The Presidential Green Chemistry Challenge Awards Program

Summary of 2005 Award Entries and Recipients

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The Presidential Green Chemistry Challenge Awards Program is a competitive incentive to create environmentally preferable chemicals and chemical processes. This year EPA celebrates an important milestone: 10 years of innovative, award-winning technologies developed by high-quality nominees.

The national policy established by the 1990 Pollution Prevention Act is aimed at reducing pollution at its source whenever feasible. By applying scientific solutions to real-world environmental problems, the Green Chemistry Challenge has significantly reduced hazards associated with the design, manufacture, and use of chemicals.

Through a voluntary EPA Design for the Environment partnership with the chemical industry and professional scientific community, this annual award program seeks to discover, highlight, and honor green chemistry.

Entries for the 2005 awards were judged by an independent panel of technical experts convened by the American Chemical Society. The judges used criteria that included health and environmental benefits, scientific innovation, and industrial applicability. Six of the more than 90 projects were nationally recognized on June 20, 2005, at an awards ceremony in Washington, D.C. All the entries submitted to the 2005 competition are summarized in this compilation. These technologies are meant to succeed in the marketplace as well: each illustrates the technical feasibility, marketability, and profitability of green chemistry.

For further information about the Presidential Green Chemistry Challenge and EPA's Green Chemistry Program, go to www.epa.gov/greenchemistry.

Note: The summaries provided in this document were obtained from the entries received for the 2005 Presidential Green Chemistry Challenge Awards. EPA edited the descriptions for space, stylistic consistency, and clarity, but they were not written or officially endorsed by the Agency. The summaries are intended only to highlight a fraction of information contained in the nominated projects. These summaries were not used in the judging process; judging was conducted on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.

Academic Award

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

Professor Robin D. Rogers, The University of Alabama

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 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 ([C_4mim]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 [C_4mim]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 combines a fundamental knowledge of ILs as solvents with a novel technology for dissolving and reconstituting cellulose and similar polymers. Using green chemistry principles to guide process 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

Metabolix is commercializing polyhydroxyalkanoates (PHAs), a broadly useful family of natural, environmentally friendly, high-performing, biobased 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 50,000 ton 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 wetlands 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 25 million tons of PHA natural plastics to replace about half of the petrochemical plastics currently used in the U.S. would reduce oil imports by over 200 to 230 million barrels per year, improving the U.S. trade balance by $6 to 9 billion a year, assuming oil at $30 to $40 per barrel.

Alternative Synthetic Pathways Awards

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

Archer Daniels Midland Company and Novozymes

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 Novozynes are commercializing enzymatic interesterification, a technology that not only has a tremendous positive impact on public health by reducing *trans* fatty acids in 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 now 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 soy bean oil, 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.

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

Emend® is a new therapy for chemotherapy-induced nausea and vomiting, the most common side effects associated with 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% of the raw materials and water used by the original one. By adopting this new route, Merck has eliminated approximately 340,000 liters of waste per 1,000 kg 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.

Alternative Solvents/Reaction Conditions Award

BASF Corporation

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

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 to 4.8 pounds of VOCs per gallon of conventional primers, a reduction of over 50%. 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% 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 businessman 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.

Designing Safer Chemicals Award

Archer Daniels Midland Company

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

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 618.4 million gallons in the U.S. in 2001. Typically, coalescing solvents constitute 2 to 3% of the finished paint by volume; this corresponds to an estimated 120 million pounds of coalescing solvents in the U.S. 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.

2005 Presidential Green Chemistry Challenge—Entries From Academia

The Application of Ultrasound (Sonication) to Catalyze Reactions in Some Industrial Processes

Dr. Finlay MacRitchie, Department of Grain Science and Industry, Kansas State University

Ultrasound has potential as a safe and clean method to catalyze reactions. It uses high-frequency sound waves to change reaction paths and speed up reactions, thus reducing or eliminating added chemicals. The methodology has so far not been scaled up for industrial application to any great extent. Dr. MacRitchie and his collaborators are working to apply ultrasound to three areas that have the potential to lead to industrial processes. These are: (1) the modification of wheat gluten to create value-added products; (2) the clarification of fruit juices; and (3) the purification of potable water. Dr. MacRitchie is using ultrasound to produce value-added products from gluten by enhancing functional properties such as solubility, gelling, foaming, and emulsifying. For example, ultrasound can increase the solubility of gluten, making it suitable for use in fortified beverages. Previous methods have used concentrated acids or enzymes, but these are not environmentally friendly. Dr. MacRitchie and his colleagues are collaborating closely with Midwest Grain Products in Atchison, Kansas, one of the major manufacturers of gluten. Presently, manufacturers mainly use enzymes to clarify fruit juices. Ultrasound offers the possibility of clarification without additional chemicals. Water contamination by microorganisms or by chemical pollutants such as pesticides is another problem to which Dr. MacRitchie will apply ultrasonics to replace traditional hazardous chemicals.

Biocatalytically Synthesized High-Performance Novel Antioxidants for Materials

Dr. Ashok L. Cholli, Center for Advanced Materials, University of Massachusetts Lowell

Industrial antioxidants are an increasingly important and fast-growing market. The antioxidants market in the U.S. is currently $1.4 billion, comprised of several low-molecular-weight antioxidants. Dr. Cholli and his group have developed high-performance macromolecular antioxidants that are synthesized in a one-step process using biocatalysts and biomimetic catalysts. These antioxidants have shown superior oxidative resistance (1- to 30-fold) and higher thermal stability compared to current low-molecular-weight antioxidants. This novel class of antioxidant technology is now ready for commercialization through Polnox Corporation. Dr. Cholli and his team at the University of Massachusetts Lowell originally developed Polnox's technology. Polnox's antioxidants have demonstrated superior performance in a wide range of materials and applications including, but not limited to, foods, oils and lubricants, fuels, plastics, and packaging. An acute oral toxicity (LD_{50}) test for these materials meets the requirements of other FDA-approved antioxidants. Scale-up to multikilogram scale has been demonstrated.

Bioinspired Thymine-Based Photopolymers: A Green Chemistry Platform for Innovation, Research, Education, and Outreach

Professor John C. Warner, School of Health and the Environment and Director, Green Chemistry Program, University of Massachusetts Lowell

Thymine-based photopolymers mimic the UV-light-induced formation and splitting of dimers in DNA. The styrene derivative vinylbenzyl thymine (VBT) offers unique polyfunctionality for polymerization, derivatization, hydrogen bonding, and pi-stacking, as well as

photocrosslinking. The applications of thymine-based photopolymers are benign, atom-economical, energy-efficient, water-soluble, and processable under ambient conditions. VBT prototypes, combining these features, demonstrate the technical feasibility of commercial applications of benign, prepolymerized photoresists: as a nontoxic, reversible hair fixative; for ambient, aqueous lithography of recyclable printed wiring boards; and for light-modulated pharmaceutical formulations. These highlight safety at the point-of-use with "light as a reagent", avoiding the danger of reactive monomers and emissions of volatile organic solvents. Immobilization of antimicrobials with VBT can substitute for chlorinated disinfectants, reduce the overuse and release of antibiotics, and preclude bacterial resistance. Success with VBT for surface-patterning conjugated-polymer nanocomposites and the facility of VBT for specific host-guest chemistry to embed analytes in sensor coatings offer links to the emerging fields of plastic electronics, functional inks, and smart textiles. VBT prototypes have driven 12 collaborations and 30 student projects; they have served 25 courses and 60 outreach events. This technology has been awarded four patents; two more patents are pending.

Professor Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

Development of Environmentally Benign Low-VOC Manufacturing Processes for Functional Materials: Towards Elimination of Transition Metals from Materials Made by Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is a controlled, transition-metal-mediated process to polymerize appropriate monomers by radical mechanisms; it was discovered in Dr. Matyjaszewski's laboratories in 1995. At present, many industrial research programs are actively incorporating this process to prepare polymers for a broad spectrum of applications. Commercial products including coatings and adhesives have been using this technology since 2002. The estimated market for well-defined functional polymers that could be made by the ATRP technology exceeds $20 billion per year.

Since 1995, Dr. Matyjaszewski's group has led efforts to develop more active catalyst systems targeted at reducing the levels of metals in ATRP systems. His group has also led the development of environmentally benign procedures for preparing many functional materials using ATRP. Previously, the most active catalysts could not be used in these systems, however, because the activity of the catalyst had to be balanced with the number of moles of initiator required to prepare low-molecular-weight functional oligomers of commercial importance. Dr. Matyjaszewski's group overcame this limitation with hybrid catalysts and two recent improvements: "Simultaneous Reverse and Normal Initiation" and "Activators Generated by Electron Transfer". As a result, Dr. Matyjaszewski's group can now apply their expanded understanding of ATRP catalysis to develop aqueous and bulk ATRP processes. The combined process controls the activity of the hybrid catalyst fully over extended time periods; it also allows recycling of the catalyst residues present in the process effluent back into reactor feed streams. Overall, the combined process eliminates all hazardous substances from the products made by ATRP and from industrial production waste streams.

Dr. Savvas Vasileiadis

Direct Step Olefin-to-Polyolefin Process with Toxic Solvent Elimination

Dr. Vasileiadis's nomination presents new catalytic processes for aliphatic (paraffin) hydrocarbon dehydrogenation into olefins and for subsequent polymerization into polyolefins.

These processes use catalytic dehydrogenation reactors in conjunction with polymerization reactors and coordination-type metal catalysts, such as titanium trichloride. In developing these processes, Dr. Vasileiadis considered materials and energy conservation coupled with environmentally benign modifications (e.g., the elimination of toxic or hazardous solvents, catalysts, and other media). Process improvements include increased polymer and olefin product yields, recycling of reactants and intermediate products for utilization within the process, reduction of toxic solvent generation, reduction of process steps, and reduction of capital and operational costs (including materials and energy costs). In 2004, Dr. Vasileiadis's technology received a U.S. patent. Dr. Vasileiadis is currently in the process of commercializing this technology.

Effective, Economical, and Relatively Benign Totally Organic Wood Preservatives to Replace the Current Copper-Rich Systems

Professors Tor P. Schultz and Darrel D. Nicholas, College of Forest Resources, Mississippi State University

Lumber for U.S. residential applications is currently treated with copper-rich preservatives. Environmental concerns have been raised about these "new" systems, however, and future disposal of metal-treated lumber may be difficult. Thus, in the future, totally organic wood preservatives will likely be required. Several problems exist with totally organic preservatives, principally: (1) the high cost of the newer organic biocides relative to the old metallic biocides; and (2) the biodegradation of organic biocides by various microorganisms, unlike metallic biocides.

Wood-decaying fungi use free radicals to degrade wood. With this basic knowledge, Professors Schultz and Nicholas combined various commercial organic biocides with an economical, benign, and commercially available antioxidant: butylated hydroxytoluene (BHT). They found that the combination was more effective than either component alone in short-term laboratory tests. Results from long-term outdoor exposure tests were even more promising. Further, they have recently confirmed their earlier hypothesis that BHT helps protect a commercial biocide against microbial degradation. Because BHT and organic biocide mixtures are synergistic and BHT reduces biodegradation of the biocide, less of the relatively expensive organic biocide is necessary to protect wood. Unlike most biocides, BHT is low-cost and safe to humans. Thus, wood treated with a biocide/BHT mixture will likely be safer to humans, have a reduced environmental impact, and be easier to dispose of than metal-treated wood. A preliminary economic analysis suggests that this concept is economical: the saving from the reduced biocide level is greater than the BHT cost.

Feedstocks for Catalytic Asymmetric Synthesis: New Route to (S)-Ibuprofen and Other 2-Arylpropionic Acids from Ethylene and Styrene Derivatives

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

One of the major challenges facing organic synthesis is the selective incorporation of abundantly available carbon, hydrogen, oxygen, and nitrogen sources into other common substrates. Professor RajanBabu and his group have discovered new, highly catalytic (substrate:catalyst ratio up to 1450) protocols for nearly quantitative (isolated yields up to >99%) and highly selective (100% regioselectivity, up to 96:4 enantiomeric ratio) codimerization of ethylene and various functionalized vinylarenes (hydrovinylation). These reactions proceed under exceedingly mild conditions (-52 °C, 1 atmosphere of ethylene) and produce highly valuable 3-arylbutenes. They consume both starting materials and leave no side products:

ideal criteria for an environmentally friendly process. A prototypical example of this hydrovinylation chemistry is the enantioselective synthesis of the widely used anti-inflammatory agent, ibuprofen, from 4-isobutylstyrene and ethylene. Several other profen drugs (e.g., naproxen, ketoprofen, flurbiprofen) could, in principle, be synthesized by this route. During these investigations, Professor RajanBabu prepared several new ligands. He also discovered new control elements that may have broader applications in the discovery of other highly selective catalytic processes. Examples include: (1) the effects of electronic and steric tuning of ligands; and (2) the role of hemilabile ligands and highly dissociated counterions in enhancing selectivity. Since the publication of Professor RajanBabu's original results, others have shown that the hydrovinylation reaction can be run in environmentally friendly supercritical CO_2.

Professor Michael J. Krische, Department of Chemistry and Biochemistry, University of Texas at Austin

Hydrogen-Mediated Carbon-Carbon Bond Formation: Catalytic Cross-Coupling with Complete Atom Economy

Elemental hydrogen is the cleanest and most cost-effective reductant available to humankind. Although catalytic hydrogenation is practiced industrially on an enormous scale, the use of hydrogen as a terminal reductant in catalytic C-C bond formation has been restricted to processes involving migratory insertion of carbon monoxide: for example, alkene hydroformylation and the Fischer-Tropsch reaction. In the absence of carbon monoxide, the capture of hydrogenation intermediates becomes untenable due to rapid CH reductive elimination of the (alkyl)(hydrido)metal intermediates. The Krische group has demonstrated that direct C-H reductive elimination manifolds are disabled upon heterolytic activation of hydrogen (H_2 + M-X $\rightarrow$ M-H + HX). This extends the lifetime of the organometallic intermediates obtained upon hydrometallation and facilitates their capture. The diverse hydrogen-mediated C-C bond formations developed in Dr. Krische's laboratory proceed with complete atom economy; several transformations have been rendered enantioselective. Moreover, implementation of this emergent technology should be expedited by the enormous infrastructure already in place for industrial-scale hydrogenation.

Professor Richard P. Wool, Department of Chemical Engineering, University of Delaware and Affordable Composites from Renewable Resources Center for Composite Materials

Materials from Renewable Resources

Professor Wool and his Affordable Composites from Renewable Sources (ACRES) research group use genetic engineering, composite science, and natural fibers to develop new, improved green materials from renewable resources. His green materials are optionally recyclable and biodegradable, thereby enhancing global sustainability. He has made a wide range of new high-performance, low-cost materials using plant oils, natural fibers, lignin, nanoclays, and carbon nanotubes. By selecting the fatty acid distribution of plant oils (triglycerides) and the molecular connectivity, he controls the chemical functional groups and molecular architecture to produce linear, branched, or cross-linked polymers. His work describes the chemical pathways used to modify plant oils and allow them to react with each other and with various co-monomers to form new materials with useful properties. When Professor Wool combines biobased resins derived from natural oils with natural fibers (plant and poultry), glass fibers, carbon nanotubes, nanoclays, and lignin, he produces new high-performance composites that are economical in many high-volume applications. His composites are used in hurricane-resistant housing, agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, electronic materials, and sports equipment. In addition, Professor Wool uses genetically engineered oils to make soft materials, such as pressure-sensitive adhesives (PSAs), foams, coatings, and elastomers.

The market for biobased materials is conservatively 100 billion pounds per year; Professor Wool's inventions are attracting considerable attention from industry.

N-Vinyl Formamide: The "Greening" of a Green Replacement for Acrylamide

Professor Eric J. Beckman, Chemical Engineering Department, University of Pittsburgh

Acrylamide is produced at volumes of over 200 million kg/year and is used worldwide to generate polyacrylamide. Acrylamide has been documented as a neurotoxin in human epidemiological studies; it is also a potential carcinogen. The 1998 Toxics Release Inventory (TRI) shows that 85 facilities released over 6.3 million pounds of acrylamide into the environment. N-vinyl formamide (NVF), an isomer of acrylamide, is readily polymerized to poly(N-vinyl formamide). NVF is neither a carcinogen nor a neurotoxin. Polymers incorporating NVF can perform most of the same applications as acrylamide polymers. Unfortunately, the current commercial production process for NVF exhibits a cost disadvantage that is tied to "green disadvantages". Professor Beckman has created an NVF synthesis that is intensified, uses lower process temperatures, produces less waste, and uses less hazardous raw materials than the current commercial synthesis. He has also found that hydrolyzed homopolymers and copolymers of NVF form covalent gels in the presence of reducing sugars. These gels are sufficiently robust to allow their use in oil recovery, replacing currently used polyacrylamide-chromium(III) gels in preventing the production of waste water during oil production. Polyvinyl amine-sugar gels can also replace chlorinated compounds during the processing of paper.

A One-Step, Anti-Corrosion, VOC-Free, Primer System to Replace Chromate Pretreatment and Pigments

Professor Wim J. Van Ooij, Department of Chemical and Materials Engineering, University of Cincinnati

Corrosion protection by paints and organic coatings is a common practice. Approximately 600,000 metric tons of chromates are used in the paint industry for chromate conversion coating and as pigments annually. The U.S. EPA, however, has identified chromates in the hexavalent state of oxidation as both toxic and carcinogenic. Chromate exposures cause a gamut of health problems, such as ulcers, irritation of the nasal mucosa, holes in the nasal septum, skin ulcers, allergic reactions, and nasal and lung cancer. The "self-healing" property of chromate makes it difficult to replace, however.

Paints are formulated with high-molecular-weight polymers for good anticorrosion properties. These polymers require solvents that are Volatile Organic Compounds (VOCs). During curing and drying of the paint, these VOCs evaporate, posing an occupational safety hazard.

Professor Van Ooij's invention is a one-step, very low VOC, anticorrosion primer system that totally eliminates chromates, yet performs as well as chromate-containing paints. He has successfully demonstrated that mixtures of organofunctional silanes and waterborne resins can be applied directly to metals as self-priming primers. His primer mimics the "self-healing" property of the chromates by including a plasma-treated pigment package to release a corrosion inhibitor slowly. Professor Van Ooij is currently commercializing this technology through a small company, ECOSIL Technologies, LLC.

Professor Xumu Zhang, Department of Chemistry, The Pennsylvania State University

Practical Asymmetric Catalytic Hydrogenation

Over 50% of the world's pharmaceuticals are single enantiomers; sales of chiral drugs were $159 billion in 2002. A growing challenge is to develop cost-effective, green chemical catalytic processes to make chiral molecules. Asymmetric chemocatalysis is one of the most competitive replacements for classic chiral resolutions, which generally require large volumes of solvents, chiral resolving agents, and even waste treatment of unwanted enantiomers. The cleanest and most cost-effective reductant available is hydrogen. Among commercial asymmetric chemocatalysis methods, asymmetric hydrogenation is dominant, accounting for over 70% of these methods. Fundamental, innovative chemical methods are needed to develop these green chemical processes. Breakthroughs in this area will have broad applicability in industry. Dr. Zhang's laboratory has developed novel transition-metal-reduction catalysts for the practical synthesis of chiral alcohols, amines, acids, amino alcohols, diols, and α- and β-amino acids. He has also investigated the fundamental factors controlling enantioselectivity. His group has invented a toolbox of practical chiral ligands for the asymmetric hydrogenation of ketones, alkenes, imines, and aromatic compounds. He has observed high activity (up to 50,000 turnovers) and enantioselectivity (up to 99% enantiomeric excess) for hydrogenation of some substrates. He demonstrates the synthetic utility of asymmetric hydrogenation in the green chemical processes with challenging asymmetric transformations for important biologically active compounds such as Lipitor®, Cymbalta®, and carbopenem.

Professor Jefferson W. Tester, Chemical Engineering Department, Massachusetts Institute of Technology

Replacing Organic Solvents and Homogeneous Catalysts with Water and Carbon Dioxide

Professor Tester and the MIT Supercritical Fluids Research Group have made significant advances in the field of green chemistry over the past five years. Their approach uses pure water, pure carbon dioxide, and water-carbon dioxide biphasic mixtures as reaction media for a range of carbon-carbon forming, oxidation, and hydrolysis reactions. Their major contributions include novel experimental apparatus designs and protocols, as well as validated models that provide technology to enable the use of water and carbon dioxide as green solvents. They have coupled experiments conducted under well-defined conditions to multiscale modeling to improve their understanding of reaction rate, selectivity, and mechanistic phenomena relevant to carrying out synthetic chemistry in these green media. They have demonstrated the feasibility of a surfactant-free acoustic technique that naturally segregates catalysts from reactants and products. This technique affords the opportunity to reduce operating costs for industrially important processes using homogeneous catalysts. Their efforts have produced new scientific methodologies and data regarding the chemical kinetics, phase kinetics, and equilibrium behavior of many model supercritical fluid mixtures. They have documented their results in over 100 publications. Other laboratories in the U.S. and other countries now utilize many of their methods, underscoring the usefulness of their experimental and theoretical methods for quantitative physical chemical kinetic analysis in hydrothermal and supercritical fluid media.

Research, Development, and Commercialization of Environmentally Benign Thermoplastic Pressure-Sensitive Adhesive Label Products

Dr. Steven J. Severtson, Department of Bio-based Products, University of Minnesota

Eliminating the problems created by pressure-sensitive adhesives (PSAs) in post-consumer waste is the most important technical barrier to expanding the use of recycled paper. Estimates are that replacement of current PSA technology with benign formulations can save tens of trillions of BTUs per year, increase the quantity of paper that can be recycled, and save the industry $650 million in non-energy-related expenses. A promising approach is the redesign of adhesive products to diminish their negative impact on paper recycling operations. Dr. Severtson has designed thermoplastic PSA products for which fragmentation of PSA films are inhibited during repulping operations. The adhesive particles that form are easily removed by standard cleaning equipment early in the recycling process, eliminating the PSA contamination. This iterative research included the study of model PSA systems and eventually led to the development of commercial products. PSA properties have been thoroughly characterized and their screening removal efficiencies have been tested when attached to various facestocks. This research has identified the surface and bulk mechanical properties of label components and the interactions between them that govern film fragmentation. Dr. Severtson's research is allowing label manufacturers to produce commercially viable, environmentally benign thermoplastic PSA labels that meet any customer requirement. This project is an impressive demonstration of academic-industrial collaboration on green technology and its successful promotion from the laboratory to the marketplace.

Solvent-Free, Crystal-to-Crystal Photochemical Reactions: The Synthesis of Adjacent Stereogenic Quaternary Centers

Professor Miguel A. Garcia-Garibay, Department of Chemistry and Biochemistry, University of California, Los Angeles

Chemical structures with adjacent stereogenic quaternary carbon centers are common in biologically active substances, including natural products, pharmaceuticals, and specialty chemicals. Despite recent advances in preparative chemistry, there have been no satisfactory procedures for preparing these structures, much less so for preparing them using environmentally benign processes. At present, most structures are obtained in low yields by circuitous routes with waste-generating purification steps. The technical challenge stems from the limitations that arise when six groups must converge with precise stereochemistry within 1.54 Å, which is the bond distance between two adjacent carbons. The method developed by Professor Garcia-Garibay consists of exposing a finely powdered crystalline ketone to a light source. Within hours, the ketone transforms into the desired product with no need for purification. Notably, the addition of six groups at the ketone α-carbons (now ~2.56Å apart) can be easily accomplished with excellent steric control by conventional methods. These substituents weaken the ketone α-bonds to extrude a CO molecule when a photon is absorbed. A short-lived biradical intermediate retains the stereochemistry of the ketone and makes the desired bond with stereoselectivity and stereospecificity that rival enzymatic processes. As an emergent technology, the photodecarboxylation of crystalline ketones is one of the most general and promising methods for synthesizing structures with adjacent stereogenic quaternary centers.

Professor Joseph M. DeSimone, Department of Chemistry, University of North Carolina at Chapel Hill and Department of Chemical Engineering, North Carolina State University

Surfactant-Free Supercritical Carbon Dioxide Fluoroolefin Polymerization Technology

Fluoropolymers exhibit a balance of high-performance properties that makes them ideal for many technologically demanding applications. Commercial fluoropolymer manufacturing practices use aqueous emulsion or suspension processes that require fluorinated surfactants that are now environmentally suspect (see "Perfluorinated Pollutant Puzzle" in *Chemical & Engineering News*, August 30, 2004). Moreover, these traditional water-based manufacturing processes strain local community water supplies and pose real health concerns when residual surfactant is not adequately isolated from the water supply. A team of researchers at UNC-Chapel Hill and NC State University has developed a more environmentally compatible process for producing fluoropolymers that uses supercritical carbon dioxide and does not require any surfactants. The process also yields more uniform products and enables easy, one-step isolation of the final polymer product. DuPont has recently licensed the technology and commercialized the process at its Fayetteville Works site in Bladen County, NC. DuPont brought the plant on line in March of 2002. The test and demonstration phase of the plant was highly successful and the Fayetteville Works site currently operates at plant-production capacity.

Professor Ajay K. Bose, Department of Chemistry and Chemical Biology, Stevens Institute of Technology

Unconventional High-Efficiency Green Synthesis

In the area of alternate reaction conditions, Professor Bose and his group have conducted microwave chemistry with limited amounts of solvents or even no solvents. Many useful synthetic reactions are exothermic and require only initiation by a short burst of microwave energy to go to completion. This "Microwave Jump Start", as devised by Professor Bose, would save energy and, thus, reduce the cost of producing pharmaceuticals. Second, Professor Bose has developed "Grindstone Chemistry" for conducting solvent-free exothermic reactions for pharmaceuticals on small and large scale by grinding reagents together. Using friction-activating agents, he has extended this method to solid/liquid and even liquid/liquid reagents. Third, he has devised water-based biphasic media for exothermic synthetic reactions that are complete in approximately 20 minutes, as compared to several hours for classical methods. For these exothermic reactions, he stirs the reagents (no solvent) and a catalyst in a large volume of water. Solid products separate as crystalline material in good yield. These solvent-free techniques constitute energy-efficient green chemistry. Indofine Chemical Company has tested Professor Bose's water-based biphasic media for the synthesis of coumarin-3-ester, obtaining excellent yield and high purity.

In the area of alternate pathways, Professor Bose and his group have used nontoxic reagents and new oxidizing agents to develop an eco-friendly alternative synthesis of Dapsone, an anti-leprosy drug also used for AIDS patients.

2005 Presidential Green Chemistry Challenge—Entries From Small Business

Advanced Marine Technologies (AMT): Reducing Nitrates in Buzzards Bay by Producing Organic Gem® Fertilizer from New Bedford's Fish Processing Wastes (A Sustainable Greater New Bedford Project)

AMT BioProducts Corporation

AMT manufactures Organic Gem® fertilizer in New Bedford, Massachusetts using approximately 7% of the 50 million pounds of fresh fish scraps typically generated by the 30 to 35 local processors each year. Organic Gem® (OG), certified by the Organic Materials Review Institute, was first made from the byproduct of AMT's nutraceutical extraction of marine cartilage. AMT has developed a unique enzymatic digestion engine (EDE) using proprietary enzymes that accelerate optimal digestion. The EDE strictly controls factors that could potentially denature enzymes and proteins; it also leaves oils, collagens, and lipids in their natural state. It is a fast, "cold" process that delivers a low-odor, efficiently absorbed fertilizer to increase plant yield and pest resistance. Presently, its markets include golf courses, turf farms, vineyards, hops, fruit trees, potatoes, cranberries, home gardens, and other crops. In New Bedford, the increased manufacture and use of OG delivers a triple economic and environmental benefit: (1) OG decreases the quantities and costs of fish wastes going to landfill illegally; (2) OG reduces nitrate discharges from the wastewater treatment plant into Buzzards Bay, a prime recreation area; and (3) OG minimizes agricultural runoff of nitrates from petrochemical-based fertilizers. With their innovative processor supply chain approach, AMT anticipates servicing 100% of the local wastes within the decade. Their plans now call for new EDE installations to bring cost savings to other processors and environmental benefits to other ports.

Biocatalytically Synthesized High-Performance Novel Antioxidants for Materials

Polnox Corporation

NOTE: This project is the result of a partnership between Polnox Corporation and Dr. Ashok L. Cholli of the University of Massachusetts. This project was judged in both the academic and industry categories. The project summary appears in the academic entries section on page 9.

A Clean and Economic Biocatalytic Process for the Key Chiral Intermediate for Atorvastatin Using Three Evolved Enzymes

Codexis, Inc.

Codexis has designed, enabled, and developed an innovative green process for commercial production of ethyl (*R*)-4-cyano-3-hydroxybutyrate, the key chiral intermediate in the synthesis of atorvastatin (Lipitor®). Previous commercial processes involve kinetic resolution (50% maximum yield) or syntheses from chiral pool precursors involving bromine chemistry. These processes ultimately substitute cyanide for halide under heated alkaline conditions,

forming extensive byproducts and requiring high-vacuum fractional distillation of the final product.

The nominated technology is an alternative process using basic feedstocks and two exquisitely clean biocatalytic reactions under neutral conditions. Codexis developed each of three enzymes using directed evolution technologies to provide the activity, selectivity, and stability required for a practical and economic process. In the first step, two enzymes catalyze the exquisitely enantioselective reduction of a prochiral chloroketone to an enantiopure chlorohydrin. In the second step, the third enzyme catalyzes the novel biocatalytic cyanation of the chlorohydrin to the cyanohydrin under neutral conditions. The evolution and development program has improved the volumetric productivity of the reduction reaction on a biocatalyst basis by approximately 100-fold and that of the cyanation reaction by approximately 1000-fold. Codexis has used the evolved biocatalysts to produce ethyl (*R*)-4-cyano-3-hydroxybutyrate at semiworks scale in such purity that there is no need for fractional distillation of the product. In July 2004, Codexis shipped over 1,000 kg of this product to a customer for testing.

MeasureNet Technology, Inc.

Data-Collection Technology that Minimizes Environmental Impact through Intelligent Design

With the growing emphasis on science education at all levels of academia, more and more educators are using electronic data collection in the laboratory. PC-based systems have advantages over traditional analog methods, but the operational and environmental costs are difficult to justify. Educators are burdened with the high energy costs, maintenance, and replacement of PCs; the environment is burdened with society's lack of a refined recycling infrastructure for the disposal of electronic equipment. Institutions face a dilemma: how to modernize their laboratories without inflating their operational and administrative overhead while remaining responsible stewards of the environment.

MeasureNet Technology's innovative design introduces students to the advantages of electronic data collection without the costs, waste, and pollution associated with PC-based systems. MeasureNet Technology's unique network design replaces up to 12 conventional PCs and interfaces with a single network controller and MeasureNet PC. This system combines improved energy efficiency, high-quality measuring capability, simplified instrument operation, and reduced maintenance. MeasureNet Technology was a winner of the 2002 Ohio Governor's Award for Excellence in Energy Efficiency. Each year, one MeasureNet System saves 16,000 kWh of electricity, prevents 18.9 tons of CO_2 emissions, saves 8.5 tons of coal, and saves $1,700 in energy costs compared to PC-based systems. Replacing just one MeasureNet PC at its obsolescence, instead of 12 PCs, keeps 26 cubic feet of waste, 66 pounds of lead, and other environmental toxins associated with PC disposal away from the nation's landfills. Simplified instrument operation and reduced maintenance allow students and educators more time for analysis and discussion, as well as more time for real learning.

Ventana Research Corporation

Development of High-Performance Environmentally Benign Lapping Fluids for Hard Disk Drive Manufacturing Applications

Magnetic hard drives are an essential component of computer hardware and handheld consumer electronic devices today. At the heart of these drives lies a giant magnetorestrictive (GMR) read/write head situated closely above a rapidly rotating magnetic hard disk. The

GMR head surfaces must be highly polished to ensure their reliable operation within hard drives. Conventional lapping fluids used to polish heads are composed of fine diamond abrasive powder dispersed within toxic nonaqueous solvents such as ethylene glycol. These solvent-based lapping fluids pose significant handling and disposal concerns for hard disk manufacturers.

Ventana Research has developed a new class of benign synthetic copolymers whose aqueous solutions have been shown to be highly effective at lapping GMR read/write heads. These copolymers have an aspartate/aspartamide backbone and pendant combs containing a phenolic oligomer phytochemical functionality (i.e., gallate esters). Besides being nontoxic and environmentally friendly, these copolymers are capable of polishing GMR read/write heads more rapidly and efficiently than conventional lapping fluids. This affords manufacturers considerable savings by increasing production rates and reducing waste disposal costs. Pace Technologies, a major worldwide distributor of polishing consumables, has begun distributing Ventana's lapping fluid to manufacturers of hard drives as well as to manufacturers of other products that require precision polishing, such as optical lenses and flat-panel displays.

A Dry and Environmentally Superior Process for the Recovery of Phosphoric Acid from Phosphate Ore

Carolina Process Associates, Inc.

The current processes used to manufacture phosphoric acid from phosphate rock are the thermal process and the wet-acid process. The thermal process is an electric reduction process that requires low-cost electricity; it is somewhat uncompetitive with the cheaper wet process. The wet process uses sulfuric acid to acidulate the phosphate rock, however, and produces vast quantities of both phosphogypsum (i.e., calcium sulfate) and process pond water. The phosphogypsum and pond water are both significant environmental problems. Currently, there are about one billion tons of waste phosphogypsum in Florida, clustered in the major phosphate-producing areas in the center and north of the state. This waste phosphogypsum contains radioactive radium sulfate and so is unsuitable for common phosphogypsum uses, such as wallboard.

The process developed by Carolina Process Associates uses almost-worthless high-magnesium phosphate rock as its first component. The poor quality of this rock makes it unsuitable for either the wet process or the thermal process. The second component is either rejected sand from the phosphate beneficiation process or another low-grade silica. The third component is a high-sulfur carbon source, such as waste petroleum coke. Carolina Process Associates uses binders to form these three components into pellets. It then roasts the pellets to generate a mixed phosphoric and sulfuric acid product and a clinker material, used as a raw material for aggregates. After chemical separation from the sulfuric acid, the phosphoric acid is suitable for commercial use in both technical and food-grade applications. Overall, the Carolina process uses waste materials, obtains a 98% yield at temperatures at least 100 to 150 °C lower than competing processes, and generates no wastes. The next step is a pilot plant to process about 500 pounds per hour.

Ecological Paint

Innovative Formulation Company

Innovative Formulation Company has developed Ecological Paint as a safe alternative to all those existing paints that do not comply with the requirements of Federal Regulation 29 CFR 1910-1200 and that also contain hazardous substances listed in California's Proposition 65. Ecological Paint was developed for chemically sensitive people and for those who suffer long-term exposure to the hazardous substances commonly found in other paints. The paint

contains no known carcinogens, neurotoxins, or volatile organic compounds (VOCs); it has no hazardous metals, formaldehydes, leads, mercury, chrome, ethylene glycol, phthalates, benzenes, hazardous air pollutants (HAPs) or APES. It has virtually no odor and is hypoallergenic. Its only solvent is water. It sacrifices no performance in achieving this and actually outperforms most other paints in many areas such as coverage, hide, and ease of application. It has none of the blocking or adhesion problems normally associated with other low- or zero-VOC products.

Ecological Paint is a multishelled, acrylated nanopolymer that is 100 percent acrylic. Its unique formulation and pigmentation shift the heat spectrum off the paint without affecting the visible color, even in the darker color spectrum; these features provide significant energy savings during the warmer months. Ecological Paint is being manufactured at the company's facility in Tucson, Arizona. It has been used in historical restorations as well as in environmentally sensitive locations.

METSS Corporation

Environmentally Friendly Aircraft Deicing Fluid

METSS Aircraft Deicing Fluid-2 (ADF-2) represents a new class of aircraft deicing fluid designed as an environmentally friendly alternative to traditional ethylene and propylene glycol-based fluids. METSS ADF-2 is composed primarily of food-grade materials derived from abundant and renewable agricultural feedstocks that are both economical and readily available. Unlike ethylene glycol-based fluids, METSS ADF-2 is nontoxic and nonhazardous to plant and animal life. It contains neither phosphates nor urea, which tend to promote eutrophication of natural waterways and may lead to fish kills. METSS ADF-2 biodegrades readily and completely to carbon dioxide and water. METSS ADF-2 has a lower Biological Oxygen Demand (BOD) and biodegrades at a slower rate than propylene glycol.

Commercial airports and military bases are increasingly concerned about the quality of storm water runoff and the effect of deicing chemicals on receiving waters. If storm water drains directly from runways and taxiways into a body of water, discharge permits require regular monitoring to determine BOD, contaminants, and other properties. Due to its low BOD, METSS ADF-2 can help airport managers achieve environmental compliance. METSS ADF-2 meets all requirements of the SAE AMS 1424D for aircraft deicing fluids. The U.S. Air Force, the Federal Aviation Administration, and Transport Canada have all approved METSS ADF-2; this product has been in commercial use since October 2003.

Harris Labs

Evapo-Rust™: Nonhazardous Rust Removal by Selective Chelation

Economic loss in the U.S. to corrosion costs $276 billion annually. Traditional methods of corrosion (or rust) removal include acids, caustics, converters, electrolysis, and mechanical. Their low purchase price is only a small portion of their true cost. These methods are major contributors to hazardous disposal, emissions, and human health problems. They use materials that are toxic, are corrosive, and can create explosive gasses and release volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Waste from these methods may contain heavy metals, paint, grease, oil, and various organic materials.

Harris Labs has invented an industrial replacement to remove and control corrosion in iron preparations. Evapo-Rust™ is nontoxic, nonhazardous, nonflammable chemical with a targeted process of removing rust (iron oxide). Evapo-Rust™ removes the iron oxide into solution by a proprietary process called selective chelation. The active ingredient in Evapo-Rust™ is an ester of a polyphosphoric acid with an amine. Following chelation, a sulfur

compound removes the iron from the chelator to form a ferric sulfate complex, regenerating the chelator. As the normal operational pH is between 6 and 7, the solution is never hazardous to handle, store, or dispose of in neat form. Personal protective equipment (PPE) is not required with Evapo-Rust™, making it an excellent industrial and consumer product. There are no air or ground transportation restrictions for Evapo-Rust™. Waste generated by Evapo-Rust™ is typically nonhazardous; the spent ferric sulfate has potential for use as a lawn and garden fertilizer. Evapo-Rust™ has been implemented in general industrial and strategic Department of Defense installations.

GreenEarth Cleaning: Dry Cleaning With Silicone Solvent

GreenEarth Cleaning, L.L.C.

Historically, solvents used for dry cleaning fabrics have been hazardous to soil, groundwater, air, and industry employees. GreenEarth Cleaning (GEC) has developed and patented a process using a cyclic siloxane (i.e., decamethylcyclopentasiloxane) that is a safe and viable alternative.

Prior to commercializing this process, GEC conducted beta-testing at 27 retail dry cleaning sites in the U.S. over a 10-month period. During this period, 2,000,000 pounds of clothing were processed, and independent, certified testing laboratories performed more than 26,000 test measurements on air and waste streams, proving the process is safe for the environment and employees. Beta-test sites also reduced the volume of their solid waste by 40-65%. The GEC silicone does not impact air quality because it is not volatile. Tests confirm that it will not impact soil or groundwater, as it degrades to SiO_2, CO_2, and H_2O within 28 days.

GEC has licensed this process at 727 locations in the U.S., Canada, England, Ireland, Sweden, Japan, Brazil, and Germany, with growing acceptance based on its health, safety, and environmental profile, as well as its operational advantages.

Green Product and Munitions Compliance Analytical Systems

Chemical Compliance Systems, Inc.

Until recently, manufacturers and regulatory agencies were restricted to qualitative, generic, and intuitive considerations of green chemicals and products (e.g., less harmful to human health and the environment) because no one had defined quantitative criteria for them. Chemical Compliance Systems has overcome this deficiency by compiling more than 75,000,000 data elements for over 210,000 chemicals and 250,000 products over the past 20 years. They have synthesized these data into quantitative green chemical and product ratings with their Green Products Compliance Analytical System (GP-CAS) and their Green Munitions Analytical Compliance System (G-MACS). G-MACS also uses the MIDAS munitions characterization database from the U.S. Army Defense Ammunition Center. Both GP-CAS and G-MACS are based upon 46 green chemical criteria, each normalized on a scale of 0% (least green) to 100% (most green). These criteria encompass a broad spectrum of ecological, health, and safety hazards. Both of these systems also identify which of 475 state, federal, and international regulatory lists include each chemical constituent of a product. Both systems can complete green analyses in 10-30 seconds. Any industry, facility, or location can utilize these systems, which have been available on the Internet since November 2003. GP-CAS and G-MACS can reap economic benefits throughout the product lifecycle. Chemical Compliance Systems can readily customize either system for special requirements and maintain confidentiality. Incorporation of these green analyses into complementary ana-

lytical systems is underway (e.g., their MSDS retrieval and manufacturing–import–export systems). No other capabilities of this type currently exist.

Montana Biotech SE, Inc.

Levan: A Renewable Raw Material for Several Industries

Levan, a polyfructan produced from sugar, can replace petrochemicals in many applications. For example, all industrial sectors use adhesives in everything from book bindings to automobiles, yet, 96% of adhesives are currently derived from a single nonrenewable resource: petroleum. A search for an environmentally friendly adhesive identified levan with a tensile strength up to 1,500 psi on aluminum. Montana Biotech SE has devised a cost-effective method to produce levan by large-scale fermentation.

Montana Biotech SE has developed two forms of levan. The water-soluble version is useful for temporary bonds and for select indoor applications. The cross-linked version can survive soaking in water for an extended time and can join difficult-to-bond plastics. Water-resistant levan can be used in the high-volume wood adhesive market. Levan could potentially be extruded to make a biodegradable plastic. Levan is safe to eat; it occurs naturally in many plants. In lab studies, levan has been shown to lower cholesterol.

Levan is a multifunctional, green, raw material. It meets three standards: (1) Safety: levan is safe for users and the environment. (2) Sustainability: levan is derived from a renewable resource. (3) Security: the feedstock is obtained from sugar beets and sugar cane, both produced in the U.S. and many regions around the world.

W.F. Taylor Co., Inc.

Meta-Tec™ Low-VOC, One-Component, Cross-Linking Adhesive: Innovative Science–Applied Technology

Traditional flooring adhesives (defined as one- or two-part reactive systems that are urethane-, epoxy-, solvent-, or water-based) include various industrial solvents and consume nonrenewable resources. The manufacturing and application processes for these adhesives can also create large amounts of hazardous waste byproducts and emissions. It is estimated that over 23 million pounds of volatile organic compounds (VOCs) are released to the environment annually from these products.

Meta-Tec™ technology is a unique class of adhesive chemistry properly designated as a low-VOC, reactive, one-part, self-cross-linking adhesive. The adhesives based on this chemistry consist of a viscous mixture of drying oils (such as soybean oil, linseed oil, and sunflower oil), inorganic fillers, renewable tackifiers (such as rosins), polymers with carboxyl functionalities, metal catalysts, and a nontoxic cross-linking agent. Although these adhesives have performance characteristics previously exhibited only by reactive systems such as urethanes and epoxies, they contain very low VOCs and use more renewable resources. With the high volume of adhesives used throughout the flooring industry, the ability of Taylor's Meta-Tec™ technology to eliminate the risks associated with volatile hazardous chemicals through reduction of VOCs promises to have a significant positive impact upon the environment and on human health. The use of just one product, Meta-Tec™ 2071 Wood Flooring Adhesive, would potentially prevent over 9 million pounds of solvents from entering the atmosphere. This product is projected to capture over 25% (25 million pounds) of the market share by the end of 2005.

MYCELX Technology: Synthesis and Use of a Curable Viscoelastic Polymeric Surface-Active Agent in the Removal of Organic Pollutants from Aqueous and Airborne Influent Streams

MYCELX Technologies Corp.

MYCELX technology uses biomimetic pathways to produce MYCELX chemistry, which is the reaction product of drying oils and methacrylate polymers. MYCELX chemistry can be considered one of the first commercially available products utilizing self-assembling synthetic pathways similar to those used by biological systems. The combination of biomolecules and synthetic acrylates in MYCELX chemistry results in novel properties that are not possessed by conventional synthetic polymers. MYCELX chemistry possesses a combination of novel properties: broad affinity, curability, and viscoelasticity. Affinity refers to the ability of MYCELX-infused substrates to bind together and immobilize disparate phases of organic compounds without future separation or desorption. Curability allows the MYCELX chemistry to be cured into practically any filter substrate and cured dry with full transfer of properties. Viscoelasticity allows MYCELX-infused filters to capture and immobilize organic compounds to filter saturation without any additional differential pressure across the filter. MYCELX-infused filters are able to remove emulsified organic compounds (e.g., from naval and marine bilge water), PCBs and other persistent organic pollutants, oil mists from air, and tramp oils in less than one second contact time without desorption. MYCELX technology has been commercialized and is used in a wide variety of industrial, marine, and commercial applications, both in the U.S. and internationally.

Mycopesticides and Mycoattractants

Fungi Perfecti, LLC

Entomopathogenic fungi kill insects and use their carcasses as platforms for disseminating spores. Because spores of certain entomopathogenic fungi repel termites and ants, however, widespread commercialization by the pesticide industry has been limited.

Fungi Perfecti has discovered that ants and flies are attracted to entomopathogenic fungi in their mycelial state, prior to sporulation. The company has received a patent for a technique to deploy the presporulating mycelium of the entomopathogenic fungus *Metarhizium anisopliae* as a natural agent to attract and kill termites and ants. More patents are pending. They have isolated cultures of fungi from naturally infected insects, cultured these fungi in the laboratory, and used a selection process to create strains that delay spore production for several weeks. The presporulating entomopathogenic mycelia emit powerful attractants and feeding stimulants, drawing select pests to a chosen locus, from which they then spread the infectious fungi throughout the targeted nest and ultimately to the queen. In choice tests, termites prefer the presporulating mycelium of *Metarhizium anisopliae* to wood as food. Research shows that diverse insect species share specific affinities to these fungi in their presporulating state. This discovery may well lead to novel methods for controlling insect pests worldwide. This mycotechnology is economical, is scaleable, and uses cell culture methods currently in practice.

New Biomass Catalytic Reforming Process for Solid Oxide Fuel Cell Power Generation

Zivatech

Zivatech's technology is based on analyzing, testing, and evaluating a new reforming process for converting biomass and other secondary waste streams into a syngas outlet stream rich in hydrogen gas for powering a directly interconnected solid oxide fuel cell (SOFC).

These waste sources are rich in methane and carbon dioxide; the new process uses an effective catalytic reformer to convert them efficiently into a syngas outlet stream. The stream is used as feed into the anode of an integrated fuel cell of a solid oxide structure.

Conversion of these waste streams to synthesis gas for use in SOFC-based electricity generation systems is of increasing importance to both commercial and remote residential energy consumers from energetic, economic, and clean energy points of view. Renewable waste biogas resources are of increased interest to the clean and highly efficient energy generation market. In addition, Zivatech's innovative process to convert carbon dioxide-rich methane gas inside an in-situ reactor using their reaction and catalysis system is under increased consideration in current and future industrial efforts. This is considered an additional benefit of Zivatech's work. Projected energy and capital savings from the use of the integrated new process are in the 30 to 35% range compared to existing natural gas- and diesel-based direct combustion technology.

The LATA Group, Inc.

New Green Technology for Eliminating Hydrogen Sulfide in Aqueous Systems, Especially Petroleum Industry Systems

Geo-Microbial Technologies and its subsidiary, the LATA Group, have been pioneers in biological research and development for nearly 20 years. Their work has resulted in biological processes and products that destroy and prevent biogenic hydrogen sulfide (H_2S) in petroleum reservoirs and water systems inherent in oil and gas production and other industrial operations. Their technology is important because deadly H_2S emissions have caused innumerable deaths and injuries, especially in the oil and gas industry.

LATA's Bio-Competitive Exclusion (BCX) technology is designed to attack the source of H_2S: the reduction of soluble sulfate (SO_4) in the water by indigenous sulfate-reducing bacteria (SRB). The BCX process is initiated and sustained by patented, environmentally friendly inorganic nitrate and nitrite formulae (named Max-Well 2000) that target and directly manipulate the indigenous microflora of hydrocarbon-bearing reservoirs and a wide variety of surface water systems. Max-Well 2000 formulae act at low concentrations as alternate electron acceptors for targeted nitrate-reducing bacteria (NRB) that flourish and out-compete SRB for essential growth nutrients needed to reduce sulfate to sulfide. The nitrite component reacts chemically with existing H_2S to form soluble, nonhazardous sulfate (SO_4); in addition, it is toxic to SRB. Certain *Thiobaccillus* NRB species that are stimulated by the nitrate in Max-Well 2000 also attack and degrade existing H_2S. The results of the growth of beneficial NRB microbial populations are the production of nonhazardous nitrogen gas, the elimination of existing H_2S, and continuous blocking of H_2S production. The oil and gas industry has responded favorably to the BCX technology, as evidenced by a growing commercial business.

Specialty Fertilizer Products

A New Polymer Coating for Increasing Efficiency of Phosphorous Use and Reducing Environmental Impact

Although phosphorus is an essential nutrient for plant growth, it can be toxic to man and the environment. Some sources of phosphorus fertilizer contain high levels of cadmium, which can accumulate in crops and have long-term toxicity to man. Phosphorus fertilizers are inefficient: crops typically take up no more than 20-25 percent of the applied phosphorus during the first year of application due to fixation of the phosphorus by antagonistic cations

in the soil. As a result, phosphorus accumulates in the soil, runs off into waterways, and causes toxic algae blooms that deplete oxygen for aquatic life.

Specialty Fertilizer Products has developed and patented a family of water-soluble, nontoxic, biodegradable copolymers made from itaconic acid (a monomer derived by fermentation of renewable agricultural resources) and maleic acid. These copolymers are applied directly to granular phosphorus fertilizers as a coating or mixed into liquid fertilizers. Used along with phosphorus fertilizers, these dicarboxylic anionic copolymers lessen or eliminate the fixation of phosphorus, increasing the availability of phosphorus to crops. The high cation-exchange capacity of these polymers interferes with the normal phosphorus fixation reactions in soil. As a result, more of the applied phosphorus accumulates in crop biomass, crop yields increase, farm profits improve, less cadmium accumulates in crops, and negative environmental impacts are lessened.

On-Site Generation of Mixed Oxidants Using Sodium Chloride Brine as a Safe Alternative for Chlorine Gas Disinfection

MIOX Corporation

Water disinfection using chlorine gas has saved countless lives in the U.S. and the world over the past 100 years. Chlorine gas is a hazardous material that is pervasive in U.S. communities and around the world. MIOX has demonstrated that on-site generation of chlorine-based mixed oxidants from low-cost sodium chloride brine is superior to chlorine gas for disinfection, even inactivating waterborne pathogens immune to chlorine gas disinfection. The MIOX process eliminates all of the hazards associated with chlorine disinfection. The technology is scalable from individual use to large municipalities. It offers significant chemistry benefits: a microflocculating effect that improves water clarification processes, reduction in byproducts of chlorine disinfection, elimination of taste and odor, maintenance of required residual chlorine in water distribution systems, and elimination of biofilms. MIOX now has over 1,000 large installations across the U.S. and in 20 foreign countries, replacing over 20 tons of chlorine gas per day, with a capacity to treat over 1 billion gallons of water per day and serve 6 million people. Since 2003, MIOX has teamed with Cascade Design, Inc./Mountain Safety Research to offer its purifier to the U.S. military, the camping and recreation markets, foreign travelers, disaster relief workers, and others.

PICKLEX®: An Environmentally Safe Metal Surface Preparation and Pretreatment Chemical

International Chemical Products, Inc.

Governments all over the world are trying to ban the use of chromate conversion coating on aluminum and other nonferrous metals. PICKLEX® replaces this traditional chromate process as well as the zinc phosphate process used to pretreat steel. PICKLEX® is an environmentally safe, nonhazardous, water-based product. In one treatment, it removes surface rust, white rust, weld scale, and laser scale from metal surfaces and also provides coating. Applied to a metal surface, PICKLEX® provides long-term rust protection. Used to prepare, treat, and coat metal surfaces prior to finishing, it requires no waste treatment or disposal at all. PICKLEX® works at room temperature and, therefore, requires no special heating system. Users can apply it easily to a metal surface with a sprayer, with a brush, or simply by dipping the metal item into a bath of PICKLEX®. The U.S. EPA's laboratory in Cincinnati, Ohio has tested this product and validated it as a nonpolluting, cost-effective conditioner for metal surfaces.

This single product is the answer to a host of pollution problems associated with many of today's metal treatment chemicals. Many small and medium-sized companies have been using PICKLEX® in its various grades since 1997 and have experienced exceptional results with zero waste for disposal. In addition, PICKLEX® 20 (a derivative of PICKLEX®) has been used by several large companies, including one that fabricates steel structures for the military.

Pantheon Chemical

PreKote® Surface Pretreatment: Replacing Hexavalent Chrome with an Environmentally Safe Solution

Hexavalent chrome (Cr(VI)) is the industry standard for corrosion protection on aluminum substrates prior to painting. Cr(VI) is toxic and hazardous. Discontinuing its use has been an EPA pollution prevention priority through Executive Order 12856 since 1993. Cr(VI) is also on the European End of Life Vehicles (ELV) Directive of nonallowable materials. In 1994, Pantheon Chemical began an extensive research program to find an environmentally safe replacement for chrome-based chemistries. Pantheon designed PreKote® Surface Pretreatment on the molecular level from environmentally safe chemicals to clean and promote paint adhesion to substrates to be coated. PreKote® is a neutral, alkaline, non-metal-based solution. After years of extensive laboratory and field tests utilizing highly advanced techniques of surface analysis and molecular modeling, Pantheon introduced PreKote® to the United States market as an efficient and green substitute for chromate chemistry.

The U.S. Air Force (USAF) has approved and implemented the use of PreKote® as an aluminum prepaint surface pretreatment process to replace Cr(VI). Following this success, the commercial aerospace market tested and has begun to use PreKote®. This technology decreases operational costs significantly (by simplifying and reducing process procedures), eliminates heavy metal waste streams, replaces toxic acids and solvents, improves the safety, health, and morale of workers, provides superior performance, and is environmentally compliant.

Recovery Systems, Inc.

Process for Treatment of Hog Waste and Production of Saleable Products from This Waste

Industrial hog production creates a large amount of liquid and solid waste, which is typically flushed into an open lagoon or sprayed onto fields, causing a number of environmental and human health problems. Recovery Systems has developed an alternative process to treat the waste and recover valuable products from it. The overall scheme consists of a processing unit on each farm and a central processing plant serving 15 to 20 farms. This process is expected to satisfy the state requirements for a waiver of the current moratorium on the expansion of hog farms in North Carolina.

In the Recovery Systems process, the waste is flushed out of the barn to a surge tank and pumped to mix tanks, where lime slurry is added to raise the pH. At this higher pH, the colloidal bonds of the solids and the urea break down to release ammonia. The lime treatment kills over 99% of all pathogens. The slurry is then pumped through an ammonia stripper; the ammonia-laden air is exhausted through a phosphoric acid reactor and the resulting ammonium phosphate is pumped to a storage tank. Next, the slurry is pumped to a solids separation tank, where coagulant and flocculent are added to separate the solids from the liquid. The solids are pumped to a vibrating screen washer, where the undigested feed is separated from the digested fecal solids. The liquid from the solids separation tank is pumped to a storage tank to be used in the flushing process. The digested solids are processed in a methane generator, which also concentrates the nutrients to produce organic fertilizer. Tests

by North Carolina State University show that the undigested feed is suitable as cattle feed and poultry litter. Well water is used to dilute the supersaturated salts in the flushing liquid. Recovery Systems will be testing its process on a one-of-a-kind U.S. EPA test hog farm in Lizzie, North Carolina.

Renewable Feedstock to Marketable Products

Changing World Technologies, Inc.

Changing World Technologies, Inc. (CWT) has successfully developed and patented a thermal conversion process (TCP) that converts renewable feedstocks into clean fuels and specialty chemicals for industrial and commercial use. The basic technology emulates the Earth's natural geological and geothermal processes: it uses heat and pressure to convert organic material into fossil fuels. The TCP accelerates these natural processes using basic chemistry and process technology in a completely enclosed system, thereby reducing the bioremediation process from millions of years to mere hours. The design of the system ensures that there is minimal odor, dust, fumes, smoke, gas, or excessive noise in the system. The TCP product streams include a clean fuel-gas, light organic oil, a carbon product, an aqueous nitrogen fertilizer, and a mineral soil amendment. The TCP does not create any negative byproducts.

A 200-ton-per-day demonstration biorefinery plant is now operating in Carthage, Missouri, using renewable turkey offal from a nearby processing plant. CWT projects that this plant will produce oil at a cost of approximately $33 per barrel with tipping fees and production credits. CWT is designing and constructing a larger plant that will operate on mixed agricultural waste. CWT estimates that large plants operating with mature versions of TCP technology using shredder residue and scrap tires could have an oil production cost of as little as $14 per barrel with tipping fees and production credits.

Renewable-Resource-Based, Environmentally Benign Deicing/Anti-Icing (D/A) Agents

MLI Associates

The new METSS/MLI technology for Deicing/Anti-Icing (D/A) agents is a fundamental, innovative chemical method that prevents pollution through source reduction. It uses abundant natural resources and agrichemical waste streams, such as biodiesel and biobased polymers. These D/A agents represent a new class of materials designed and used as alternatives to traditional glycol-based fluids. The first technical focus of the project has been to understand the synergism between components of D/A agents in order to reduce the use of environmentally destructive D/A agents, such as chloride salts and glycols. A second focus has been to use waste streams from critical biofuel energy independence products in D/A formulations.

This chemistry has led to a wide array of products, many of which are now in or near commercial use. The METSS/MLI biomass-based fluids are infinitely soluble in water, are nontoxic, and act as corrosion inhibitors for ferrous metals. They can be applied to a wide variety of surfaces. Sales of these fluids in the highway and facilities market have reached over 16 million gallons per year. METSS's aircraft deicing fluid has Federal Aviation Administration (FAA) approval and has begun commercial sales; a deicing product for runways has been sold to the U.S. Air Force. These products reduce the nation's reliance on petroleum, assist the use of biofuels, and reduce impacts on health and the environment relative to traditional glycol-based fluids.

Cleary Chemical Company

ROACH TERMINAL™ Insect Control: A Nontoxic Alternative that Prevents the Development of Pest Cockroach Populations

Cleary Chemical Company has developed and commercialized Roach Terminal™, an insecticidal bait supplied as a gel or in a bait tray. In 1999, the U.S. EPA registered Roach Terminal™ as a biopesticide. Roach Terminal™ has been tested successfully on the German cockroach, the most important household pest worldwide. This insect, like many others, stores uric acid as a source of nitrogen for retrieval during neogenesis of tissue and embryo development.

Roach Terminal™ has a novel mode of action. The active ingredient, termed a nutritional metabolism disrupter, is a composition of oxypurinol and xanthine, which act in concert to inhibit xanthine oxidase, a key enzyme in the metabolic pathway that produces uric acid. Oxypurinol is a metabolite of a human gout medication; xanthine is found naturally in foods. Cleary incorporates this active ingredient into an inert bait matrix designed to enhance the effects of the active ingredient and to attract the target pests. The insects founder when they deplete their reserves of uric acid precipitately during mating, molting, or embryo development and then cannot replenish their uric acid supply. Because they are not killed by direct toxic action, the dead insects do not contain any toxin that can move into the environment by secondary consumption. Roach Terminal™ affects insecticide-resistant and susceptible cockroach strains equally, indicating that there is no cross-resistance from other mechanisms.

Rynex Holdings, Ltd.

RYNEX® Dry Cleaning Solution

Rynex Holdings, Ltd. has developed, demonstrated, and implemented an environmentally safe and effective dry cleaning solvent that is economical and recyclable. RYNEX® replaces traditional hazardous dry cleaning solvents including perchloroethylene and Stoddard solvent. It is composed of an oxygenated surfactant, specifically dipropylene glycol *t*-butyl ether (DPTB), and water. This patented technology effectively removes water- and oil-soluble stains without the damage to delicate fibers that can occur with other dry cleaning and wet cleaning methods. RYNEX® is a complete solvent with no hazardous air or water pollutants. It has the advantage of attracting water molecules to form a water-solvent complex that exhibits extraordinary cleaning capabilities. The performance of RYNEX® is better than that of all other solvents available to the dry cleaning industry today. RYNEX® has low volatility and is not flammable, carcinogenic, bioaccumulative, or persistent in the environment. It separates from water to allow the removal of dirt, grease, and soil without additional soaps. RYNEX® cleans water-soluble and oil-soluble stains, providing effective detergency and compatibility with existing machinery. It has superior cleaning abilities; it does not cause fabrics to shrink or cause any types of dyes to bleed. Its enhancements include greater optical brightness in garments that are also softer to the hand. Twelve major dry cleaning distributors are currently selling RYNEX®. It is being used in over 100 locations in the U.S., Europe, and Asia.

Atmospheric Glow Technologies, Inc.

Sterilization of Medical Devices with Atmospheric Plasma

Atmospheric Glow Technologies (AGT) has developed an innovative method for cold sterilization of medical and dental devices using the exhaust of the patented One Atmosphere Uniform Glow Discharge Plasma® (OAUGDP®). The OAUGDP® operates in air at atmos-

pheric pressure to produce reactive chemical species that include oxygen species, excited molecular oxygen species (singlet oxygens), superoxide, ozone, and oxygen radicals. The longer-lived species can be convected outside of the plasma device to sterilize objects beyond the plasma volume. AGT has performed studies that demonstrate the ability of this technology to neutralize bacterial endospores on objects with complex shapes, such as hemostats and quick disconnects. Recently, AGT successfully passed the Association of Analytical Chemists (AOAC) Sporicidal Activity of Disinfectants Test (Official Method 966.04). This test requires the sterilization of 720 successive carriers. Analysis by AGT indicated that the carriers harbored extraneous organic debris and loads of up to 10^9 endospores per carrier before treatment. Materials compatibility studies performed by AGT indicated no obvious alteration in high-density polyethylene or stainless steel following treatment. AGT is maturing the OAUGDP® technology to provide an alternative means of low-temperature sterilization that will ultimately reduce reliance on chemicals such as ethylene oxide and its common nonreactive diluent, dichlorodifluoromethane (CFC-12), that pose a threat to human health and the environment.

Stoller ROOT FEED for Crop Production: Reduction in Fertilizer Pollution, More Efficacy of Pesticides, Increased Yield, Increased Quality, and Increased Crop Plant Disease and Insect Tolerance

Stoller Enterprises, Inc.

Stoller ROOT FEED is a proprietary crop health product, formulated to improve the use of fertilizer nutrients and, therefore, to decrease nutrient pollution by using minerals, sunlight, and crop production inputs more efficiently. The technology is based on signaling mechanisms for enhanced crop production. It recognizes that our crop systems are producing at about one-fourth to one-third of the genetic potential of the crop seed.

Fundamental to Stoller's technology is an understanding of: (1) the transcriptional regulation of DNA (crop genes) by plant growth regulators, minerals, and small molecules; (2) the management of translation (synthesis and functionality of proteins–the "workers" in cells that make growth happen); and (3) the physiological control of cell growth to enhance crop performance. Included in Stoller's model is an understanding that the plant growth regulator, auxin, has a major influence on plant growth and that the mineral calcium acts as a second messenger to assist with the signaling mechanisms.

The Stoller ROOT FEED technology is also innovative with development of an understanding that roots of the crop plant are the "control center" ("brains") of the plant, both practically and scientifically. ROOT FEED is delivered directly to the roots by drip irrigation, the most efficient and water-saving way of irrigating crops, for maximum crop regulation and performance.

Stoller STIMULATE: A Natural Product for Improving Crop Plant Performance and Enhancing Pest Resistance

Stoller Enterprises, Inc.

Stoller formulates STIMULATE with the natural plant growth regulators, auxin, kinetin, and gibberellin. These plant growth regulators are present in fruits and vegetables; Stoller often uses them at concentrations lower than are present naturally in food.

The focus in crop production has been on ameliorating the imbalance of nitrogen, phosphorus, and potassium in fertilizers. By focusing on fertilizer, farmers are generally producing at only a small fraction of the genetic potential of crop seeds. Stoller has developed a model

that places the growth regulator auxin at the top of plant growth and development control, an accurate estimate based on recent scientific literature. At least two premises of the Stoller model are critical to improving crop production. The first is that stress (environmental or biological) or lack of crop performance is most likely the result of an imbalance of the plant growth regulators (often referred to as hormones) in a crop plant. The second is that the half-life of the hormones has to be short in a particular organ of the plant for the rapid signaling required for "on time" plant growth control. The hormones are either hydrolyzed or conjugated after they signal a particular physiological event.

Judicious and timed application of Stoller STIMULATE in drip-irrigated crops increases crop yields; it reduces fertilizer and water use by 50% per unit of crop production. It also reduces the use of insecticides and fungicides by 50 to 100% by enhancing a plant's resistance to insects and tolerance to disease organisms.

Coastwide Laboratories

Sustainable Earth® Cleaning Products Designed for Health and the Environment

Commercial cleaning products are used daily by professionals in schools, hospitals, and commercial facilities. Although cleaning is beneficial, cleaning products commonly contain chemicals harmful to human and environmental health. High concentrations of these chemicals can negatively impact ground-level ozone concentrations, aquatic ecosystems, worker safety, and human health. Coastwide Laboratories has adopted a strategy that uses green chemistry to develop products that meet rigorous performance, environmental, and human health criteria. The strategy involves: (1) fully assessing all ingredients to understand their potential human health, environmental health, and lifecycle impacts; (2) creating a product development standard, Sustainable Earth® Green Chemistry standard 114 (SEGC 114), to establish positive criteria for product efficacy as well as human and environmental health benefits; and (3) formulating products to meet SEGC 114. This strategy results in entirely new formulations with remarkable benefits. Sustainable Earth® (SE) cleaning products combine reagents determined to be safer for human and environmental health with a hybrid surfactant system containing a stabilized oxidizing compound. This system eliminates conventional, potentially problematic ingredients such as alkyl glycol ethers, alkali builders, alkylphenol ethoxylates, EDTA, and ethanolamine. SE products have increased functionality and performance, use fewer, more benign ingredients, and reduce waste and emissions. Current SE products include cleaners for glass, floors, carpets, and washrooms, as well as an odor eliminator, floor finish, wax stripper, and dust mop treatment. In 2004, sales of SE products were $1.1 million.

Microcide, Inc.

Technology of Safe, Biodegradable, Non-Polluting Products as Alternatives to Toxic Microbicidal Chemicals

Almost all traditional, widely used disinfecting and sanitizing products contain ingredients that are toxic or potentially toxic, are environmentally hazardous, or have a high potential for accidents. For example, oxidizing chemicals, such as hypochlorite, peracetic acid, hydrogen peroxide, ozone, and chlorine dioxide, kill microorganisms by indiscriminate oxidation of organic matter, potentially destroying antioxidants, nutrients, and vitamins while forming unknown or toxic byproducts, including cancer-causing free radicals. The non-oxidizing microbicidal quaternary ammonium compounds (QACs; other traditional

disinfectants) inhibit butyl cholinesterase in blood plasma, liver, pancreas, and the white matter and are unsafe for use on fruits and vegetables because they leave large residues.

Microcide uses ingredients listed by the FDA and EPA in volumes 21 and 40 of the Code of Federal Regulations (CFR) as biodegradable, generally recognized as safe (GRAS), food additives, safe, and/or nonpolluting. With these ingredients, Microcide develops broad-spectrum microbicidal products as alternatives to toxic and oxidizing chemicals for the food processing, personal care, and health industries. Their products use surface-active agents at low pH. Raising the pH diminishes the microbicidal properties, allowing safe environmental disposal and biodegradation of the products after use. These products selectively kill microorganisms on food-contact surfaces, on fresh fruits and vegetables, and on body parts (including mucosal and skin surfaces) without covalent chemical reactions. The technology presents alternative products safe for manufacturing, transportation, and use without accident potential. Two of Microcide's products, PRO-SAN and PRO-SAN L, are EPA-registered pesticides.

WaterSavr™ Evaporation Control

WaterSavr Global Solutions, Inc.

WaterSavr™, as first developed, reduces drinking water evaporation from reservoirs and canals effectively and economically. It is a process-controlled powder that is a mixture of calcium hydroxide and long-chain fatty alcohols (*n*-cetyl and *n*-stearyl alcohols). When added to water, WaterSavr™ yields a self-spreading and self-assembling monolayer film that is two nanometers thick and has unlimited width and length. WaterSavr™ reduces evaporation by up to 40%. The United Nations Environmental Programme Centre has designated WaterSavr™ as an Environmentally Sound Technology. WaterSavr™ has been tested in the Western U.S., as well as in China, India, Morocco, and Spain.

Research is continuing to expand the usefulness of this rapid-spreading monolayer by adding functions to it. Following successful field and lab trials, WaterSavr Global Solutions submitted a mosquito larva control version to the U.S. EPA for registration as a pesticide. Other research focuses on pathogen and pollutant detection through thin-film optimization of the air/water interface and the inherent advantage of surface sensors over volume sensors. All versions of WaterSavr™ are biodegradable. The basic WaterSavr™ product reduces evaporative losses at a fraction of the cost of new water production, whereas the mosquito-control version reduces the use of less environmentally friendly chemicals and maintains the active ingredients at the air/water interface where larvae must breathe.

WT-HSC13: A High-Strength, Low-VOC Aerosol Adhesive

Westech Aerosol Corporation

Westech's WT-HSC13 high-strength canister adhesive is formulated to limit volatile organic compounds (VOCs), dramatically reducing toxicity and air pollutants. WT-HSC13 contains no chlorinated or cancer-causing solvents (e.g., methylene chloride). Methylene chloride is a concern in some geographical areas and Westech has excluded it from the formula. The South Coast Air Quality Management District (SCAQMD) for Los Angeles, Orange County, Riverside, and San Bernardino requires the VOC level to be less than 80 grams per liter. WT-HSC13 is the only solvent-based canister adhesive on the market that complies with this regulation. Using an alternative solvent, cyclohexane, Westech's new formula makes the manufacture of furniture, countertops, RVs, automotive headliners, manufactured homes, and many other products a safer process for workers, the environment, and the local population. This product provides a substantially high bonding strength and

contains more than double the solids or rubber content of other adhesives currently on the market, resulting in double the coverage. This new technology in chemistry provides a much-needed solvent-based adhesive. It is strong, affordable, environmentally safe, and adheres to even the strictest regulations with regard to emissions and pollutants.

2005 Presidential Green Chemistry Challenge—Entries From Industry And Government

3D Trasar Bio Control

Nalco Company

Open recirculating cooling water systems are used by industry for heat rejection. They are one of the largest users of fresh water (5% of total use); in industrial/power generation systems, they account for up to 70% of a plant's water use. The warm, nutrient-rich waters of a cooling system provide an ideal growth medium for microbes. Unchecked, microbial proliferation increases the use of water and energy, shortens equipment life, and increases health risks.

The biocides used to control microbial activity in cooling systems are among the most toxic chemicals added to or discharged from these systems. The necessary dose of biocide depends on time-variable factors such as water chemistry and microbial activity, but operators often dose systems with excessive biocides to ensure control and preserve a margin for error. Nalco's 3D Bio Control puts a fluorescent BioReporter molecule, resauzurin, in the water to continuously monitor the total microbial activity throughout the system. Nalco then adds biocide only when the BioReporter molecule responds to microbial activity. This method of continuous monitoring and control allows the most efficient use of biocide, ensures microbial performance, reduces absorbable organic halide (AOX) formation, and reduces toxic discharge. Following commercialization in April 2004, Nalco had deployed 550 units capable of 3D Bio Control to the field by the end of the year.

Airflex® EF811 Vinyl Acetate Ethylene (VAE) Emulsion Polymer: A Binder for Environmentally Friendly, High-Performance, Cost-Effective Architectural Coatings

Air Products Polymers, L.P.

Air Products Polymers, L.P. has solved a regulatory compliance problem for paint manufacturers by developing a safer chemical. The architectural coatings industry is being challenged to implement strict environmental regulations that significantly reduce the level of volatile organic compounds (VOCs) added to water-based paints as solvents. Vinyl acrylics, the workhorse polymer for architectural coatings, typically require significant levels of added solvent. Many of the polymers used in paints currently require added solvent to form a film that will adequately protect the painted surface. Historically, paint performance has been significantly compromised as solvent levels are reduced.

Air Products Polymers has developed Airflex® EF811 emulsion, a new vinyl acetate–ethylene (VAE) copolymer that solves this formulation challenge. Airflex® EF811 emulsion can be formulated at very low solvent levels, replacing vinyl acetate. Airflex® EF811 emulsion provides superior performance and is priced similarly to vinyl acrylics. Prior to the development of Airflex® EF811, the higher cost of VAEs versus vinyl acrylics had inhibited adoption of this technology into the large coatings market and its vinyl acrylic segment. Airflex® EF811 is being purchased or evaluated by most major U.S. paint companies. Broad replacement of vinyl acrylics with Airflex® EF811 emulsion will significantly reduce solvent use, improving indoor and outdoor air quality.

DuPont Company

Bioderived Solvents, Surfactants, Fuel Additives, and Monomers

Many applications of renewable resources require their transformation into platform molecules, followed by their ready conversion into commercial products. Levulinic acid is one such platform molecule. Biofine, Inc. (winner of the 1999 Presidential Green Chemistry Challenge Award in the Small Business Category) discovered a manufacturing process to make levulinic acid from cellulosic biomass. This process is currently moving toward large-scale commercial production.

DuPont is taking the next step by developing commercially viable processes that use levulinic acid, converting it into a host of desired products. DuPont uses novel catalytic transformations along with other techniques of green chemistry. DuPont is developing processes to replace petroleum-derived solvents, monomers, and transportation fuels with products derived from levulinic acid. For example, DuPont has discovered several new, high-yield routes to levulinic acid esters that are attractive additives to either diesel fuel or gasoline. Using levulinic acid in ways such as these can reduce dependency on petroleum while consuming cellulosic waste.

Savannah River National Laboratory

BioTiger™: Biocatalyst for Accelerated Cleanup of the Environment

BioTiger™ is a novel, surfactant-producing consortium of 12 nontoxic microbial strains that remediates polycyclic aromatic hydrocarbons (PAHs) and heavy metals. The BioTiger™ consortium is highly resilient and effective; it was isolated from an oil refinery in Poland that had been exposed to extreme environmental conditions, petroleum hydrocarbons, heavy metals, and associated solvents for over a century. This environmental biocatalyst has properties and capabilities not demonstrated elsewhere.

The BioTiger™ strains produce biosurfactants during in situ and ex situ remediation. The biosurfactants increase the solubility of PAHs, increasing both the access of the bacteria to PAHs and the efficiency of bioremediation. The biosurfactants also bind metals and other contaminants, allowing them to be flushed from contaminated soil. Potentially, the biosurfactants could be used as cleaning or degreasing agents. Using microbes can reduce treatment time for petroleum-contaminated soil to as little as 90 days, producing cost savings. BioTiger™ can also save money by removing petroleum products from mixed radioactive waste, allowing its less costly disposal as low-level radioactive waste.

Broin and Associates

Broin Project X™: A Method for Producing Ethanol Using Raw Starch

Broin and Associates has created a unique, novel process for the large-scale production of ethanol and its coproduct, distiller's dried grains. The process represents the next step in the evolution from the conventional, high-temperature liquefaction process. Broin's new technology delivers fermentable sugars from granular starch directly to the yeast (the production organism) in a controlled manner, avoiding the high-temperature starch liquefaction step. The Broin Project X™ (BPX) ethanol production process addresses several principles of green chemistry. It uses novel biocatalysts; it results in higher ethanol yield, lower energy input, reduced safety issues (due to reduction in ammonia), reduced plant capital costs, reduced use of fresh water, reduced environmental emissions, increased flexibility in coprod-

uct applications (due to improved quality), and reduced transportation costs (due to increased density and flow properties of the coproduct). The nominated process represents a new dislocating technology that owes its existence to the realization of several manufacturing and environmental benefits. It is the most novel development in the history of the fuel ethanol industry, the nation's largest renewable-based industry. Since the spring of 2004, the BPX™ process has been implemented in three U.S. commercial ethanol facilities totaling almost 150 million gallons in annual ethanol capacity.

SC Johnson

Chemistry-Based Design Process to Create Environmentally Benign Consumer Products: The Greenlist™ Process

SC Johnson is a chemical user, not a manufacturer, but is working to minimize the hazard of the chemicals it uses. The Greenlist™ process is an environmental classification system for chemicals; it is based on four to seven specific criteria for chemicals within functional material categories. These categories include surfactants, solvents, propellants, resins, packaging, chelants, insecticides, antimicrobials/preservatives, fragrance raw materials, waxes and candle fuels, and thickeners. SC Johnson may add others, such as colorants and inks, in the future. SC Johnson selected criteria to be meaningful and discriminating within each functional category. These criteria include biodegradability, aquatic toxicity, human toxicity, European Union environmental hazard classification, preferred source/supply, vapor pressure, octanol/water coefficient, and others appropriate for specific categories. The Greenlist™ process assigns an environmental classification (EC) score for each raw material based on its average score against the criteria used for its category. SC Johnson lowers the final EC score for some chemicals to account for other significant concerns including persistence, bioaccumulation, and toxicity (PBT); endocrine disruption; carcinogenicity; reproductive toxicity; and others. The final EC scores range from Best (3) to SC Johnson Restricted Use Material or RUM (0).

Greenlist™ sets new environmental standards that surpass regulatory requirements and drive product innovation. Product formulators may access the company's global databases to find the EC score of each chemical. Formulators have increased their use of Better or Best chemicals in products by over 13,000,000 kg in the past three years. In addition, SC Johnson has replaced all polyvinylchloride (PVC) and chlorine-bleached paperboard in its product packaging, eliminating over 1,700,000 million kg of PVC and 100,000 kg of chlorine-bleached paperboard. By measuring its progress with Greenlist™, SC Johnson is institutionalizing sustainability and improving its environmental footprint.

Cytec Industries Incorporated

Cylinderized Phosphine as a Safer, More Environmentally Friendly Alternative to Traditional Fumigants for Stored Products

Agricultural fumigants are used to control pests that infest stored products such as dried fruits and nuts, grains such as wheat, rice, and corn, and nonfood commodities such as tobacco. For over fifty years, stored products have typically been fumigated with methyl bromide or metallic phosphides. Methyl bromide is being phased out in accordance with the Montreal Protocol on ozone-depleting substances; therefore, an alternative fumigation method is needed. Metallic phosphides (typically aluminum or magnesium phosphide) release phosphine gas when exposed to the ambient moisture in the air. Phosphine gas by itself is a very effec-

tive fumigant with no known chronic toxicity. The efficient release of phosphine gas from the metallic phosphides, however, requires certain temperature and humidity levels that may not be reached in practice; as a result, unreacted phosphide residues are often left after fumigation. These residues must be deactivated and disposed of in a time-consuming and often dangerous process. Typically, they are hazardous waste.

Cytec Industries has developed and commercialized a new technology for the stored product fumigation market. Cytec supplies phosphine gas in recyclable cylinders. With cylinderized phosphine, workers can easily adjust phosphine concentrations from outside the fumigation space, applying only the amount necessary for complete fumigation. As a result, fumigation requires less phosphine. Further, cylinderized products leave no unreacted residue or byproducts. Cytec's cylinderized phosphine products are inherently safer than traditional fumigants: they require less worker exposure and do not significantly impact the environment. Cytec's two products, ECO_2FUME and $VAPORPH_3OS$, are currently used by some of the largest food processing, milling, and storage facilities.

Solutia Inc.

Dequest PB–Carboxymethyl Inulin: A Versatile Scale Inhibitor Made from Chicory Roots

Fouling of surfaces by mineral salts is a major problem in water-bearing systems, because scaling reduces heat transfer efficiency and interferes with the operational performance of industrial processes. Previously, scale inhibitors were either products with poor biodegradability, moderate toxicity, and good performance (e.g., polyacrylates) or biodegradable products with limited applicability (e.g., polyaspartates). Carboxymethyl inulin (CMI), developed by Solutia and Cosun, provides a cost-effective, safe, and versatile alternative to traditional antiscalants. In 2004, Solutia began marketing this very first inulin derivative, CMI, in the U.S. under the trade name Dequest PB.

CMI is based on inulin, an oligosaccharide harvested from the roots of chicory. CMI has excellent scale-inhibitor properties. It combines good biodegradability, very low toxicity, and excellent scale-inhibition performance characteristics for various types of scales, particularly sulfate scales. The product can be used in many applications, but is especially well-suited for use in environmentally sensitive areas, such as off-shore oil production. For example, CMI is used in the Norwegian off-shore oil drilling sector of the North Sea. CMI also is a suitable replacement for poorly biodegradable scale inhibitors in water and process water treatment applications. In addition to CMI, Solutia and Cosun are developing a wider range of inulin-based products with different functionalities.

Novartis Pharmaceuticals Corporation

Development of Green and Practical Processes Utilizing Dialkyl Carbonates as Alkylating Reagents

In the last five years, Novartis's green chemistry project has developed an environmentally friendly methylation process that employs 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) or 1,4-diazabicyclo[2.2.2]octane (DABCO) as novel catalysts to promote methylation reactions of phenols, indoles, benzimidazoles, and carboxylic acids with dimethyl carbonate under mild conditions in nearly quantitative yields. Similarly, Novartis has developed a novel and green process using dibenzyl carbonate with catalytic amounts of DABCO or DBU to benzylate nitrogen, oxygen, and sulfur atoms. Either microwave irradiation or an ionic liquid provide additional rate enhancement. By combining DBU or DABCO, microwave irradiation, and an ionic liquid, Novartis can perform alkylation reactions that previously took up to several days efficiently in high yields within minutes. Novartis's technology avoids toxic or

carcinogenic reagents such as methyl iodide, dimethyl sulfate, benzyl chloride, and benzyl bromide. It also eliminates the use of a stoichiometric amount of base if applicable substrates contain no acidic protons. Their novel technology has the additional benefit of rapid reaction times, ease of operation, and use of readily available catalysts and ionic liquids. These features should make this newly developed chemistry of great benefit to humans and the environment. The United States Patent and Trademark Office has granted four patents to Novartis for these novel inventions. In addition, leading peer-reviewed journals have accepted six publications. By the end of 2004, these papers had been cited thirty times by other scientists, confirming the utility and value of these inventions.

Development of Nike Brand Footwear Outsole Rubber as an Environmentally Preferred Material

Nike Global Footwear

One of the Nike brand's long-term, corporate environmental goals is to eliminate from its products all substances known or suspected to be harmful to human health or the health of biological or ecological systems. To move towards this corporate goal, Nike brand's footwear organization began an effort to eliminate many of the toxic substances from the process of manufacturing footwear rubber outsoles, which are common to the athletic footwear manufacturing industry. Nike's general strategy included developing an assessment protocol to identify toxic chemicals to avoid; assessing certain of Nike's rubber formulations against the protocol; testing; and commercializing the new rubber formulation. The project resulted in a new environmentally preferred rubber formulation for outsoles that replaces a traditional Nike rubber formulation (Formula A). A representative sample of the new environmentally preferred rubber contains 96% fewer toxics by weight than the original formulation, provides equal performance, looks the same, and costs no more than traditional rubber. Nike continues to work at improving its formulation. Currently, Nike is also trying to establish a consortium of companies to pool resources to develop an enhanced assessment protocol and open the protocol to scientific peer review.

Nike implemented an internal footwear sustainability index to measure its footwear development teams on their use of environmentally preferred materials. The index helped drive rapid adoption of the new rubber. After about two years, nearly all footwear development groups (basketball, soccer, running, etc.) have used the environmentally preferred rubber in some shoes. In Nike's spring 2005 production season, 58 million pairs of shoes out of approximately 100 million pairs total will contain the new material. In producing these shoes, Nike will use approximately 14,415 metric tons of environmentally preferred rubber.

Development of a Water-Based Adhesive, Primer, and Release Coating for Post-it® Super Sticky Notes

3M Office Supplies Division Laboratory

3M's Post-it® Super Sticky Notes are an excellent example of the benefits of green chemistry and the importance of integrating 3M's core values into decision-making. In 2003, 3M introduced Post-it® Super Sticky Notes: a new, enhanced Post-it® Notes product designed for use on vertical and hard-to-stick surfaces. In the late 1980s, 3M developed a prototype of this enhanced Post-it® Note using solvent-based formulations for the adhesive, primer, and release coatings. At the same time, 3M launched an initiative to reduce volatile organic compound (VOC) emissions by 90% by the year 2000. Rather than install pollution control equipment to control the VOC emissions from the proposed production process, 3M delayed introducing the product until it could develop new, water-based formulations. 3M's new water-based microsphere adhesive, primer, and release coating formulations yield the desired perfor-

mance, generate fewer air emissions, have a reduced environmental risk profile, and are less expensive to manufacture than the original, proposed solvent-based formulations. The new formulations result in lower VOC emissions (33,400 pounds controlled or 2,170,000 pounds uncontrolled) and lower Toxic Release Inventory (TRI) emissions (20,500 pounds controlled or 1,024,000 pounds uncontrolled) annually than if 3M had implemented its proposed solvent-based process.

Pfizer Global Research and Development

Discovery and Development of an Environmentally Benign Commercial Route to Sildenafil Citrate

Pfizer has emphasized green chemistry objectives during the discovery and development of the commercial route to sildenafil citrate, the active ingredient in the important medicine Viagra™. The commercial synthesis generates only 4 kg of organic waste per kg of sildenafil, substantially less than is typical for pharmaceutical products. The key breakthrough in achieving this exceptional result was the discovery of a new, convergent synthetic route with a clean cyclization reaction as the final step, eliminating purification operations. Subsequent careful chemical development and diligent solvent recovery have optimized the environmental performance.

Achievements include a nine-fold yield increase from the starting pyrazole to sildenafil citrate. The commercial route reduces organic waste by 14-fold, eliminating 4,000 tons of organic waste; it also reduces aqueous waste by 5-fold, eliminating over 3,900 tons of aqueous waste. An environmentally benign catalytic hydrogenation reaction replaces a reduction using tin chloride (tin is a toxic heavy metal). Hydrogen peroxide (a worker safety issue) has been eliminated. Three chemical steps are combined, using a single solvent that is recovered. None of the reactions in eight chemical steps requires a work-up involving extraction, again leading to low organic waste. Pfizer has implemented many technological achievements at the outset of commercial manufacture.

GlaxoSmithKline

Discovery and Development of a Green Process for Radafaxine

GlaxoSmithKline has identified and fully evaluated two viable commercial routes of manufacture for Radafaxine, a compound that has shown antidepressant activity in animal models of depression. Radafaxine is an (S,S)-enantiomer. The corresponding (R,R)-enantiomer is associated with undesirable effects. The key challenge was to separate the two enantiomers efficiently and minimize the environmental impacts associated with the undesired enantiomer.

Route B3, an initial improvement on the traditional synthesis, uses an original and innovative dynamic kinetic resolution to synthesize the desired single enantiomer. This simple process has several advantages and produces the desired enantiomer without expensive and environmentally unacceptable chiral catalysts or templates. It also replaces the environmentally undesirable solvents dichloromethane and acetonitrile.

The second process, multicolumn chromatography (MCC), improves on route B3, retaining all of its advantages. The MCC process also re-epimerizes and recycles the undesired enantiomer, delivering an overall process with significant environmental benefits. Detailed analysis demonstrates that the MCC-based process meets all commercial and quality criteria; in addition, it reduces the use of valuable resources and greatly decreases the process liquid waste streams.

The traditional synthesis required 260 kg of input material and 194 kg of solvent per kg of product. The mass intensity of the MCC process is approximately 20 kg of input material per kg of product, an incredibly low number for a pharmaceutical product. The MCC process uses only 19 kg of solvent per kg of product, with potential for further recovery. GlaxoSmithKline performed a pilot study on medium-to-large scale in-house MCC equipment during 2003. At peak production, GlaxoSmithKline calculates that the MCC process could reduce the overall waste load by 5,000 metric tons per year.

Duraflame® All-Natural Manufactured Firelog

Duraflame, Inc.

Duraflame, Inc. is America's leading marketer of manufactured firelogs. Headquartered in Stockton, California, Duraflame is a privately held company that has been in business for more than 30 years.

What started out as an effort to recycle the sawdust produced by wood milling operations has grown into a way of doing business for Duraflame. The company's Research and Development Department regularly experiments with resources to determine unique approaches to product development and is continually striving to create convenient, environmentally responsible products to meet consumer needs.

Faced with a shrinking supply of petroleum wax and a rise in restrictions on wood-burning fireplaces by air quality districts (particularly in the Western States), the company has focused on developing manufactured firelogs using materials that are both cleaner burning and recycled or renewable. In 2004, Duraflame introduced a new all-natural firelog made from recycled biomass products such as wood sawdust, ground nut shells, recycled cardboard, and plant waxes (rather than petroleum wax) as a combustible binder. Standard petroleum wax-sawdust firelogs produce approximately two-thirds less of the key air pollutants associated with residential wood combustion than does an equivalent natural wood fire. In contrast, Duraflame's new all-natural firelogs produce only about one-quarter of the emissions of an equivalent natural wood fire. The Duraflame® All-Natural Firelog is now available in supermarkets across the U.S. and Canada.

Economic Destruction of Methyl Bromide from Air Streams Using Nonhazardous Aqueous Solution

Value Recovery, Inc.

Methyl bromide is a critical chemical fumigant used to protect imported and exported goods from conveying unwanted insect pests. It is also an ozone-depleting substance slated for elimination by 2015 under the Montreal Protocol, in part because emission control was not believed to be practical. Efforts to find replacement substances have, to date, not been successful; thus, methyl bromide remains in use.

The novel technology developed by Value Recovery takes advantage of methyl bromide's reactivity to separate it from air. The fumigation chamber containing methyl bromide is vented into a special scrubber filled with an aqueous solution of ammonium thiosulfate and other nonhazardous compounds. The gas passes through the liquid in tiny bubbles that enhance gas-liquid mass transfer. The nucleophilic substitution reaction involving bromide (leaving group) and thiosulfate (nucleophile) takes place in the aqueous phase. Industrial-scale trials using a container filled with produce fully confirm numerous laboratory results: one pass through the scrubber removes more than 85% of the methyl. Value Recovery's technology is very inexpensive due to the simplicity of the process, the low cost of equipment, the inexpensive reactants, and the ease of disposal of the used liquor.

U.S. Army Engineer Research and Development Center

Environmentally Friendly Water Treatments for Control of Corrosion, Scale, and Bioactivity in Heating and Cooling Systems

Presently, heating and cooling water treatment requires manual handling of toxic and corrosive chemicals, some of which (hydrofluoric acid, for example) are extremely hazardous. The U.S. Army Corps of Engineers Engineer Research and Development Center (U.S. Army ERDC) led a team of researchers to develop green water treatments to control corrosion, scale deposit, and microbiological growth in heating systems (boilers and condensate lines) and cooling systems (cooling towers). The goal was to provide a safer and more environmentally friendly water treatment program that exceeded industry standard performance criteria and at a cost equal to or less than conventional water treatments for heating and cooling systems. U.S. Army ERDC teamed with: the Garratt-Callahan Chemical Company; Trevino Mechanical, a small business mechanical sub-contactor; SurTech Corporation to perform the field demonstrations; and the Illinois State Water Survey for verification of field data.

The research team worked to develop, run field demonstrations on, and evaluate three formulations based on two chemicals previously recognized as Presidential Green Chemistry Challenge Winners: tetrakis hydroxymethyl phosphonium sulfate (THPS) for control of biological growth and polyaspartate for control of mineral scale. In addition, the formulations contained a filming soya amine to control corrosion in condensate pipelines. The team also used state-of-the-art automated equipment to minimize the hazards of chemical handling. The researchers applied the water treatment formulations and monitored their performance at three military installations for a period of two years. As a result, U.S. Army ERDC developed performance specifications for the use of green chemicals in water treatment for heating and cooling systems at public and private central energy plants.

Bunge North America

Enzymatic Degumming of Soybean Oil with PLA_1 Enzyme

Crude soybean oil contains between two and three percent phospholipids, commonly known as gums. Following centrifugation to remove most of the gums, the traditional, chemical refining process neutralizes the free fatty acids (FFA) with sodium hydroxide, converting them to sodium soaps. Sodium hydroxide also reacts with the neutral oil, however. An emulsion forms between the sodium soaps, phospholipids, and neutral oil. This heavy phase, called soapstock, is removed by centrifugation, reducing the yield.

Bunge North America has developed an efficient degumming process using the enzyme phospholipidase A_1 (PLA_1). PLA_1 selectively cleaves the SN-1 fatty acid from the phospholipid, yielding a *lyso*-phospholipid. This *lyso*-phospholipid is water-soluble and separates easily from the oil phase without emulsifying any of the neutral oil. The enzymatic reaction occurs at a buffered pH of roughly 4.5; thus, the neutral oil does not saponify and soaps do not form. The heavy phase containing the *lyso*-phospholipids can either be added to soybean meal as an energy source or possibly purified as a lecithin with new properties. The fatty acids generated from the enzymatic reaction are recovered along with the FFA originally present in the oil in a subsequent deodorization step. Bunge is currently using its PLA_1 process at a refinery in Indiana with a capacity of 750 metric tons per day. Compared to the chemical refining process, this one plant is reducing carbon dioxide emissions by over 30 metric tons daily.

Enzyme-Based Technology for Decontamination of Toxic Organophosphorus Compounds

U.S. Army, U.S. Army Edgewood Chemical Biological Center

The U.S. Army Edgewood Chemical Biological Center (ECBC) has developed and patented a technology designed to neutralize chemicals such as nerve agents and related pesticides. The technology consists of enzymes in a dry granular form that can be added to water or water-based application systems (e.g., fire-fighting foams and sprays; aircraft de-icing solutions). The enzymes quickly detoxify these hazardous chemicals before they can contaminate wider areas. Because the enzymes are catalytic, only small quantities are required, greatly reducing transportation and storage requirements. They are also nontoxic, noncorrosive, and environmentally safe. Initially intended to decontaminate equipment, facilities, and large areas, the enzymes could potentially be used in shower systems to decontaminate personnel and casualties. Genencor International, the premier manufacturer of industrial and specialty enzymes in the U.S., will utilize its state-of-the-art fermentation manufacturing technology to produce the enzymes. The enzymes will be sold to companies that produce and sell fire-fighting foams, sprays, and other potential matrices. These companies will formulate the enzymes into products for purchase by fire departments, HazMat groups, and other first-responders. Genencor is marketing the enzymes under the general name DEFENZ™.

Equinox® Technology: A Greener Approach to Microbiological Control

Lonza Inc.

Because of its high biocidal efficacy and low cost, chlorine is one of the most predominant biocides used by the U.S. papermaking industry, with an estimated 60 million pounds of chlorine biocides used annually. The widespread use of chlorine in papermaking creates highly toxic chlorinated byproducts, such as trihalomethanes and dioxin, which are broadly referred to as absorbable organic halogen (AOX).

Lonza has developed Equinox® as a nontoxic alternative to reduce the amount of chlorine biocides used by the papermaking industry. Equinox® is based on 5,5-dimethyl hydantoin, which interferes with the natural tendency of chlorine to random oxidations and in the process enhances chlorine's bactericidal properties. By markedly improving the stability of chlorine, Equinox® has shown that it can reduce chlorine use by over 90%. Because chlorine is reduced, the amount of AOX is similarly reduced by up to 95%. Since its commercial introduction in 2002, Equinox® has treated over 36 billion gallons of paper mill water, eliminating the use of an estimated 2.4 million pounds of chlorine and preventing the generation and release of over 128,000 pounds of AOX into the environment. Equinox® is now used in paper mills throughout the U.S. and Europe. Equinox® has other uses as well, but in the papermaking industry alone it has the potential to eliminate the formation of 3.3 million pounds per year of AOX pollutants. By reducing the amount of toxic AOX compounds released into the environment, Equinox® provides an environmentally safer alternative to the historically high use levels of chlorine biocides.

Formula 1™ Laundry System

Ecolab

Formula 1™ is a new, single-product system designed for on-premises commercial laundry operations. Its unique dispensing and packaging system (patent pending) produces a dilute detergent solution from a 100% active concentrate on-site. The concentrate is a non-aqueous, heterogeneous slurry that contains $C_{12\text{-}14}$ linear alcohol ethoxylates, two polymeric water conditioning agents, a proprietary enzyme support matrix, and sodium carbonate. This

single-product system can replace three or four current products with no loss in performance. The Formula 1™ technology delivers many benefits to the consumer and to the environment. These include fewer wash steps and, therefore, water savings, energy savings, and shorter cycle time; fewer different products required; reduced product waste; reduced plastic packaging; significantly lower shipping weight; and increased worker safety. Formula 1™ contains no caustic soda, chlorine, or nonylphenol ethoxylates. The marriage of product chemistry, dispenser, and packaging gives on-premise laundry operators a revolutionary new way to clean that is significantly more environmentally friendly.

The Formula 1™ Laundry System has been in commerce since January 2004; there are currently over 1,000 users in North America. If half of the over 50,000 potential user locations in North America used the Formula 1™ Laundry System, they would save 8.2 billion gallons of water, 47 million therms of natural gas, and 5 million pounds of plastic each year.

Dow AgroSciences and the U.S. Department of Agriculture (USDA) Agricultural Research Service

GF-120™ NF Naturalyte™ Fruit Fly Bait

Tephritid fruit flies are important quarantine pests that can devastate fruit and vegetable production and limit movement of produce. Previously, a wide range of insecticide baits had been used to control these fruit flies; the results were often inconsistent, however, due to a lack of understanding of fly attractiveness, feeding biology, and quality control. The active ingredients in these baits were organophosphates. The organophosphates were generally used at rates as high as 0.5 to 1.0 pounds per acre to overcome their inadequacy. The International Atomic Energy Association and others had developed irradiated sterile insect techniques (SIT), but this tool works best with low insect populations. An improved bait system using an environmentally sound active ingredient was needed (1) to reduce population levels so that sterile insect and other integrated pest management solutions could be used and (2) to protect fly-free regions such as the U.S.

Dow AgroSciences had already developed spinosad, a new reduced-risk insecticide active ingredient that was successful in spray applications. Dow AgroSciences combined its project management, industrial manufacturing, quality control, and formulation science skills with USDA's knowledge of fruit fly biology and behavior. Together, Dow AgroSciences and USDA developed a superior bait technology, GF-120™ NF, to protect fruits and vegetables from the Mediterranean fruit fly and similar pests. This is the first bait plus active ingredient (spinosad) that contains only organically acceptable components; it is so attractive to flies that farmers need less than 0.003 pounds of spinosad per acre. Between 2000 and 2004, farmers used GF-120™ NF to treat over six million acres. GF-120™ NF is now the fruit fly bait of choice in much of the world.

Pfizer Global Research and Development

Green Chemistry in the Redesign of the Celecoxib Process

Pfizer redesigned the celecoxib manufacturing process with green chemistry objectives as some of the project's primary goals, resulting in dramatic environmental and worker safety improvements in the manufacture of the active ingredient in the medicine, Celebrex®. These improvements followed the elucidation of two unprecedented reaction mechanisms responsible for the formation of isomeric impurities whose presence required a subsequent recrystallization with its concomitant loss of yield and expense for resources. Celecoxib made by Pfizer's new process is pure enough to permit final isolation directly from the reaction mix-

ture; such isolations are very rare in the pharmaceutical industry. Pfizer's new mechanistic understanding increases the process efficiency significantly with respect to raw materials, solvents, energy, and waste.

The environmental and safety improvements are also significant. In total, Pfizer has eliminated 5,200 metric tons per year of organic solvents. Pfizer has also completely removed tetrahydrofuran and 35% hydrochloric acid (212 metric tons/yr). Pfizer has partially replaced organic solvent washes during isolation by water. In addition, raw materials have been reduced by over 150 metric tons per year. By eliminating the recrystallization and using the heats of reaction and other temperature parameters judiciously, Pfizer is saving more than 4 billion BTUs per year. Pfizer has also improved worker safety by reducing the number of unit operations required per batch and improving the process payload (product produced/reactor volume), resulting in the need for fewer batches to fulfill demand.

Green Chemistry in the Redesign of the Pregabalin Process

Pfizer Global Research and Development

Application of green chemistry principles to the synthesis of Pregabalin, the active ingredient in the medicine Lyrica®, has delivered dramatic environmental and worker safety improvements concomitant with significantly enhanced process efficiency. Lyrica® is used to treat patients with neuropathic pain, epilepsy, and generalized anxiety disorder. It was approved in Europe in 2004 and currently is under review by the U.S. Food and Drug Administration.

Development of high-throughput enzyme screening technology, elucidation of product inhibition in biocatalysis, and the application of medium- and large-bioreactor engineering to enhance catalytic efficiency has resulted in a new catalytic and enantioselective process with all four reaction steps conducted in water. At the projected peak of annual production, this new process will eliminate 11 million gallons of organic solvents each year, including tetrahydrofuran, ethanol, methanol, and isopropanol. This process is also projected to eliminate 1,600 metric tons per year of (S)-mandelic acid waste associated with classic chemical resolution and 500 metric tons per year of Raney nickel. Pfizer is recycling the undesired enantiomer using successful product partitioning, epimerization, and subsequent resubmission to a biocatalytic transformation. This recycling, combined with overall process improvements, will save over 800 metric tons of starting material per year. Using a food-grade enzyme, Pfizer's biocatalytic route has improved process throughput, increased process yield by over 50%, significantly reduced metal catalyst requirements, and delivered a highly efficient, environmentally responsible process for manufacturing the pharmaceutical Pregabalin.

A Green Process for the Synthesis of Quinapril Hydrochloride

Pfizer Global Research and Development

Pfizer emphasized green chemistry objectives in redesigning its process to manufacture quinapril hydrochloride (HCl), the active ingredient in the important cardiovascular medicine, Accupril™. The resulting process employs more efficient chemical transformations with dramatic environmental and worker safety improvements. Process yields have increased by 30%; process throughput has quadrupled. The process has eliminated methylene chloride and dicyclohexylcarbodiimide. Operations that caused loss of yield due to the intermolecular cyclization of quinapril HCl have been minimized. Overall, Pfizer's improvements have eliminated the isolation of one intermediate, two drying steps, and a hydrogenation step.

The environmental and safety improvements are dramatic. Pfizer's process has eliminated the use of approximately 30 metric tons per year of dicyclohexylcarbodiimide and the subsequent generation of 30 metric tons per year of solid dicyclohexylurea waste. The process has also eliminated the use of approximately 1,100 metric tons per year of methylene chloride. The volume of solvent has been reduced dramatically; aqueous and organic wastes have been reduced by 90%. Pfizer's process reduces raw material, water, and energy use significantly. The new process was readily transferred to Pfizer's manufacturing facilities.

Eli Lilly and Company

An Improved Approach to the Preparation of Duloxetine and Atomoxetine

Eli Lilly has developed and demonstrated new, more efficient, synthetic routes for two of its 3-aryloxy-3-arylpropylamine pharmaceutical products. Duloxetine hydrochloride is the active ingredient in the product Cymbalta®, used to treat depression. Atomoxetine hydrochloride is the active ingredient in the product Strattera®, used to treat attention deficit/hyperactivity disorder. Each of these improved syntheses avoids using an N-methyl protecting group and produces the drug substance in a direct fashion using a monomethylamine intermediate. Eliminating the traditional protecting group to produce these drug substances reduces the combined environmental footprint by an average of 44%, as measured by the weight of materials used to produce one kilogram of product (E-factor). These combined improvements reduce the use of (1) solvents by an average of 27%, (2) water by 58%, and (3) raw materials by 78%. At peak production volumes for both drugs, estimated in the tens to hundreds of metric tons per year, these reductions could provide expected savings of 2.5 to 25.5 million pounds of raw materials per year. Further, manufacturers must often incinerate pharmaceutical aqueous waste streams to destroy the biological activity associated with their trace components, necessitating additional fuel consumption. Water reductions from the new syntheses alone should result in secondary fuel savings of 1.5 to 14.5 million cubic feet per year.

The new synthesis for duloxetine was demonstrated on a pilot plant scale in 2002; Eli Lilly is now developing its pilot plant process into an improved commercial process. The new synthesis for atomoxetine is currently being used at an Eli Lilly production facility.

Rohm and Haas Company

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Invention and Commercialization of Environmentally Friendly Acrylic Thermosets

Thermosetting binders are used ubiquitously in composite building and construction materials such as fiberglass insulation, air filters, and engineered wood products. The most common thermosetting resins are formaldehyde-based resins, which require expensive abatement equipment as well as special handling and transport.

TSET™, the Rohm and Haas acrylic thermoset formulation, is a formaldehyde-free, curable, aqueous solution of poly(acrylic acid), triethanolamine, and sodium hypophosphite. Although hypophosphite catalysis of esterification was used earlier in permanent press fabric applications, TSET™ chemistry is a significant departure from these early chemistries. TSET™ is novel: from the very beginning, Rohm and Haas's objective was to synthesize an alkyl phosphinic acid polymer backbone. Rohm and Haas obtained higher degrees of crosslinking by combining steps that had never before been combined. These steps include: the dual use of the esterification catalyst as a chain transfer agent in synthesizing the polymer backbone; the mobility of the polyol within the curing resin (which becomes transport-limited at high degrees of cure); increased reactivity of primary alcohols such as triethanolamine

(further activated by the β-tertiary amine) relative to the secondary alcohols of cellulosics; and the higher cure temperatures available in heat-resistant noncellulosic substrates.

By combining these steps, Rohm and Haas has created a class of acrylic thermosets that are an ideal green chemistry alternative to the industrially ubiquitous phenol-formaldehyde resins. With TSET™, the only byproduct of cure is water; there are no formaldehyde wastes, emissions, or exposures. Acrylic thermosets are nonreactive, nonflammable, recyclable, and benign at ambient conditions, simplifying handling, transport, storage, application, and cleanup. TSET™ has been in commerce since 2002; several leading building products companies are currently using it. By the end of 2004, TSET™ will have replaced approximately 100 million pounds of phenol-formaldehyde resins; by the end of 2010, TSET™ is poised to eliminate over 400 million pounds of formaldehyde-based resins.

Irbesartan (Avapro®) Greenness Project

Bristol-Myers Squibb Company

Irbesartan, which is chemically synthesized, is an angiotensin II receptor antagonist used to treat hypertension and renal disease in Type 2 diabetic patients. Although clinical trials had demonstrated the medical benefits of Irbesartan, the original synthetic process was difficult to manage from an environmental, health, and safety (EHS) perspective. The primary concerns included a potential runaway bromination reaction, severe skin and eye irritation from an intermediate product, and negative environmental effects of several organic solvents. Previously, Bristol-Myers Squibb (BMS) had mitigated some of the negative EHS impacts of the original synthesis, but the bromination in the first synthetic step remained a concern. This bromination created a nonbiodegradable byproduct that required incineration and, thereby, created a significant waste disposal problem.

To address that problem and further minimize EHS impacts, BMS has modified the bromination and crystallization processes it uses in the synthesis and modified the recrystallization process for the active pharmaceutical ingredient. These modifications have increased yield, saved energy, reduced the use of hazardous materials, reduced waste, and improved workplace health and safety. Based on projected five-year production of Irbesartan, BMS expects to save over 680 metric tons of solid chemicals, over 40 million liters of solvents, and 4.4 million liters of water.

Metal-, Phenol-, and Ash-Free Antiwear Hydraulic Additive: Providing Performance Only Achieved Previously with Zinc-Containing Additives

Afton Chemical Corporation

The use of heavy metals in lubricants presents environmental concerns, due primarily to zinc contamination coming from hydraulic oils. The global antiwear hydraulic lubricant market is approximately 980 million gallons. Roughly 95% of this global market is based on lubricants containing zinc dialkyl dithiophosphate (ZDDP) as the antiwear additive. Only approximately 5% of this market is based on lubricants containing the less toxic, environmentally friendly, ashless, antiwear additive technology. Of the lubricants using ashless additive technology, the majority are based on conventional mineral oils with, globally, only approximately 3% based on biodegradable fluids. The slow growth in the use of antiwear hydraulic fluids based on ashless technology is due, in part, to problems in the field, where performance equivalent to fluids based on ZDDPs had not been achieved previously. This is especially true for biodegradable hydraulic fluids.

Afton has identified an additive technology that is not only ashless, but also phenol-free. When used in mineral oils, Afton's product performs as well as, if not better than, ZDDP-based fluids. This is the first ashless, mineral oil-based technology to be tested against new, more severe requirements and approved by original equipment manufacturers (OEMs). Also, this ashless additive technology, along with boosters in biodegradable oils, is the first to be approved against new specifications designed for environmentally friendly fluids. Afton's HiTEC 543 contains an amine salt of a sulfurized phosphite that provides antiwear protection over a wide temperature range in dry and wet conditions, a thiadiazole corrosion inhibitor that provides compatability with yellow metals, a three-way phenol-free antioxidant system, and a dispersant. Afton received its first commercial order for this new product in April 2003.

U.S. Army Engineer Research and Development Center

Mold Prevention through the Novel Use of In Situ Electrochemistry to Eliminate Water Seepage in Concrete Structures

Electro-Osmotic Pulse (EOP) technology eliminates water seepage through concrete by the novel use of in situ electrochemistry. It prevents mold growth and eliminates the use of harmful volatile organic compounds (VOCs), such as from petroleum-based coatings used for waterproofing. EOP has led to a revolution in waterproofing technology through the application of electro-osmosis (forced movement of an aqueous solution containing a net electric charge due to an external electric field) to control water transport through below-grade concrete structures such as foundations, basements, and tunnels. Unlike many conventional waterproofing methods, EOP reaction chemistry is inherently nontoxic and releases no VOCs. EOP improves air quality in below-grade spaces by reducing the interior concrete surface moisture below 55% relative humidity, such that mold cannot grow. Further, it costs about 40% less to install than traditional waterproofing methods.

EOP combines the novel application of an asymmetric, dual-polarity pulse with long-life ceramic-coated electrode materials. The anodes are inserted into the concrete wall on the interior of the structure; cathodes are placed either in the soil directly outside the structure or in the structure itself, near the exterior. A direct current (DC) power supply produces a low-voltage, dual-polarity pulse. This sets up an electric field between the electrodes, creating an electro-osmotic pressure sufficient to overcome the external hydraulic pressure and to reverse the flow of water seepage, actually causing moisture to move toward the outside of the basement walls. During 2003 and 2004, the Army has installed EOP systems in the basements of 382 family houses on military bases.

Rhodia Inc.

Natural, Guar-based Chemistry Reduces Drift and Increases Retention of Crop Sprays

Supported by patented research, peer-reviewed publications, and market acceptance, Rhodia's natural, guar-based chemistry is an innovative, effective, and environmentally sound alternative that allows crop protection sprays to be applied more precisely to their targeted areas, remain on targeted crops longer, and minimize waste and drift associated with traditional application aids. Rhodia's product, AgRHO™DR 2000, is a natural, plant-based polymer; it contains new guar derivatives developed by Rhodia specifically for the market needs of this product. The guar base of AgRHO™DR 2000 eliminates the need for solvent-based formulations and is fully biodegradable, compatible with other spray ingredients, and safe for use and handling. Farmers now apply AgRHO™DR 2000 to more than 16 million

acres of soybeans in the United States. This represents nearly 15 percent of the total sprayable soybean acres, with significant potential for further market growth. Through its ongoing research and pending patent applications, Rhodia expects that AgRHO™DR 2000 technology could be applied to other crops covering more than triple the current sprayable acreage within the next five years.

A Novel Cleaning System Using Less Toxic, Safer Chemicals

JohnsonDiversey, Inc.

The nominated process cleans and sanitizes the polyethersulfone ultrafiltration (UF) membranes used in the dairy industry. The current commercially available cleaning process has been a three-cycle alkaline/acid/chlorinated alkaline system. Conventional alkaline cleaners typically consist of strong alkaline solutions of sodium and potassium hydroxide with a small amount of nonionic surfactants. The acid cleaners typically consist of high levels of phosphoric and nitric acids. The current sanitizer contains sodium hypochlorite at 200 ppm in solution. The current procedure also requires large volumes of water to rinse and neutralize the membrane.

JohnsonDiversey's technology uses peroxygen chemistry to develop more efficient cleaners and germicides with safer and more environmentally preferable chemicals. This new technology consists of an aqueous solution of hydrogen peroxide, phosphorus-based acid, phosphonate, and an anionic surfactant. This new technology yields safer cleaners by formulating them at a more neutral pH. Hydrogen peroxide provides a good bleach alternative that sanitizes more gently than chlorinated alkaline sanitizers. Overall, this technology cleans and sanitizes effectively using less toxic chemicals than current alternatives; it is also safer with respect to human health and environment. This technology has a great economic impact by performing the cleaning and sanitization at lower temperatures. JohnsonDiversey's cost analysis shows that it saves energy by up to 43%, reduces plant downtime by up to 18%, and decreases water use by up to 33%. This technology also decreases wastewater generation and improves the long-term stability of the UF membrane. During pilot plant studies, JohnsonDiversey's peroxygen products demonstrated superior performance versus the current competitive products. Compared to a typical system, JohnsonDiversey's new system would save $700,000 per year, on average, in a dairy plant.

Oxygen-Enhanced Combustion for NO_x Control

Praxair, Inc.

The abundance of coal and forecasts of high costs for alternative fossil fuels, such as natural gas, suggest that the use of coal to generate power will continue for some time. Coal-fired utilities are also, however, major emitters of pollutants, such as nitrogen oxides (NO_x). Praxair's Oxygen-Enhanced Combustion (OEC) technology for NO_x control is a unique combination of reduced NO_x emissions and enhanced combustion. In OEC, a small portion of the combustion air in a staged combustion system is replaced with oxygen, increasing the local temperature under fuel-rich conditions. These higher flame temperatures enhance reactions, converting NO_x to N_2 in the flame zone. In various trials from laboratory-scale furnaces to a nominal 125-megawatt power plant, oxygen-enhanced staged combustion reduced NO_x emissions by as much as 60% without the added operational problems commonly associated with staged combustion. An OEC system operated for most of the 2003 and 2004 ozone seasons at the Northwest Utilities 125-megawatt Mt. Tom Station, achieving NO_x emissions of less than 0.15 pounds per million Btu.

By minimizing NO_x formation in the combustion zone, OEC reduces or eliminates the need for post-combustion cleanup technologies that require ammonia, such as selective catalytic reduction (SCR). By minimizing the need for SCR systems, Praxair's OEC technology also minimizes the production, transportation, and storage of ammonia. Because ammonia is hazardous, minimizing its use increases the safety of both plant personnel and the public. Replacing ammonia with oxygen also reduces atmospheric emissions of ammonia, thereby reducing the associated impacts on respiratory health. Further, because ammonia production requires natural gas, minimizing ammonia also helps preserve this important natural resource. Based on some broad assumptions for 600 coal-fired plants in 22 states, OEC technology could eliminate the use of over 500 million pounds of ammonia per year and atmospheric emissions of over 30 million pounds of ammonia in flue gas per year.

Pacific Northwest National Laboratory

Self-Assembled Monolayers on Mesoporous Silica Technology: A Green Alternative Synthesis of a Novel Adsorbent for Mercury Source Reduction

Until now, there had been no effective technology for removing mercury from groundwater down to 2 parts per billion, as required by the maximum contamination limit for drinking water set by the U.S. Food and Drug Administration (FDA) and the U.S. EPA. Thiol self-assembled monolayers on mesoporous silica (thiol-SAMMS) can absorb mercury from low-volume waste streams, but the original synthesis of thiol-SAMMS created its own environmental problems. SAMMS used to be functionalized in toluene. The resulting waste stream consisted of water, methanol, toluene and traces of mercaptan. It was impractical to separate this mixture; therefore, the mixture was usually disposed of as hazardous waste.

In response to this problem, scientists at the Pacific Northwest National Laboratory (PNNL) have created and patented a green chemical process to synthesize SAMMS more efficiently. PNNL scientists use supercritical carbon dioxide ($scCO_2$), a green solvent that allows complete silane deposition and yields a higher quality product. With this new process, PNNL can conduct SAMMS deposition faster and more efficiently. A reaction that normally took several hours in refluxing toluene (110 °C) is complete in only a few minutes in $scCO_2$; the reaction now produces a defect-free silane monolayer with no residual silane left in solution. The only byproduct is the alcohol from the hydrolysis of the alkoxysilane. The CO_2 and the alcohol are readily separated; each is then captured and recycled. The SAMMS emerges from the reactor clean, dry, and ready to use. This new synthesis produces higher-quality SAMMS at one-third of the original cost, with virtually no waste. PNNL is working with an oil and gas filtration equipment company to conduct pilot-scale tests of mercury removal from water produced during off-shore oil drilling. PNNL expects to commercialize the SAMMS technology through licensing agreements within the next two years.

Pfizer Global Research and Development

Separation of Racemic Tetralone

Sertraline is the active ingredient in Zoloft®, used to treat depression. Pfizer has emphasized green chemistry objectives in the separation of racemic tetralone, the starting material for the Sertraline process. Consequently, the Sertraline process is more environmentally friendly, solvent use is more efficient, process atom economy is better, waste streams are reduced, and worker safety is enhanced.

Pfizer uses a relatively new technology, multicolumn chromatography (MCC), to separate its current racemic raw material, 4(*R,S*)-tetralone. Pfizer has also demonstrated that the pharmaceutically undesired enantiomer, 4*R*-tetralone, which constitutes 50% of the process

input, can be racemized, reprocessed, and separated as 4*S*-tetralone by MCC. Thus, the racemic starting material can be used in the downstream processing more efficiently, greatly reducing the 4*R*-tetralone waste stream, which is toxic to aquatic organisms. Other benefits of starting with 4*S*-tetralone include: more than doubling the overall yield, reducing by one-half the volumes of ethanol (saving 800,000 gallons per year), monomethylamine (saving 65.2 metric tons per year), and catalyst (saving 4.1 metric tons per year), eliminating a classical resolution step (saving 160 metric tons of D-(-)-mandelic acid per year), eliminating the undesired Sertraline mandelate waste stream (nearly 500 metric tons per year), eliminating 50% caustic (saving 150 metric tons per year) in the process and the subsequent waste steams associated with the mandelate salt break, and eliminating a methanol recrystallization step (saving 600,000 gallons per year). The new process could potentially reduce the raw material requirement of 4(*R,S*)-tetralone by 180 metric tons annually. In summary, Pfizer has dramatically improved its process by using raw materials and energy more efficiently and by reducing and eliminating waste streams. Pfizer is currently using MCC separation as part of its synthesis of Sertraline and plans to begin recycling 4*R*-tetralone as soon as it receives approval from the U.S. Food and Drug Administration (FDA).

Crane & Company, Inc.

Substitution with Carbon Dioxide Eliminates A Major Use of Sulfuric Acid

Crane & Company, Inc. produces specialty papers with highly technical specifications, mostly from cotton and other natural and synthetic fibers. Company products include 100% cotton social stationery, commercial printing papers, reprographic papers, synthetic fiber nonwovens, and currency and security papers. To reuse preconsumer products that either do not meet specifications or have been reclaimed from finishing operations (referred to as "broke"), Crane must process the paper into a slurry form. Because many of its papers have a high degree of permanent wet strength, Crane must use an alkaline substance and high temperatures to make the slurries. In its traditional papermaking method, Crane then adjusted the pH of the slurried broke with sulfuric acid before adding the broke to the papermaking stock.

Crane's Research and Development Department initiated a toxics use reduction project aimed at replacing the sulfuric acid with a less toxic chemical. The research was successful, and Crane is now using its improved process to repulp off-specification papers. The company has replaced sulfuric acid with an innovative liquid carbon dioxide system. It has also reduced the amount of sodium hypochlorite it uses by specifying cleaner raw materials. It controls the temperature and pH of the process more closely as well. Crane reduced its use of sulfuric acid by approximately 697,000 pounds and sodium hypochlorite by 576,000 pounds between 1999 and 2000, a combined reduction of about 46%. Overall, these improvements have reduced the costs of pulp production by 3%.

Emerson & Cuming

Tin- and Copper-Compatible Conductive Adhesive for Lead-Free Electronic Circuit Assembly

Tin/lead eutectic solder is currently the most common product used to attach electronic components on circuit boards. Lead, however, is a known toxin. Because lead can leach into the environment, Europe recently passed legislation mandating recycling of consumer electronics containing lead by 2006. This has prompted electronic circuit assemblers to seek an alternative attachment product. Conductive adhesives have also been used for years, but their use has been limited to attaching components terminated with palladium/silver, silver, and

gold (noble metals) on both ceramic hybrid boards and flexible polyester circuits. Previous conductive adhesives were not stable on low-cost tin- and tin/lead-terminated components.

Emerson & Cuming's novel and patented chemistry allows it to achieve stable contact resistance and stable adhesion under damp-heat and high-temperature aging conditions with tin, tin/lead, and copper finishes. Compatibility with these finishes was not possible in the past. This compatibility was achieved by preventing galvanic corrosion on these less expensive, non-noble metal finishes. The incorporation of a corrosion inhibitor and a low-melting alloy into the adhesive formulation prevents oxidation on these finishes under extreme environmental conditions and leads to stable performance over time. About 30 electronic circuit assembly companies currently purchase the Emerson & Cuming adhesive. Over the last three years, this product has effectively eliminated the use of 2.3 metric tons of tin/lead eutectic solder; in five years, it should replace 100 metric tons of solder a year.

Highland Supply Corporation

Using Chemistry and Engineering Technology to Reduce Volatile Organic Compound (VOC) Emissions and Eliminate Hazardous Process Waste in the Printing Industry

Highland Supply Corporation (HSC) manufactures decorative packaging for the floral industry using flexographic and rotogravure printing presses as part of its production processes. Until 1988, HSC used only solvent-based inks that contained 50% or more VOCs by weight. During 1988, however, the executive management of HSC accelerated its efforts to develop a viable water-based ink system and issued a corporate policy directing the reduction of VOC emissions and hazardous air pollutants (HAPs), which are harmful to human health and the environment. HSC researched installing air pollution control equipment, but chose to replace its solvent-based ink system with a cleaner water-based system. Commercially available water-based inks contained approximately 20% VOCs by weight, however, and had lower print quality. HSC elected to develop its own water-based ink system to reduce VOC content further and to increase print quality.

Within the last five years, HSC has refined its technology: now its water-based ink system contains less than 0.70% VOCs by weight. HSC continues aggressive research to lower this percentage. By switching from solvent-based to water-based printing inks in all of its facilities, HSC has reduced VOC emissions and eliminated HAPs and hazardous process waste. Water-based inks also cost about 40% less than solvent-based inks to print the same area. Its Highland, Illinois plant released 198.5 tons of VOCs in 1989, but releases less than two tons per year today. In 1989, HSC spent over $100,000 to dispose of hazardous process waste from that plant; today there are no such wastes, so it spends nothing. The company now recycles all of its water-based inks by reformulating excess inks into useful ones. HSC thoroughly reviews product information and controls all items that enter its facilities based on strict environmental, health, and safety criteria.

The Dow Chemical Company

VORANOL VORACTIV* Polyols for Flexible Polyurethane Foams*

Polyurethane is the material of choice for cushioning materials in automotive seating, mattresses, and furniture. Its performance is unrivaled by competitive materials. Global production of flexible polyurethane foam is over 2 million metric tons (4.4 billion pounds) each year. Foam producers blend a polyether polyol, an isocyanate, water, a surfactant, and a fugi-

tive tertiary amine catalyst together in a mix-head to form a reacting mixture that generates the foam. Most foams use either bis(dimethylaminoethyl)ether or triethylenediamine as the fugitive amine catalyst. These amines are undesirable for a number of reasons. First, they may be hazardous to the skin or eyes and, hence, require careful handling. Second, workers could be exposed to them during handling and processing of polyurethane chemicals. And third, they are released slowly from the foam during use and, hence, can provide odor and degrade indoor air quality.

VORANOL VORACTIV polyols embed the amine catalyst covalently into the polyol structure, eliminating amine catalyst emissions both during the foaming process and from the finished product. This technology results in performance that exceeds current industry standards, provides greater yields, and makes smoother, more consistent foam block shapes, reducing waste from trimming. Dow Chemical has been selling its VORANOL VORACTIV polyols in the U.S. since 2002; in 2004, its global sales exceeded $25 million.

Wash 'n Walk™ Floor Care System

Ecolab

Ecolab has introduced a revolutionary floor care system that removes kitchen grease from foodservice floors. This system uses a novel no-rinse procedure, leaving enzymes on the floor to digest and break down the grease deposits that accumulate over time. Formulated to clean kitchen floors, Wash 'n Walk™ incorporates a patent-pending blend of surfactants, water conditioners (including Trilon M), lipase, and spore-forming, fatty-acid-degrading microbes that break down the hard-to-degrade fatty acid components of floor grease. This chemistry provides immediate cleaning, comparable to industrial-strength floor cleaners, as well as long-term deep cleaning by removing imbedded organics left in pores, cracks, corners, and crevices. Its key benefits include: (1) clean floors; (2) clean grout, reducing the potential for growth of odor-producing bacteria; (3) a significant increase in the coefficient of friction (i.e., increased slip resistance) of kitchen quarry tile floors, reducing worker accidents. In addition to institutional and industrial floors, the environmentally friendly formula of Wash 'n Walk™ cleans flooring and grout in household kitchens.

Ecolab introduced Wash 'n Walk™ in January 2004; by November 1, 2004, over 30,000 customer sites were already using this product. Ecolab has introduced this product in Canada and will expand to global sales in 2005. Globally, Ecolab estimates that there are over one million potential institutional and industrial users for this technology.

WOODSTALK™ Strawboard

Dow BioProducts Ltd.

Dow Chemical and Dow BioProducts have implemented a revolutionary process for manufacturing fiberboards using 100% waste straw as the fiber raw material. After harvesting wheat grain, the remaining stalks are typically burned in the fields or plowed into the topsoil. Historically, field burning has been the preferred method of disposal; however, CO and CO_2 emissions from open-air field burning can be significant, especially in the wheat belt areas of Kansas, Iowa, and Manitoba. Smoke from these burning fields decreases visibility and poses health concerns.

In the WOODSTALK™ process, Dow BioProducts takes straw that would have been burned as waste in the fields and manufactures it into fiberboard composite panels. WOODSTALK™ fiberboard competes head-to-head with traditional fiberboard made from wood particles (i.e., particleboard, medium-density fiberboard, and plywood). WOODSTALK™ fiberboard uses polymeric methylene diphenyl diisocyanate (pMDI) instead of formaldehyde-based resins and, therefore, emits substantially less aldehyde than do traditional

wood-based composite panels. Overall, the WOODSTALK™ process uses waste from a renewable resource, reduces CO and CO_2 emissions associated with the wheat harvest, and substantially reduces the aldehyde emissions from wood-based composite panels that are a growing concern with indoor air quality. Each year, Dow BioProducts uses over 255 million pounds of waste straw that would have generated 175,000 tons of CO_2 had it been burned. Dow BioProducts does this today while being competitive with traditional indoor wood-based fiberboard products.

Rust-Oleum Corporation

Zero-VOC, Zero-HAP, No-Odor Industrial Coatings

Sierra Performance Coatings by Rust-Oleum have eliminated the traditional use of solvents to manufacture and apply industrial coatings. Through a number of patented and trade secret processes, Sierra has developed a way to combine uniquely designed resins and resin systems into a line of industrial coatings that has zero volatile organic compounds (VOCs), zero hazardous air pollutants (HAPs), and no odor. As a commercial product line, these coatings reduce VOC and HAP emissions, which translates into broad-based benefits for end-users (paint applicators, workers, and building occupants) and the environment.

Sierra Performance products range from single-component (1K) acrylic and acrylic-urethanes to two-component (2K) epoxies and acrylic-epoxies. The 1K compositions are unique resin systems that achieve application and finished properties by manipulating particle size, molecular weight distribution, and chemical composition without solvents. These compositions, combined with other traditional paint and coatings raw materials, activate upon the evaporation of water. The principal component of the 2K products is a proprietary, advanced-molecular-weight epoxy polymer with a unique molecular weight distribution that produces high-performance coatings that cure quickly without requiring solvents to reduce viscosity or aid coalescence.

Rust-Oleum's development of alternative processes and material compositions has made possible new designs for waterborne resins, coatings, and paint products that meet the demanding performance requirements of institutions and industry, without any airborne environmental emissions or worker safety issues. Since Rust-Oleum introduced the Sierra Performance product line in 2004, the company has sold 90,500 gallons of coatings. The switch to Sierra coatings has reduced VOC emissions, conservatively, by 200,000 pounds.

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Award winners are indicated with *.

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