 10,000-fold, whereas Sea-Nine™ antifoulant's bioaccumulation was essentially zero. Both TBTO and Sea-Nine™ were acutely toxic to marine organisms, but TBTO had widespread chronic toxicity, whereas Sea-Nine™ antifoulant showed no chronic toxicity. Thus, the maximum allowable environmental concentration (MAEC) for Sea-Nine™ antifoulant was 0.63 parts per billion (ppb) whereas the MAEC for TBTO was 0.002 ppb.

Hundreds of ships have been painted with coatings containing Sea-Nine™ worldwide. Rohm and Haas Company obtained EPA registration for the use of Sea-Nine™ antifoulant, the first new antifoulant registration in over a decade.

Program Information

Additional information on the Presidential Green Chemistry Challenge program is available from:

- The Green Chemistry Web site at
  http://www.epa.gov/greenchemistry and
- The Industrial Chemistry Branch of EPA by e-mail at greenchemistry@epa.gov or by telephone at 202-564-8740.

Disclaimer

Note: The summaries provided in this document were obtained from the entries received for the 1996–2016 Presidential Green Chemistry Challenge Awards. They were edited for space, stylistic consistency, and clarity, but they were neither written nor officially endorsed by EPA. These summaries represent only a fraction of the information that was provided in the entries received and, as such, are intended to highlight the nominated projects, not describe them fully. These summaries were not used in the judging process; judging was conducted on all information contained in the entries.

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