The Presidential Green Chemistry Challenge Awards Program

Summary of 2006 Award Entries and Recipients

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Introduction

The Presidential Green Chemistry Challenge Awards Program is a competitive incentive to create environmentally preferable chemicals and chemical processes. Each year the United States Environmental Protection Agency (U.S. EPA) celebrates innovative, award-winning technologies developed by high-quality nominees. The year 2006 marks the eleventh year of the program.

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 the hazards associated with designing, manufacturing, and using chemicals.

Through a voluntary U.S. 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.

An independent panel of technical experts convened by the American Chemical Society judged the entries for the 2006 awards. The judges used criteria that included health and environmental benefits, scientific innovation, and industrial applicability. Five of the more than 90 entries were nationally recognized on June 26, 2006, at an awards ceremony in Washington, D.C. This compilation summarizes the entries submitted for the 2006 awards. 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 U.S. 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 2006 Presidential Green Chemistry Challenge Awards. U.S. EPA edited the descriptions for space, stylistic consistency, and clarity, but they were not written or officially endorsed by the Agency. The summaries are intended only to highlight a fraction of the information contained in the 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 U.S. EPA.

Academic Award

Biobased Propylene Glycol and Monomers from Natural Glycerin

Professor Galen J. Suppes, Department of Chemical Engineering, University of Missouri-Columbia

Innovation and Benefits

Waste glycerin from biodiesel fuel production could flood the current market for glycerin and negatively impact the economic viability of biodiesel. However, if a high-value use existed for the glycerin byproduct, production costs would be lower and biodiesel could compete as a viable alternative fuel. Professor Suppes found such a use for waste glycerin by developing an inexpensive method to convert glycerin into propylene glycol, which can replace ethylene glycol in automotive antifreeze.

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

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

Professor Suppes's system couples a new copper-chromite catalyst with a reactive distillation. This system has a number of advantages over previous systems that perform this conversion. The new catalyst system uses a lower temperature and lower pressure than do previous systems (220 °C versus 260 °C and <10 bar versus >150 bar), converts glycerin to propylene glycol more efficiently, and produces less byproduct than do similar catalysts. Propylene glycol made from glycerin by Professor Suppes's method is also significantly cheaper than propylene glycol made from petroleum.

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

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

Small Business Award

Arkon Consultants and NuPro Technologies, Inc.

Environmentally Safe Solvents and Reclamation in the Flexographic Printing Industry

Innovation and Benefits

Flexographic printing is used in a wide array of printing, but uses millions of gallons of solvent. Arkon and NuPro developed a safer chemical processing system that eliminates hazardous solvents, reduces explosion potential and emissions, and increases worker safety in the flexographic printing industry.

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

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

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

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

Greener Synthetic Pathways Award

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

Merck & Co., Inc.

Innovation and Benefits

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

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

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

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

Greener Reaction Conditions Award

Codexis, Inc.

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

Innovation and Benefits

Using cutting-edge genetic methods, Codexis has developed an enzyme-based process that greatly improved the manufacture of the key building block for Lipitor®, one of the world's best-selling drugs that lowers cholesterol by blocking its synthesis in the liver. The new enzymatic process is dramatically faster and more efficient than the processes that have been in use. The result is increased yield and improved worker safety. At the same time, the new process has reduced waste, the use of solvents, and the need for purification equipment.

Atorvastatin calcium is the active ingredient of Lipitor®, a drug that lowers cholesterol by blocking its synthesis in the liver. Lipitor® is the first drug in the world with annual sales exceeding $10 billion. The key chiral building block in the synthesis of atorvastatin is ethyl (*R*)-4-cyano-3-hydroxybutyrate, known as hydroxynitrile (HN). Annual demand for HN is estimated to be about 200 metric tons. Traditional commercial processes for HN require a resolution step with 50 percent maximum yield or syntheses from chiral pool precursors; they also require hydrogen bromide to generate a bromohydrin for cyanation. All previous commercial HN processes ultimately substitute cyanide for halide under heated alkaline conditions, forming extensive byproducts. They require a difficult high-vacuum fractional distillation to purify the final product, which decreases the yield even further.

Codexis designed a green HN process around the exquisite selectivity of enzymes and their ability to catalyze reactions under mild, neutral conditions to yield high-quality products. Codexis developed each of three enzymes using state-of-the-art, recombination-based, directed evolution technologies to provide the activity, selectivity, and stability required for a practical and economic process. The evolved enzymes are so active and stable that Codexis can recover high-quality product by extracting the reaction mixture. In the first step, two evolved enzymes catalyze the enantioselective reduction of a prochiral chloroketone (ethyl 4-chloroacetoacetate) by glucose to form an enantiopure chlorohydrin. In the second step, a third evolved enzyme catalyzes the novel biocatalytic cyanation of the chlorohydrin to the cyanohydrin under neutral conditions (aqueous, pH ~7, 25–40 °C, atmospheric pressure). On a biocatalyst basis, the evolved enzymes have improved the volumetric productivity of the reduction reaction by approximately 100-fold and that of the cyanation reaction by approximately 4,000-fold.

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

Designing Greener Chemicals Award

Greenlist™ Process to Reformulate Consumer Products

S.C. Johnson & Son, Inc.

Innovation and Benefits

SC Johnson developed Greenlist™, a system that rates the environmental and health effects of the ingredients in its products. SC Johnson is now using Greenlist™ to reformulate many of its products. For example, "Greenlisting" Saran Wrap® resulted in converting it to low-density polyethylene, eliminating the use of nearly 4 million pounds of polyvinylidene chloride (PVDC) annually.

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

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

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

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

Entries from Academia

Bioinspired 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. Vinylbenzyl thymine (VBT), a styrene derivative, offers unique polyfunctionality for polymerization, derivatization, hydrogen bonding, π-stacking, and photocrosslinking. The applications of thymine-based photopolymers are benign, atom-economical, energy-efficient, water-soluble, and processable under ambient conditions. VBT prototypes combine these features, demonstrating 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. Antimicrobial surfaces made with VBT copolymers can be substituted 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 14 collaborations and 36 student projects; they have served approximately 27 courses and 70 outreach events. This technology has been awarded four patents; three more patents are pending.

Bromine-Free, TEMPO-Based Catalyst System for the Oxidation of Alcohols

Dr. Robert L. Augustine, Center for Applied Catalysis, Seton Hall University

The selective oxidation of alcohols to the corresponding carbonyls is one of the more important transformations in synthetic organic chemistry. A large number of oxidants have been reported in the literature, but most of them are based on transition metal oxides such as those of chromium and manganese. Because most of these oxidants and their reduced compounds are toxic, their use creates serious problems in handling and disposal, especially in large-scale, commercial applications. A common alternative is the Anelli process, which replaces the metal oxides with NaOCl and TEMPO. The Anelli reaction is carried out in a two-phase (CH_2Cl_2–H_2O) system using TEMPO as a catalyst and NaOCl as the oxidant. A co-catalyst, KBr, increases the reaction rate. Dr. Augustine's oxidation procedure is an extension of the Anelli process that does not require any organic solvents and replaces KBr with the more benign $Na_2B_4O_7$ (borax). In the absence of organic solvents, the reactant alcohol comprises about 38 percent of the total reaction volume compared with only about 2.5 percent in the classic reaction using dichloromethane. This has positive cost, environmental, and process safety implications. A further advantage to the solvent-free reaction is the isolation of the product aldehyde by phase separation from the aqueous solution; this saves even more energy because there is no solvent to remove.

Dr. Augustine's process can oxidize a number of primary alcohols, producing the corresponding aldehydes in very good to excellent yields. His process also oxidizes secondary alcohols to ketones in very good to excellent yields.

The Center for Applied Catalysis has been collaborating with the NutraSweet Corporation to scale up this reaction. NutraSweet is currently using Dr. Augustine's process to manufacture an aldehyde, 3,3-dimethylbutanal, on a commercial scale.

Professor Kaichang Li, Department of Wood Science and Engineering, Oregon State University

Development, Characterization, and Commercial Applications of Environmentally Friendly Adhesives for Making Wood Composites

The wood composites industry is one of the biggest manufacturing sectors in the United States. Together, the United States and Canada consumed 7.4 billion pounds of wood adhesives in 2000. At present, the predominant adhesives used to make wood composites are phenol-formaldehyde, urea-formaldehyde, and other formaldehyde-based resins. Formaldehyde is a known human carcinogen. It is released to the air during both production and use of wood composites made with formaldehyde-based resins.

Professor Li, inspired by the superior properties of the adhesive proteins secreted by mussels, has developed several environmentally friendly adhesives that can replace formaldehyde-based adhesives in wood composites. Professor Li developed his adhesives using renewable materials such as soybean flour, lignin, condensed tannins, and brown-rot-fungus-degraded wood to mimic the mussel adhesive proteins. Professor Li first converted soy protein to a strong, water-resistant wood adhesive by modifying it with the key functional groups found in mussel adhesive protein, including the catechol, amino, and mercapto (-SH) groups. He then developed new adhesives that contain one polymer with catechol moieties and another polymer with abundant amino groups. He also developed unique curing agents for soy flour and lignin. One of Professor Li's soy-based adhesives has been in commercial production since April 2005 to replace urea-formaldehyde resins in wood composites for interior use. Professor Li is working with Hercules Incorporated and Columbia Forest Products to commercialize other soy-based adhesives, including some to make wood composites for exterior use.

Professor Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

Dramatic Reduction of Copper Catalyst Content in Atom Transfer Radical Polymerization

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

Since 1995, Professor 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 and "green" materials using ATRP. Previously, the most active catalysts could not be used in many 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. Professor Matyjaszewski's group has overcome this limitation with hybrid catalysts and two recent improvements: Activators Generated by Electron Transfer (AGET) and Activators ReGenerated by Electron Transfer (ARGET). In ARGET, the most recent discovery, environmentally friendly reducing agents such as FDA-approved tin octanoate, sugars, or ascorbic acid reactivate the copper catalyst continuously, reducing the amount of catalyst by 1,000-fold. ARGET can be conducted in benign solvents including

water, carbon dioxide, ionic liquids, and biphasic solvents, in addition to bulk polymerization. The new processes will eliminate all hazardous substances from the products made by ATRP and from the waste streams of industrial production.

Employing Low-Cost, Benign Antioxidant and Metal Chelator Additives in Totally Organic Wood Preservative Systems

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

Lumber for U.S. residential applications is treated with copper-rich preservatives. Starting in 2010, however, minor use restrictions will be placed on copper-treated lumber sold in the United States. Further restrictions will undoubtedly occur, and future disposal of metal-treated lumber will become more difficult and expensive. A need exists for lumber treated with organic preservatives, but at this time no organic-treated lumber is available for residential exterior applications. Several problems exist with the development of totally organic wood preservatives, including (1) the newer organic biocides are expensive relative to metallic biocides; and (2) unlike metallic biocides, organic biocides can biodegrade by various biotic and abiotic pathways.

Fungi use metal-mediated reactions to form the free radicals that degrade wood. Using this basic knowledge, Professors Schultz and Nicholas combined numerous commercial organic biocides with butylated hydroxytoluene (BHT), an economical, benign, commercial antioxidant, and found synergism in short-term laboratory tests. (BHT is a food preservative, among other uses.) Their results from long-term outdoor tests were quite promising. Recently, they confirmed their earlier hypothesis that BHT helps protect a commercial biocide against microbial degradation. Because BHT is synergistic when combined with organic biocides and reduces biodegradation of the biocide, less of the relatively expensive organic biocide is necessary to protect wood. In their most recent work, Professors Schultz and Nicholas have shown that the metal chelator, ethylenediaminetetraacetic acid (EDTA), also has synergistic activity with organic biocides.

Wood treated with an organic biocide/nonbiocide mixture will be safer, have less environmental impact, and be easier to dispose of than metal-treated lumber. A preliminary economic analysis suggests that the savings from the reduced use of biocide are greater than the cost of the BHT. This technology can be employed with any organic biocide and, thus, is universal.

Ethylene in Catalytic Asymmetric Synthesis: A General Route for 2-Arylpropionic Acids including (S)-Ibuprofen from Styrene Derivatives and a Practical Solution to the Exocyclic Stereochemistry Problem

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 moieties into other common substrates. Professor RajanBabu and his group have discovered new, highly catalytic (substrate:catalyst ratios up to 1450:1) protocols for nearly quantitative (isolated yields up to 99 percent or more) and highly selective (100 percent regioselectivity, up to 96:4 enantiomeric ratio) co-dimerization 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.

Cyclic and acyclic 1,3-dienes also undergo efficient heterodimerization with ethylene, giving 1,2-addition products. Professor RajanBabu has realized yields up to 99 percent for several 1-vinylcycloalkenes and 1-substituted-1,3-butadienes. Phospholanes with suitably placed hemilabile ligating groups and phosphoramidites derived from binaphthol are excellent ligands for an asymmetric variation of this reaction; the latter gives 99 percent yields and >95 percent enantiomeric excesses for selected substrates. These discoveries open the door to expeditious syntheses of several biologically relevant classes of compounds, including many steroid derivatives.

Professor Anil N. Netravali, Fiber Science Program, Cornell University

Green Composites: Environment-Friendly and Fully Sustainable

Fiber-reinforced composites have many applications due to their favorable mechanical properties. Most composites on the market today, however, use nondegradable polymeric resins and fibers derived from petroleum. Professor Netravali uses plant-based, yearly renewable feedstocks to fabricate fully sustainable and environmentally friendly green composites. His chemically modified soy proteins have mechanical and thermal properties that make them suitable for use as resins. He reinforces these resins with plant-based fibers, yarns, or fabrics to make fully sustainable, environment-friendly, green composites. After use, his green resins and composites biodegrade fully during composting.

Soy protein is commercially available as isolate (SPI), concentrate (SPC), and flour (SF); it contains 18 amino acid residues, many of which have reactive amine, hydroxyl, or carboxyl groups. Soy protein can be processed into a lightly cross-linked resin, mainly through its cystine residues. Dehydroalanine residues formed from alanine can react with lysine and cystine to form additional cross-links. The resulting resin is too weak and brittle, however, for use in composites.

Professor Netravali has chemically modified SPC and SPI with Phytagel®, a linear D-glucose/D-glucuronic acid/L-rhamnose (2:1:1) tetrasaccharide, to form complex, interpenetrating network-like (IPN-like) structures that are also strongly hydrogen-bonded. Phytagel® forms a strong cross-linked gel with soy protein by ionic and hydrogen bonding in the presence of the mono- or divalent ions (ash and mineral) present naturally in soy protein. The resulting structure has excellent mechanical properties. Professor Netravali has obtained even better mechanical and thermal properties by dispersing exfoliated nanoclay particles in the IPN-like resin to form nanocomposite resins whose properties are better than those of common epoxy resins. He has used his modified soy resins with plant-based fibers such as flax and ramie to form green composites with excellent mechanical properties. Currently, Professor Netravali is working with Nissan, USA to mass manufacture green composite panels for automobile interiors.

Green Materials from Biomass

Professor Richard P. Wool, Department of Chemical Engineering, University of Delaware and Center for Composite Materials

Professor Wool is developing new, improved, green materials from biomass that are optionally recyclable and biodegradable, thereby enhancing global sustainability. He and his group have synthesized a wide range of high-performance, low-cost materials using plant oils, natural fibers, lignin, chicken feathers, nanoclays, and carbon nanotubes. By selecting the fatty acid distribution of plant oils (triglycerides) and their molecular connectivity, he controls chemical functional groups and molecular architecture to produce linear, branched, or cross-linked polymers. He uses new rigidity percolation processes to describe the resulting thermal and mechanical properties. His green materials include pressure-sensitive adhesives, foams, coatings, elastomers, rubbers, composite resins, carbon nanotubes dispersants, and nanoclay exfoliants. His work describes the chemical pathways used to modify plant oils and allow them to react optimally with each other and with various other monomers to form new materials with useful properties. Professor Wool combines his biobased resins with natural fibers (plant and poultry), glass fibers, carbon nanotubes, nanoclays, and solubilized lignin to produce new low-cost composites that are economical in many high-volume applications. His high-performance composites are used in hurricane-resistant housing, agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, electronic materials, and sports equipment. He has also derived pressure-sensitive adhesives (PSA), foams, coatings, and elastomers from genetically engineered oils. He found that these materials are both biodegradable and biocompatible with human tissue.

Professor Wool is president of Cara Plastics, Inc., which is producing his patented biobased resins for this 100-billion-pound market through its manufacturing partner, DynaChem, in Illinois. Mass production will begin in 2006. His inventions are attracting considerable attention from many other industrial partners as well. Overall, his new high-performance materials will provide significant energy savings (approximately 100 trillion Btu by 2020), CO_2 reductions (approximately one million metric tons of carbon equivalents per year), and NO_X reductions.

Greener Approaches to Functionalized Nanoparticle Synthesis and Nanoscale Patterning

Professor James E. Hutchison, Department of Chemistry and Director, Materials Science Institute, University of Oregon

Nanoscience and nanotechnology promise to revolutionize many areas of science and technology. Concerns have arisen, however, about the biological and environmental impacts of the materials and processes used to manufacture nanoparticles. Professor Hutchison's goals are the rational design of safe, high-performance, nanoscale materials, the efficient, inexpensive manufacture of these materials, and their incorporation into products and devices that offer environmental benefits. He chose three initial targets for his research: (1) finding alternatives to the hazardous reagents and solvents frequently used to produce nanomaterials; (2) developing efficient nanomaterial syntheses that increase yields and reduce complicated purifications; and (3) discovering bottom-up manufacturing approaches to nanodevices that eliminate the waste inherent in traditional top-down approaches.

During the last eight years, Professor Hutchison and his group have used this approach as a powerful driver for innovation in nanoscience. The examples in his nomination (synthesis, functionalization, and purification of nanoparticles; biomolecular nanolithography) illustrate the efficacy of this strategy as well as its health, environmental, and economic benefits. One of his syntheses, for example (1) eliminates the toxic substances diborane and benzene; (2) eliminates a processing step; (3) can be carried out in air without elaborate equipment; (4) produces over ten-fold more material; (5) scales up easily; and (6) reduces the cost from

approximately $300,000 per gram to $500 per gram. Professor Hutchison's work in this area has two patents; a number of other patent applications are pending.

Professor Urmila Diwekar, Departments of Bio, Chemical, and Industrial Engineering, and Institute for Environmental Science and Policy, University of Illinois at Chicago

Greener by Design: An Efficient, Multiobjective Framework under Uncertainty

Professor Diwekar and her group have developed an efficient, integrated framework for computer-aided green process design that combines chemical synthesis with process synthesis, design, and operation. Even in the presence of multiple, conflicting objectives, her framework uses new, efficient, optimization algorithms to provide cost-effective, environment-friendly designs that also explicitly identify trade-offs. The framework quantifies and characterizes uncertainties inherent in group contribution methods for chemical synthesis and in environmental impact assessments and includes them in the design process.

Because the property data needed to assess environmental impacts are not available for many molecules, scientists have turned to computational chemistry and molecular simulations to predict these properties. Previous simulations have, however, been computationally intensive and have produced large errors in predicted properties. Professor Diwekar's new framework reduces computational intensity and predictive errors for environmental property prediction by an order of magnitude compared to other molecular simulations. Her framework has wide applicability ranging from molecular simulations to designing profitable greener chemicals, chemical processes, environmental control technologies, and energy systems. It can also be used for effective environmental management and operations including nuclear waste disposal and renewable energy systems.

In the last five years, Professor Diwekar's work has resulted in 25 research papers in peer-reviewed journals (including five invited papers), three invited chapters (one in The Encyclopedia of Chemical Technology), two American Institute of Chemical Engineers (AIChE) graduate research awards (a 2001 Separations Division Award and a 2002 Environmental Division Award), a patent application, industrial implementation, and several conference and invited presentations. Results of Dr. Diwekar's work are currently being used in both continuous and batch chemical production and in energy systems. This is the first framework that considers chemical synthesis, process synthesis, and design under uncertainty together when confronted with multiple and conflicting objectives encountered in the selection of environment-friendly chemicals and technology designs for large-scale systems.

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

High-Performance Macromolecular Antioxidants for Materials: A Green Chemistry Approach

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 small business and academic categories. The abstract appears in the small business section on page 25.

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

Hydrogen-Mediated Carbon-Carbon Bond Formation

Elemental hydrogen is the cleanest and most cost-effective reductant available to humankind; industry uses it on an enormous scale. The vast socioeconomic impact of catalytic hydrogenation portends an equally powerful approach to reductive C–C bond formation mediated by hydrogen. The field of hydrogen-mediated C–C bond formation had lain fallow, however, since the discovery of the Fischer-Tropsch reaction and alkene hydroformylation, which are restricted to the insertion of carbon monoxide.

In an exciting and groundbreaking advance, Professor Krische's research team has discovered that the organometallic intermediates arising transiently in the course of catalytic hydrogenation may be intercepted by a variety of reacting partners. This finding led them to develop a broad new family of hydrogenations that form C–C bonds, adding a new dimension to one of chemistry's oldest and most widely used reactions. The diverse hydrogen-mediated C–C bond formations developed in Professor Krische's laboratory proceed with complete atom economy; several of these transformations are enantioselective. Moreover, the enormous infrastructure already in place for industrial-scale hydrogenation should expedite implementation of this emergent technology.

Novel, One-Step, Chromate-Free Coatings Containing Anticorrosion Pigments 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. Each year, the paint industry uses approximately 600,000 metric tons of chromates for chromate conversion coatings and as pigments. 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, including 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 in coatings makes it difficult to replace, however. In addition to chromates, 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 and contributing to smog formation.

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 coatings. His primer mimics the self-healing property of the chromates by including commercial pigments such as zinc phosphate into the structure of the primer; these pigments leach out only on demand.

Professor van Ooij is currently commercializing this technology through a small company that he founded, ECOSIL Technologies, LLC. He has provided samples under secrecy agreements to several companies including DuPont, PPG, Sherwin Williams, Hentzen Paints, and BASF. ECOSIL submitted a nomination in the small business category; see page 28 for that abstract.

Practical Asymmetric Catalytic Hydrogenation

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

Over 50 percent 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. Asymmetric hydrogenation accounts for over 70 percent of the current methods for commercial asymmetric chemocatalysis. Fundamental, innovative chemical methods are needed to develop these green chemical processes. Breakthroughs in this area will have broad applicability in industry.

Professor Zhang and his group have developed novel transition-metal-reduction catalysts for the practical synthesis of chiral alcohols, amines, acids, amino alcohols, diols, and α- and β-amino acids. They have also investigated the fundamental factors controlling enantioselectivity. They have invented a toolbox of practical chiral ligands for the asymmetric hydrogenation of ketones, alkenes, imines, and aromatic compounds. They have observed high activity (up to 50,000 turnovers) and enantioselectivity (up to 99 percent enantiomeric excess) for the hydrogenation of some substrates. They have demonstrated 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 Zhang's technology has numerous patents. He is commercializing it through Chiral Quest, Inc., which is providing his chiral technology to pharmaceutical and fine chemical companies including Phoenix, Pfizer, Merck, and Eli Lilly. Phoenix Chemicals Ltd. is currently manufacturing the Lipitor® sidechain using Chiral Quest's technology.

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 Supercritical Fluids Research Group at MIT have advanced the use of near- and supercritical carbon dioxide and water as benign alternatives to toxic organic solvents. Their technologies limit the use of auxiliary chemicals to carbon dioxide and water, eliminating additional surfactants, catalysts, and co-solvents. Their goal is the improved understanding of chemical reactions under extreme conditions in an effort to identify industrially relevant processes that are both economically attractive and environmentally benign. They have focused on two areas: (1) the clean and energy-efficient production of specialty chemicals in supercritical carbon dioxide; and (2) the use of water near its critical point to remediate chemical wastes and generate renewable energy. Their major contributions are novel experimental designs and protocols, precise and accurate measurements of phase behavior and reaction rate constants, and advanced theoretical models and engineering analysis of chemical kinetics. Their recent successes include the use of carbon dioxide as both solvent and reactant for the formation of important, nitrogen-bearing, heterocyclic compounds and the adaptation of power ultrasound technology to improve the selectivity and yield of a model Diels-Alder reaction in emulsions of carbon dioxide and water. The group's efforts have been documented in over 120 publications. Laboratories in the United States and in other countries now use many of the methods first introduced by the MIT Supercritical Fluids Research Group. Their detailed analyses enable generalization of their results from the laboratory bench to industrial processes.

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

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

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 on adjacent carbons.

Professor Garcia-Garibay's method consists of exposing a finely powdered crystalline ketone with appropriate substitution at the α-carbons to a light source. Within hours, the ketone transforms into the desired product with no need for purification. Notably, one can use conventional methods to add six groups at the ketone α-carbons (approximately 2.56 Å apart) easily and with excellent steric control. 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.

Entries from Small Businesses

Acetylene: A Viable Fuel Alternative for the Internal Combustion Engine

Go-Tec, Inc.

Go-Tec has developed an environmentally clean dual- and multi-fuel composition for use in internal combustion engines. It contains acetylene as the primary fuel, along with a secondary, combustible fuel to prevent early ignition and knock. The secondary fuel is often ethanol or methanol, but may include other alcohols, ethers, esters, diesel (to fuel diesel engines), or another suitable fluid, such as mineral spirits. Go-Tec has used its acetylene-based fuels successfully in a number of prototype vehicles with gasoline or diesel engines.

Engines using Go-Tec's acetylene-based fuel produce little or no carbon monoxide (CO), oxides of nitrogen (NO_X), oxides of sulfur (SO_X), volatile organic compounds (VOCs), or hydrocarbon (HC) emissions; they do not require catalytic converters. In addition, this fuel offers no buildup of residues in the engine, no particulate emissions, longer engine life, and greater fuel efficiency. With the low emissions realized in preliminary tests, Go-Tec's fuel may be suitable for use indoors, opening up many other applications. Go-Tec is proceeding toward commercialization of this technology.

Alternative to Methyl Bromide to Overcome Nematode Damage to Crops: Stoller Root Feed™

Stoller Enterprises Inc.

Worldwide, nematode damage costs food producers as much as $1.75 billion each year. Currently, producers control nematodes by fumigating with methyl bromide, a highly toxic gas. Stoller has developed products to replace methyl bromide for nematode control.

Stoller products are a combination of some or all of three types of materials that occur naturally in plants: minerals, plant hormones, and small molecules. They are applied exogenously, preferably in water-efficient, drip irrigation systems. Stoller serendipitously discovered that their products not only enhanced crop yield and quality (their original objective), but also strongly suppressed nematodes, resulting in much larger and more nutritious crops. An entomologist at Texas A&M University observed that Stoller products suppressed insects in a tomato field. Following this observation, Stoller used university studies to examine whether their products enhanced tolerance to insects and diseases. A study done by a graduate student in Peru showed that Stoller products suppressed the root-knot nematode: treated plots had healthy white roots and untreated plots had brown roots. Subsequent studies were done at the University of California Davis with grapes, broccoli, and sugar beets, at Auburn University with cucumbers and peppers, at the University of Florida with tomatoes. In all cases, crop canopy increased, root mass increased, and nematodes were reduced to varying degrees, but always with very desirable yields and crop quality. Additional studies are in progress.

The entomologist also suggested that if Stoller Root Feed™ could overcome nematodes, it should also overcome Phylloxera, the pest that devastated European grapes. An initial study in California in 2005 showed very good recovery from Phylloxera damage to grapes. Stoller is currently studying physiology and gene regulation to determine the mechanism of action by which Root Feed™ overcomes nematode damage to crops. Stoller is currently selling its products in over 40 countries for use on over 70 different crops under numerous climate conditions.

iSoy Technologies Corporation

Biocatalytic Production of Biobased Personal Care Products

Heightened awareness of the skin-damaging effects of ultraviolet (UV) radiation by the public has lead to robust growth in the market for sun and skin care personal products. The market for active ingredients in these products is $100 million in the United States. Approximately 90 percent of the sunscreens in the U.S. market rely on synthetic organic chemicals as their active ingredients. The most common active ingredients tend to bioaccumulate and persist. They also show estrogenic activity in mice and may be endocrine disruptors in humans.

SoyScreen™ is a highly innovative product that meets all the criteria for a green chemical and a green production process. It is made by biocatalysis of renewable feedstocks: ethanol, ferulic acid, and soybean oil. Ferulic acid is 4-hydroxy-3-methoxycinnamic acid, a phenolic compound widely distributed in plants. The biocatalyst is immobilized *Candida antarctica* lipase B in a solvent-free, packed-bed reactor. This enzyme efficiently transesterifies the ethyl ester of ferulic acid onto the glycerol backbone of vegetable oil. The result is a mixture of feruloylated monoacyl- and diacylglycerols. The biocatalyst retains good activity for months under continuous operation. The desired feruloylated acylglycerols are separated from unreacted ethyl ferulate and ferulic acid by molecular distillation or liquid carbon dioxide extraction. Recovered ethyl ferulate and ferulic acid are returned to the process, resulting in very high atom efficiency. The manufacturing process does not use any organic solvents.

The resulting nontoxic, biodegradable product has excellent properties as a UV-A and UV-B absorber, free-radical trap, and antioxidant, making it a superior substitute for conventional petroleum-based sunscreen active agents and skin care ingredients. Human sensitivity skin testing of SoyScreen™ has confirmed its safety and lack of allergic response. In November 2005, iSoy Technologies constructed a pilot plant for commercial synthesis. It plans to introduce SoyScreen™ into the market in a variety of skincare products in 2006.

GreenBlue (Green Blue Institute)

CleanGredients™ Information Technology for Green Chemistry

CleanGredients™ is an online database of environmental fate and toxicology data and other information on cleaning product ingredients. CleanGredients™ uses a peer-reviewed framework to evaluate and compare chemicals within functional classes. It enables developers and manufacturers to showcase ingredients with lower inherent environmental or human health hazards. It also enables formulators to identify ingredients for environmentally preferable cleaning products easily.

CleanGredients™ facilitates the ongoing development and implementation of green chemistry in the cleaning products industry. It has the potential to expand into other industry sectors. CleanGredients™ grew out of recommendations of the Unified Green Cleaning Alliance and a partnership between GreenBlue and the U.S. EPA's Design for the Environment (DfE) Program. The steering and technical advisory committees for the Alliance drew members from leading organizations in industry, government, and the nonprofit sector. The committees established the overall format and identified the specific attributes used in the CleanGredients™ database. Interested participants, now numbering around 300, serve as peer reviewers.

Formulators can search the database by general ingredient information and physical properties to identify suitable candidate ingredients for particular applications. The database displays candidate ingredients along with key environmental information, allowing formula-

tors to consider environmental factors easily when they select ingredients. For surfactants, the database displays company and product name, as well as acute aquatic toxicity and biodegradability. For each candidate ingredient, the database contains manufacturer information, material safety data sheets (MSDSs), and technical data sheets, as well as information on other human and environmental fate and toxicity attributes including mammalian toxicity, level of volatile organic compounds (VOCs), irritancy, sensitization, degradation products of concern, and others. A revised beta version of CleanGredients™ has been available for public review as of January 2006 at www.cleangredients.org.

Commercialization and Broadening of Market for an Environmentally Friendly Cleaner and Degreaser

IPAX Cleanogel, Inc.

IPAX has improved its formula for Green Unikleen, an environmentally safe degreaser, and brought its technology into new markets, making its product more available to both consumers and commercial/industrial users. The product has been used for 10 years in the auto industry to replace hazardous solvents in parts cleaning operations and has eliminated literally thousands of tons of hazardous waste. During the past three years, IPAX has serviced parts washers at the DaimlerChrysler Detroit Axle Plant, saving DaimlerChrysler approximately 63,750 gallons of hazardous waste.

Green Unikleen is a biodegradable, nontoxic, noncaustic, concentrated cleaner and degreaser that can be used with any manual or mechanical cleaning equipment. Its formula includes sodium silicate, Biosoft S-100, Neodole 23-5 (Shell Oil; includes a mixture of $C_{12\text{-}13}$ alcohol ethoxylates), a tetrasodium salt, and Surco SXS (40-42 percent sodium xylene sulfonate and up to 2 percent sodium sulfate in water).

IPAX's activities are now focused on broadening the reach of their technology to permit access to their product in other markets, including the consumer market. To this end, IPAX has: (1) secured every key certification available to the company and its products; (2) secured an endorsement by a well-known medical authority; (3) enlisted distributors with expertise in reaching new markets; and (4) applied for a patent on the new formula. Green Unikleen is the only product in the world to have received Green Seal GS-34 (degreasing) certification. Since November 2005, IPAX has been exporting components of its formula to China, where they are incorporated into consumer and commercial/industrial products. In addition, IPAX has introduced this highly versatile product as an environmentally preferable hand cleaner for those with multiple chemical sensitivities. All of these activities are designed to facilitate bringing IPAX's green cleaning technology to more markets.

Development of High Performance, Environmentally Benign Hard Disk Drive Polishing Fluids and Corrosion Inhibitors

Ventana Research Corporation

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 these 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. Each year, commercial polishing operations produce over 100,000 gallons of ethylene glycol polishing waste, which is not recyclable. Aqueous polishing fluids are critical to the industry, but water can corrode the sensitive electronic circuitry.

Ventana Research has developed a new class of benign synthetic copolymers whose aqueous solutions have high corrosion inhibition properties and are 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 with less waste than conventional lapping fluids. This affords manufacturers considerable savings by increasing production rates and reducing waste disposal costs.

Since 2004, Pace Technologies, a major worldwide distributor of polishing consumables, has been distributing Ventana's lapping fluid to manufacturers of hard drives as well as manufacturers of other products that require precision polishing such as optical lenses and flat-panel displays. In 2005, Ventana received a Phase II Small Business Innovation Research (SBIR) grant from the National Science Foundation to continue developing its polishing fluid. Ventana has also developed a series of new corrosion inhibitors and paint primers from its phytochemical precursors and spun them off as a separate technology.

Innovative Formulation Company

Ecological Paint Antimicrobial Clear Coat

Ecological Paint Antimicrobial Clear Coat is a self-curing water-based paint formulated to address public health concerns linked to the transference of bacteria and mold on public and private surfaces that people are likely to touch. Innovative Formulation has developed an antimicrobial, mold and bacteria retardant paint that is totally nontoxic and contains no volatile organic compounds (VOCs). Their Clear Coat is the first nontoxic antimicrobial paint product; other advertised non-VOC paints use solvents such as methyl ethyl ketone, acetone, and other ketones.

Clear Coat uses a sophisticated silver nanoparticle cage technology. For hundreds of years, silver has been acknowledged as effective in stopping the growth and spread of bacteria. Innovative Formulation has designed a dispersal system that releases silver ions in a uniform, non-clumping manner, providing comprehensive antimicrobial coverage of all treated surfaces. The nano emulsion polymer carrying system in Clear Coat is a single-component, fully crosslinked acrylate. Clear Coat uses pharmaceutical-grade pigments.

Toxic chemicals are a health hazard. The paint produced in the United States during 2001 contained almost 5 million kilograms of VOCs. The origin of many respiratory conditions in the U.S. population is unknown, but it is, in the company's opinion, related to toxic chemicals in the atmosphere. Airborne toxic chemicals may also be related to the high incidence of liver and pancreatic cancers in the United States.

Innovative Formulation has created a completely safe antimicrobial paint that is virtually free of hazardous chemicals. No other paint company in the United States can legitimately and accurately make such representations. Innovative Formulation has been producing its Clear Coat since December 2005 at a plant in Tucson, AZ. A major fast food chain is currently using Clear Coat and a major hotel chain is testing the product.

MLI Associates

Environmentally Benign Deicing/Anti-Icing Agents

Each year, the U.S. market for deicing/anti-icing (D/A) products consumes over 100 million gallons of liquids and 20 to 25 million tons of salt. Historically, rock salt and glycol solutions have represented the bulk of D/A chemicals. Over time, however, it has become apparent that these effective, low-cost, but corrosive chemicals carry a severe cost in damage to infrastructures, vehicles, and the environment. For example, highway salt has found its way

into both surface water and underground aquifers, whereas the high biological oxygen demand (BOD) of glycols has had negative effects on marine organisms.

MLI D/A technologies are based on an innovative chemical method that prevents pollution through source reduction. This method uses abundant natural resources, agrochemical waste streams, and low-value streams such as carbohydrates derived from corn, glycerin-containing byproducts of biodiesel manufacture, and biopolymer wastes. Some of these D/A agents represent a new class of materials designed as alternatives to traditional salt and glycol-based fluids. The MLI chemistry has led to development of a wide array of products, many of which are now in or near commercial use. These products reduce the nation's reliance on petroleum, assist the commercialization of biofuels, and reduce impacts on health and the environment relative to traditional glycol-based fluids. The MLI biomass-based fluids are infinitely soluble in water, are nontoxic, and act as corrosion inhibitors for ferrous metals. During 2005, MLI received a patent for D/A agents made from byproducts of biodiesel manufacture. Also in 2005, MLI released Caliber® FC-B antifreeze and Caliber® SBA-2 additive for chloride D/A products in collaboration with Archer Daniels Midland. Current sales of MLI D/A agents are 15 million gallons per year. Applications for these products include aircraft-related uses, airport runways, roadways, bridges, facilities, landscape, and consumer markets.

ExSact: A "Green" Gasoline Technology

Exelus, Inc.

Alkylate is a clean, high-octane blending component of gasoline made primarily by alkylating isobutane with butenes. Alkylate is an ideal replacement for MTBE (methyl tertiary-butyl ether) in reformulated gasoline: it has a low vapor pressure, a high octane value, and is not water soluble. Most U.S. refineries produce alkylate. The current technology for alkyation, however, requires either hydrofluoric acid (HF) or concentrated sulfuric acid as the catalyst. These liquid acid catalysts pose many problems. HF is deadly, causing severe burns and tissue damage. It also tends to form stable aerosols, so that an accident could create a lethal cloud over the point of release. The 50 HF units in the United States threaten as many as 15.6 million people living nearby. Sulfuric acid is somewhat safer, but its use creates a byproduct mixture of hydrocarbons and sulfuric acid that must be disposed of or regenerated. Sulfuric acid units use considerable amounts of catalyst, requiring the transport and storage of large amounts of this acid.

ExSact solves these problems by replacing dangerous liquid acids with a noncorrosive, environmentally friendly solid acid. This breakthrough catalyst is safe enough to be held in hand and is benign in the open environment. Previous solid acid catalysts have not been commercially successful because they tend to deactivate rapidly by coking during alkylation. Exelus has engineered every aspect of their new catalyst to reduce coke formation. They have optimized both the distribution and strength of the acid sites. They have chosen a pore structure that creates the proper reaction environment near the active sites. Their ExSact technology represents the first commercially viable solid acid alkylation process in the world. A pilot plant has been demonstrating the technology since December 2005, and Exelus expects the first commercial deployment of its technology in mid-2006.

Super Trap Inc.

GEL-COR™: A New, Environmentally Compatible Bullet-Trapping Medium for Small-Arms Firing Ranges

There are over 10,800 small-arms firing ranges in the United States for sport shooting and for training military and law-enforcement personnel. These ranges collect over 80,000 tons of lead every year, often in soil berms, where the lead can leach into the environment. Containing and recovering lead and other heavy metals from ranges in a safe and environmentally acceptable manner is vital to controlling soil and ground water pollution.

GEL-COR™ is an engineered ballistic material designed to collect impacting bullets fired on small-arms training ranges in a safe and environmentally compatible way. It captures the spent bullets and contains the heavy metals that would otherwise escape into the environment. GEL-COR™ is a mixture of recycled tire-tread rubber chunks, a hydrated superabsorbent polymer gel (a copolymer of acrylamide and potassium acrylate), and three salt additives. This resilient material stops incoming bullets, captures them intact with few exceptions, and does not make any detectable metal dust. The gel-rubber mixture contains approximately 40 percent water by mass, which prevents it from burning if it is exposed to tracer rounds, pyrotechnics, or other sources of ignition. The salt additives (including tricalcium phosphate, aluminum hydroxide, and calcium carbonate) immobilize the lead and copper in the trapped bullets and keep them from leaching into the environment. The mixture maintains an alkaline pH, minimizing the solubility of lead hydroxide in the trap and stabilizing the gel. Exposed lead surfaces react with the salts to form insoluble lead aluminum phosphate (plumbogummite), one of the safest and most stable lead compounds. Copper reacts to form an insoluble copper phosphate. GEL-COR™ is the first resilient medium that contains no toxic additives and will not burn, even if exposed to a source of ignition. GEL-COR™ is an important step in ensuring that live-fire ranges are safer and more environmentally compatible.

GreenEarth Cleaning, L.L.C.

GreenEarth Cleaning: Dry Cleaning With Silicone Solvent

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 cyclic siloxane (decamethylcyclopentasiloxane) that is a safe and viable alternative. Commercial drycleaners license the use of this process in their independent operations.

Prior to commercializing this process, GEC conducted beta testing at 27 retail dry cleaning sites in the United States over a 10-month period. During this period, two million 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 percent. The GEC silicone does not influence 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 481 locations in the United States and over 500 locations in ten other countries, with growing acceptance based on its health, safety, and environmental profile, as well as its operational advantages.

High-Efficiency Olefin to Polyolefin Process with Toxic Solvent Elimination

ZIVATECH Corporation

ZIVATECH has developed novel catalytic processes to dehydrogenate aliphatic (paraffin) hydrocarbons into olefins and, subsequently, to polymerize them into polyolefins. These processes use catalytic dehydrogenation reactors in conjunction with polymerization reactors and coordination-type metal catalysts, such as titanium trichloride. This technology replaces the conventional cracking and refining of paraffins, which require more energy. In developing these processes, ZIVATECH considered materials and energy conservation coupled with environmentally benign modifications (e.g., eliminating toxic or hazardous solvents, catalysts, and other media). Process improvements include increased polymer and olefin product yields, recycling of both reactants and intermediate products 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 2005, this technology received a U.S. patent. ZIVATECH is currently in the process of licensing and scaling up this technology.

High-Performance Macromolecular Antioxidants for Materials: A Green Chemistry Approach

Polnox Corporation

Industrial antioxidants are an increasingly important and fast-growing market. The antioxidant market generates annual sales of approximately $2.1 billion, based mainly on low-molecular-weight products with limited thermal stability, relatively low material protection, and higher material diffusion rates. Polnox Corporation is developing 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. They demonstrate superior performance in a wide range of materials and applications including, but not limited to, foods, oils and lubricants, fuels, plastics, and packaging. They are cost-effective, safe to use, and have a superior price-to-performance ratio. An acute oral toxicity (LD_{50}) test for these materials met the requirements of other FDA-approved antioxidants.

Dr. Cholli and his team at the University of Massachusetts Lowell originally discovered the technology. In January 2004, Dr. Cholli formed Polnox Corporation to commercialize his antioxidants. Polnox has scaled up the synthesis of two core antioxidants to the mini-pilot scale (multikilogram scale). During 2005, Polnox initiated validation testing of its core antioxidants at six Fortune 500 companies. They expect to enter into one or more joint development and marketing partnerships in 2006, including production and sales for a number of industrial markets.

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

Recovery Systems Inc.

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 a process to treat the waste and recover valuable products from it. A standard 5,000-head farm is expected to generate about $170,000 per year in products; there are about 2,000 hog farms in North Carolina alone.

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 col-

loidal bonds of the solids and urea break down to release ammonia. The lime treatment kills over 99 percent 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, NC. In 2005, U.S. EPA issued a contract to Recovery Systems to fund the necessary construction permit.

W.F. Taylor Co., Inc.

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

Traditional flooring adhesives are one- or two-part reactive systems that are urethane-, epoxy-, solvent-, or water-based; they 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. These products are estimated to release over 23 million pounds of volatile organic compounds (VOCs) to the environment annually.

Meta-Tec™ technology is a unique class of adhesives that are low-VOC, reactive, one-part, and self-cross-linking. The Meta-Tec™ adhesives 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 by reducing 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. Between 2002 and 2004 (latest available data), this product was used to install over 60 million square feet of wood flooring products. The company expects this product to capture over 25 percent (25 million pounds) of the market by the end of 2005.

Montana Polysaccharides Corporation

Multipurpose Exopolymer as a Raw Material

Levan, an unusual polysaccharide, is being developed as a raw material to replace petrochemicals in many industries. This polymer of fructose has an extremely low intrinsic viscosity so that it requires less energy to handle, does not swell in water, is heat- and acid-stable, and causes no skin or eye irritation, even on prolonged, direct contact. Levan is a strong adhesive, forms oxygen-barrier films, can be derivatized to make powerful surfactants, can be extruded into plastics, and can replace petrochemicals in certain personal care products.

Cost is a critical factor in determining commercial success of a raw material. Levan is made from sucrose, the disaccharide of glucose and fructose, which currently sells for $0.17 per kilogram. Levan is an exopolymer. Unlike products from corn, soy, and waste biomass that require significant amounts of energy and solvents for separation from cells, levan is naturally exported from producing cells. Either sugar beets or sugar cane can be the source. Sugar beets are grown on marginal lands. Processing energy needs are minimal; some beet sugar processors sell excess electricity to the grid. Sugar cane is an excellent CO_2 sink. The byproduct, glucose, is a basic feedstock for numerous chemicals, providing additional revenue.

Levan is a multifunctional, 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: sucrose, the feedstock, comes from sugar beets and sugar cane, both produced in the United States and in many regions around the world. Montana Polysaccharides has been producing levan in 5,000-liter fermenters since 2003. During 2005, the company initiated sales of levan in the adhesive and personal care industries.

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. Fungi Perfecti has isolated cultures of fungi from naturally infected insects and, through a selection process, cultured these fungi in the laboratory to create strains that delay spore production for several weeks. The presporulating entomopathogenic mycelia emit powerful attractants, trail-following elicitors, 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 Corporation

ZIVATECH's technology is based on analyzing, testing, and evaluating a new reforming process to convert biomass and other secondary waste streams into a syngas outlet stream rich in hydrogen gas, which then powers an interconnected solid oxide fuel cell (SOFC) to generate power directly.

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, which converts it into electric current. Conversion of these waste streams to synthesis gas for use in SOFC-based electricity generation systems is of substantial and increasing importance to both commercial and remote residential energy consumers from energetic, economic, and

clean energy points of view. ZIVATECH's SOFC technology saves oil, natural gas, and coal deposits, while reducing pollution.

Renewable waste biogas resources are increasingly important to the energy generation market. ZIVATECH's innovative process to convert carbon dioxide-rich methane gas inside an in situ reactor using their reaction and catalysis system is under consideration for current and future use as an energy source by industry. This will be enhanced by an increased knowledge of processes that convert carbon dioxide mixtures into other chemicals and fuels, eliminating greenhouse gas emissions and other pollutants. Projected energy and capital savings from the integrated new process are in the 30–40 percent range compared to current 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. In addition, H_2S is corrosive; the National Association of Corrosion Engineers estimates the cost of corrosion at nearly $300 billion per year worldwide.

LATA's Bio-Competitive Exclusion (BCX) technology is designed to attack the source of H_2S: the reduction of soluble sulfate in the water by indigenous sulfate-reducing bacteria (SRB). The BCX process is initiated and sustained by patented, environmentally friendly inorganic nitrate and nitrite formulas (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 formulas at low concentrations act 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; in addition, it is toxic to SRB. 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. In 2005, LATA successfully completed sulfide control field projects for major oil companies, leading to treatment expansions in the United States and Canada.

ECOSIL Technologies LLC

New One-Step, Chromate-Free Anticorrosion Coatings for Aluminum Alloys and Hot-Dip Galvanized Steel

Corrosion protection by paints and organic coatings is a common practice. Each year, the paint industry uses approximately 600,000 metric tons of chromates for chromate conversion coatings and as pigments. 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, including 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. In addition to chromates, paints are for-

mulated 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.

ECOSIL's invention is a one-step, low-VOC primer system for use on aluminum alloys and hot-dip galvanized steel. The new primer eliminates chromates totally, yet performs equally well. Its major components are water-dispersed resins, an organofunctional silane, and selected pigments. With the addition of a suitable corrosion inhibitor, the primer without topcoat attains a B-117 resistance of over 2,000 hours on both substrates. The resin component is an epoxy-based bisphenol-A or epoxy-novolac resin with small amounts of polyurethanes or acrylates.

ECOSIL is currently commercializing this technology. The advantages of their primer over other technologies that replace chromates, plus the huge chromate market for pretreatments and pigments, have attracted the attention of many companies including DuPont, PPG, Sherwin Williams, Hentzen Paints, and BASF. ECOSIL is collaborating with two large paint companies on its primer system. Professor Wim van Ooij, the founder of ECOSIL, also submitted a nomination in the academic category; see page 15 for that abstract.

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

Specialty Fertilizer Products

Although phosphorus is an essential nutrient for plant growth, it can be toxic to humans 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 has developed and patented a family of water-soluble, nontoxic, biodegradable copolymers made from itaconic acid (a monomer derived from renewable 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 adverse environmental effects are lessened.

New Water-Based Organic Corrosion Inhibitor

HALOX

In 2004, the anticorrosive pigments market for North America totaled approximately 33 million pounds and had a value of approximately $55 million. Strontium chromate, barium phosphosilicate, barium borosilicates, modified phosphates, and zinc phosphate accounted for the majority of anticorrosive pigments. These and other traditional corrosion inhibitors include known carcinogens, flammable oils and solvents, hazardous air pollutants, marine pollutants, and chemicals that cause eutrophication of ecosystems.

HALOX® 510 is the trade name for 1,3-propanediamine, *N,N*-dimethyl-, monobenzoate, a water-based organic corrosion inhibitor for direct-to-metal coating applications. It replaces corrosion inhibitors formulated with heavy metals such as hexavalent chromium,

cadmium, lead, strontium, barium, and mercury. It contains no nitrites or other toxic chemicals, no eutrophication chemicals such as phosphates, and no marine pollutants such as zinc oxide and zinc phosphate. Its applications include direct-to-metal finishes (e.g., railcar coatings), automotive finishes, light industrial primers for metals, weld seam flash rust protection, temporary corrosion protection, general maintenance coatings (e.g., hand rails, metal decking), and synthetic and semisynthetic metalworking fluids. HALOX® 510 imparts both anti-flash rust and long-term corrosion properties to waterborne coatings for steel, aluminum, galvanized steel, cast iron, and zinc alloys. HALOX® 510 interacts strongly with a corroding metal at the active anodic sites, forming a thin coating over the metal and restricting the access of other corrosive ions to the metal. Its alkaline pH also reduces the corrosion rate of the underlying metal. It is added to paint during manufacture or prior to applying the paint. It prevents ferrous substrates from flash rusting caused by the presence of water and oxygen as the paint dries. In addition, it does not adversely affect paint gloss.

HALOX® 510 has been in commerce since 2003. In November 2004, The Sherwin-Williams Company approved HALOX® 510 for its automotive products division.

MIOX Corporation

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

Water disinfection using chlorine gas has saved countless lives in the United States 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 using chlorine gas for 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 United States 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 a miniature version of its purifier to the U.S. military, the camping and recreation markets, foreign travelers, disaster relief workers, and others. Thousands of these devices are currently deployed in Iraq and Afghanistan.

PostSaver USA

PostSaver®

PostSaver® is a patented invention that can substantially reduce the leaching of toxic wood preservatives from treated wood commodities in ground contact. A PostSaver® wrap will extend the useful service life of treated wood commodities using only a fraction of the preservative typically required for ground contact. PostSaver® wrap is a thick, UV-stabilized polyethylene film that has an internal bitumen coating. The bitumen inner layer protects wood in contact with this tar-like substance; the outer polyethylene film layer hinders decay and insect attack further and prevents water absorption. PostSaver® wrap adheres to wood commodities such as posts, lumber, and poles under slight pressure and heat from a mechanical applicator.

PostSaver® wrap is unlike typical wood preservative groundline-remedial treatment wraps; it does not contain additional toxic preservatives to supplement the wood preservatives that have already leached from wood in service. In contrast, PostSaver® wrap is applied to new wood prior to its being put into service. PostSaver® wrap can reduce the leaching of any wood preservatives in a treated commodity, can reduce the actual loading of toxic, wood-preservative chemicals needed to protect wood in ground contact, and can help extend the service life of durable heartwood species. PostSaver® may also expand the use of more leachable, less toxic wood preservatives such as borates.

PostSaver® wrap currently has worldwide sales in over six countries. During 2005, PostSaver USA had manufacturing and implementation sites located in Coos Bay, OR and Mechanic Falls, ME.

Practical Asymmetric Catalytic Hydrogenation

Chiral Quest, Inc.

NOTE: This project is the result of a partnership between Chiral Quest, Inc. and its founder, Professor Xumu Zhang of The Pennsylvania State University. This project was judged in both the academic and small business categories. The abstract appears in the academic section on page 15.

A Preproduction System for Re-Refining Used Oil Using Closed-Loop, Patented, Atomization Technology

FluidPhase Technologies Inc.

Only 14 percent of the approximately 2.4 billion gallons of lubricating oil used per year in the United States is recycled to reusable lubricating oil. Many companies that recycle oil use a simple thermal cracking operation that yields a highly unstable, low-grade fuel oil with low consumer acceptability.

FluidPhase is building a preproduction unit based on atomization in supercritical fluids to recycle lubricating oil into a highly stable, purified base lubricating oil in a cost-effective and environmentally friendly manner. Their new, innovative technology is a continuous process that mixes waste fluid with a supercritical fluid. The process exploits the difference in the solubility of the desired and the undesired components in the supercritical fluid. During the process, jet spray micro-orifices atomize waste oil into a supercritical fluid. The atomization process dissolves the reusable elements of the oil, leaving behind impurities and waste particles. Thus, polychlorinated biphenyls (PCBs) are removed early in the process, along with metals, sludge, and water. Undissolved components are separated by gravity, and the dissolved fluid is separated from the supercritical fluid. The system uses supercritical propane or another environmentally friendly solvent that is contained and recycled online. The byproducts from the extraction are used as binder material for asphalt, eliminating their disposal in landfills.

This preproduction system for re-refining used oil reached the pilot plant stage during 2005. The pilot plant has the capacity to process 30 liters per hour of used oil in a continuous process; it has all the components of a larger commercial system. Members of the National Oil Recyclers Association have expressed interest in this technology.

ArchAngel Enterprises, LLC

Stalosan F Microbial and Environmental Control for Use in Housing of All Animals

Stalosan F is an all-natural product that improves hygiene and environmental conditions for livestock when applied to damp surfaces. It has lower toxicity and provides greater safety than existing alternatives. Stalosan F is a pink powder that acts as a drying agent. It is composed of human-grade, high-quality minerals including three forms of very pure phosphate, a structural clay material, a combination of iron and copper salts, and an essential oil. This formulation makes it safer than many sulfate-based alternatives. Its low pH inhibits pathogens. Stalosan F addresses the problem of odor abatement and ammonia in external environmental bacteria, viruses, fungi, and fly larvae, all of which interfere with livestock production and pose potential harm to humans. Stalosan F also controls moisture at variable levels, where increased water pressure leads to increased water binding capacity. It can bind up to four times its own weight of water. It can be applied by hand or with a power blower.

Stalosan F is suitable for all animals, including cats, dogs, and rabbits, with special attention to livestock, including pigs, cows, poultry, horses, and sheep. Stalosan F virtually eliminates offensive odors for neighboring residents and ammonia levels within the production facility. This, in turn, creates a better environment for livestock to grow and thrive.

Stormøllen A/S, the Denmark-based manufacturer of Stalosan F, is selling this product in the agriculture markets of 64 countries. ArchAngel represents this company in the United States. Most recently, the U.S. EPA has evaluated Stalosan F for registration and found it to be safe for humans and animals. ArchAngel is anticipating U.S. EPA registration in spring 2006.

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 uses green chemistry to develop products that meet rigorous performance, environmental, and human health criteria. Their 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 many types of cleaners, as well as an odor eliminator, floor finish, wax stripper, and dust mop treatment. In 2005, Coastwide introduced seven new SE products; its sales of all 21 SE products were $2.3 million.

Entries from Industry and Government

3D Trasar BioControl

Nalco Company

Microbes grow well in the warm, nutrient-rich waters of cooling systems. Unchecked, microbes coat the heat exchanger surfaces, impeding heat transfer and increasing energy costs. Biocides are added to control microbial activity. Although 99 percent of the microbial population resides on the inaccessible surfaces of a cooling system, the industry standard was to monitor only floating microbes because there was no method to monitor the total population. The result was either excessive biocide dosing (to preserve a margin for error) with resultant discharge of biocides and corrosion products into natural waterways or insufficient biocide dosing; either case increased energy use and public health concerns.

3D Trasar BioControl adds a fluorescent molecule, Resazurin, to the water in cooling systems. When Resazurin interacts with active microbes, it reacts and its fluorescence changes: BioReporter (Resazurin) + microbial respiratory enzymes = BioProduct (Resorufin). Continuous monitoring of the fluorescence of both Resazurin and Resorufin allows instantaneous measurement of the total microbial activity in the system. Oxidizing biocide is added to the system only in response to increasing microbial activity. Oxidizing biocides also react with Resorufin and Resazurin, but at a much slower rate than the reaction with microbes. Fluorescent detection of the degradation of Resorufin by the oxidizing biocide is used to determine the precise endpoint for biocide addition.

With 3D Trasar BioControl, biomonitoring and control are continuous and comprehensive; biocide is applied only when microbial activity is detected and before the population enters the log growth phase. Continuous monitoring avoids the use of excess biocide to catch up after rapid microbial growth has occurred. 3D Trasar BioControl allows the most efficient use of biocide, ensures microbial control, reduces the formation of absorbable organic halide (AOX), and reduces toxic discharge. During 2005, Nalco deployed over 1,200 new 3D BioControl units for a total of over 1,700.

ACCOLADE™ Synthetic-Based Drilling Fluid System

Halliburton Energy Services

In 2001, Halliburton introduced a revolutionary synthetic-based drilling fluid (SBF) called the ACCOLADE™ system. ACCOLADE™ is the first SBF to couple superior environmental compliance with exceptional drilling performance, allowing operators to drill with high efficiency while they minimize environmental impact in sensitive offshore areas. Halliburton formulated ACCOLADE™ to exceed U.S. EPA's environmental criteria for sensitive areas; ACCOLADE™ is the highest rated of all drilling fluids for its low toxicity and high biodegradability. The system far exceeds all regulations governing discharge of cuttings generated with SBF for drilling offshore in the Gulf of Mexico.

ACCOLADE™ contains no commercial clay or lignite additives; it is the only organophilic clay-free synthetic fluid on the market. The base oil is a blend of 50 percent vegetable oil esters (from palm and cocoanut oils) and an internal olefin. The ester component of the base fluid makes ACCOLADE™ more biodegradable than conventional SBFs. ACCOLADE™ is characterized by desirable rheological properties over a range of temperatures from 40 to 350 °F, properties that provide unprecedented control over viscosity and equivalent circulating density. The gel strength of the fluid develops quickly, but is fragile. With ACCOLADE™, downhole mud losses normally associated with tripping, running cas-

ing, cementing, and breaking circulation are an average of 41 percent lower than those in wells using traditional SBFs. To date, ACCOLADE™ has saved approximately 350,000 barrels (14.7 million gallons) of drilling fluid and has reduced total drilling additives. This reduction translates into fewer crane lifts, reduced transportation expense, and less exposure of workers to potentially hazardous operations.

Through 2005, 20 different operators had used ACCOLADE™ to drill over two million feet of holes for more than 190 oil wells in the Gulf of Mexico. In 2005, ACCOLADE™ also had its first international use, in Venezuela.

Milliken & Company

Alternative Green Adhesives for Textile Composites in Commercial Buildings: TractionBack™ and 180 Walls™

Indoor air quality can have a drastic impact on the health, comfort, and well-being of building occupants. The U.S. EPA has identified it as one of today's top five environmental health risks. Typically, the thick, blended acrylic latex adhesive used to install carpet tiles emits volatile organic compounds (VOCs) for several months to years after installation. Chemicals used to prepare walls and install wall coverings emit VOCs as well.

Milliken has developed floor and wall coverings that do not require adhesives for on-site application and, as a result, improve indoor air quality. Milliken's innovative TractionBack™ high-friction coating for modular carpet tiles and its 180 Walls™ pressure-sensitive wall coverings demonstrate the sustainable benefits of safer chemicals. TractionBack™ is a polyolefin coating of amorphous polypropylene copolymers, polyolefin polymers, and tackifying resins, both biobased and petroleum-based. 180 Walls™ contains a proprietary water-based, acrylic adhesive that allows textile installation with essentially no VOC emissions; it replaces poly(vinyl chloride)- (PVC-) based vinyl wall coverings. These floor and wall coverings provide the design and building industry, facility managers, and homeowners with green solutions.

Milliken's adhesive solutions for textile composites (1) eliminate chemical pollutants such as floor primers, sealants, and other VOCs; (2) eliminate biological pollutants such as mold and bacteria; and (3) reduce sanding and surface preparation, which create particulates. Additional environmental benefits include: (1) reduced energy during production; (2) reduced waste during installation; (3) reduced waste sent to landfill because individual tiles are easy to reposition or replace, extending overall product life; (4) reduced down-time for building spaces; and (5) elimination of PVCs. TractionBack™ is currently available on 95 percent of the Milliken floor coverings. 180 Walls™ has been on the market since March 2005; it is currently available as the adhesive for 100 percent of Milliken's wall covering products.

Aminopyralid: Increasing Protection of Endangered Species through Improved Management of Non-Native Plants While Maximizing Land Use and Significantly Reducing Herbicide Volume and Application

Dow AgroSciences LLC

According to U.S. government policy, endangered plant species have potential scientific, medical, ecological, aesthetic, recreational, educational, and historic value. A wide range of programs has been put into effect in an effort to preserve them from extinction. Noxious and invasive weeds threaten endangered plant species by transforming ever-increasing amounts of habitat into monocultures with little to no biodiversity. Infestation of federal land with invasive weeds is increasing at a rate of 4,600 acres per day. Invasive weeds also reduce the productivity of farm and rangeland by approximately $20 billion per year at a time when pressure for additional agricultural output is mounting.

Aminopyralid belongs to the pyridine carboxylic acid class of auxinic herbicides. It is the first noncrop herbicide ever registered by U.S. EPA as a reduced-risk pesticide; it is registered for use in range, pasture, industrial, and wheat applications. It provides superior control of invasive weeds at rates of application 4 to 20 times less than those for competitive products, while reducing risk to people, nontarget organisms, and the environment. Use of aminopyralid for invasive weed control maximizes land use and helps protect habitat for endangered species. It also reduces the amount of herbicide active ingredient applied to the environment. Aminopyralid degrades relatively quickly; its half-life is approximately 30 days. Its synthesis includes a novel, one-step electrochemical reduction process in aqueous solution that results in substantial, high-purity yields.

Dow AgroSciences projects that once aminopyralid becomes established in the marketplace, it will reduce the total yearly environmental load of broadleaf herbicides applied in the United States by 2.4 million pounds, equivalent to a net 15-percent reduction. Against only one invasive species, Canada thistle, Dow AgroSciences predicts that hay growers will save $14.3 million each year in herbicide costs and eliminate $9.3 million in crop losses.

Beneficiation and Use of Coal Combustion Fly Ash: A Major Success in Reducing Solid Waste and Increasing Supplies of Construction Materials While Reducing Greenhouse Gas Emissions

Separation Technologies LLC

Coal combustion generates approximately 55 percent of all electric power in the United States. Over 70 million tons of fine coal ash, known as fly ash, are recovered annually; most of it is disposed of in landfills or settling ponds. Using fly ash as a supplement in concrete reduces the use of ordinary Portland cement, but concrete specifications limit the amount of unburned carbon in the fly ash.

Separation Technologies (ST) has developed and implemented innovative, patented processes to reduce unburned carbon and detrimental ammonia in coal fly ash. The treated fly ash is suitable for use in concrete, and the separated carbon is a fuel for utility boilers. ST takes advantage of the differing surface chemistries between unburned carbon particles and mineral particles in fly ash. When these particles collide, charge transfer (triboelectric charging) occurs and the carbon particles separate from the mineral particles in an electric field. ST has also developed an economical process to remove ammonia as a gas from fly ash.

ST's technology is operating commercially at eight large, coal-fired electric power plants in the United States, Canada, and the United Kingdom to beneficiate coal ash into raw materials for concrete production and to recover unburned carbon in the ash for its fuel value. Cumulatively, ST has produced four million tons of concrete-grade fly ash with a corresponding reduction in solid waste and emissions of greenhouse gas (CO_2).

Broin and Associates

BFRAC™ and BPX™: Launching the Biorefining Revolution

Ethanol is one of the most economical and viable alternative fuels. Broin is the second-largest producer in the industry, making more than 600 million gallons of ethanol per year. Broin has been working to usher in the biorefinery revolution by increasing the efficiency and sustainability of ethanol production.

BFRAC™ is a Broin technology that fractionates corn or other cereal grains into bran, germ, and endosperm. It then uses the optimal fractions for ethanol production and refining. Broin developed this technology in collaboration with Satake USA, Inc., a world leader in rice and flour milling. BPX™ is a complementary Broin technology that removes the cooking step in traditional dry-mill ethanol production and replaces it with simultaneous saccharification of raw starch and fermentation of the resulting sugars in an advanced enzyme technology. Broin developed this technology in collaboration with Novozymes North America, Inc., a world leader in enzyme development and a major enzyme supplier. BFRAC™ and BPX™ not only increase ethanol production efficiency by enabling higher alcohol levels during fermentation and during beer production, but also result in the production of a higher-protein distillers dried grain from the no-cook plant material. An added environmental benefit is reduced dryer stack emissions.

The BPX™ process is currently in use at ten plants managed by Broin. In May 2005, Broin started up BFRAC™ and BPX™ operations at a retrofitted 50-million-gallon-per-year ethanol biorefinery in Coon Rapids, IA. Broin is currently marketing the majority of its over-40-percent protein distillers grains from the BFRAC™ and BPX™ processes as Dakota Gold HP (HP = high protein). This low-fat, high-fiber, high-protein product is opening new markets to distillers grains in the swine and poultry feeding industries.

Cargill, Incorporated

Biobased Polyols

Cargill has demonstrated an innovative approach to delivering environmental responsibility along with cost-effective performance to the polyurethane industry. Cargill's hydrolytically stable, biobased polyols can replace traditional petroleum-based polyether polyols and copolymer polyols. The Cargill polyols produce commercially competitive, flexible urethane foams that meet industry requirements and provide superior performance in both load-bearing properties and resistance to UV degradation. Production of Cargill polyols reduces the risk of exposure to hazardous feedstocks used to manufacture conventional petrochemical-based polyols: ethylene oxide, propylene oxide, styrene, and acrylonitrile. Cargill polyols use the carbon that annual renewable plants remove from the air during photosynthesis. As a result, the net emissions of carbon dioxide from Cargill polyols are lower than emissions from conventional urethane polyols and Cargill polyols have a smaller environmental footprint than do conventional polyols. In addition, Cargill polyols diversify the industry's existing supply options and can mitigate the risks associated with the uncertainty and volatility of petroleum supply and pricing. Each million pounds of Cargill polyol saves 2,200 barrels of crude oil.

Most other commercial, soy-based polyols are better suited for rigid urethane foams, suffer from inconsistent product quality, have poor reactivity, compromise polyurethane performance, and have problems with odor and color. The U.S. market for polyols to produce urethanes is over 3 billion pounds and is growing at 3–4 percent annually. For the first time, Cargill's renewable-derived technology has made it possible to displace a substantial portion of the 1.5 billion pounds of petroleum-based polyols presently used in flexible urethane foam each year. Cargill's technology has the potential to replace 100 percent of the petroleum-based polyols. By the end of 2005, Cargill had produced over 500,000 pounds of these polyols for two major customers; it is planning to build a 200-million-pound-per-year plant by 2008. Cargill biobased polyols can also replace petroleum-based polyols in other urethane applications such as rigid foams, coatings, adhesives, sealants, and elastomers.

Bioderived Solvents, Surfactants, Fuel Additives, and Monomers

DuPont Company (DuPont Central Research and Development)

Many applications of renewable resources require the transformation of these resources into platform molecules, which then are readily converted 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 to convert levulinic acid into a host of desired products. DuPont uses novel catalytic transformations along with other techniques of green chemistry to develop products derived from levulinic acid that can replace petroleum-derived solvents, monomers, and transportation fuels.

The largest opportunity for biobased feedstocks is the production of bioderived fuel additives. DuPont has discovered several new, high-yield routes to levulinic acid esters that are attractive additives to either diesel fuel or gasoline. As another example, DuPont can catalytically hydrogenate levulinic acid and primary amines in a single, high-yield step to a variety of pyrrolidones; these are widely used as solvents and surfactants. Levulinic acid can also be hydrogenated in very high yield to γ-valerolactone, which has several uses including as an intermediate for "green" nylon 6 or nylon 6,6 and as a potential replacement for γ-butyrolactone, the intermediate for a variety of polymers. Using levulinic acid in ways such as these can reduce dependency on petroleum while consuming cellulosic waste.

Closing the Loop with "Benign by Design" Biobased Fabrics and Backings

Interface Fabrics

Interface Fabrics has successfully developed and introduced into the market a sustainable quality textile fabric that uses biobased fibers, environmentally preferable textile finishing dyes and chemicals, and a biobased textile coating. Technical innovations in yarn development, dyeing, weaving, and finishing of biobased fibers were necessary to produce a fabric that meets the stringent standards of the commercial interiors market. The base material for the biobased Terratex® fabric and the BioBac™ textile coating is a homopolymer of polylactic acid (PLA). The fabric is woven from Ingeo™ PLA fiber; BioBac™ is made from NatureWorks™ PLA resin. PLA Terratex® is an alternative to petroleum-derived fibers like polyester; BioBac™ replaces traditional acrylic or styrene-butadiene rubber latex coatings. The biodegradability of PLA allows its reassimilation into plants as a nutrient, thereby closing the loop on raw material utilization. PLA Terratex® composts successfully in a commercial composting facility under standard operating conditions.

Interface Fabrics has developed a stringent dye and chemical protocol to screen all ingredients used to dye and finish PLA Terratex® fabric; the company then selects only those that are not harmful to health or the environment. To date, Interface Fabrics has screened 279 chemicals used in about 147 dyes, finishes, and auxiliaries, approving only about 30 of these chemicals. The protocol excludes ingredients that are carcinogens, mutagens, persistent, bioaccumulative, or toxic chemicals (PBTs), skin sensitizers, etc. Many of these are in common use in fabrics today. To validate the benign nature of its protocol, Interface subjected fabric samples of six different color palettes to hazardous waste characterization and synthetic precipitation leaching analysis. It screened for 179 chemicals of concern, including volatile organic compounds (VOCs), semi-volatile organic compounds, metals, polychlorinated biphenyls (PCBs), pesticides, and carbonyls. It detected only copper, fluoride, nitrate, and sulfate, all at concentrations only marginally above the reporting limit.

Cytec Industries Incorporated

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

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 50 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 effective 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; 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 fumigating stored products. 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 the Roots of Chicory

Fouling of surfaces by mineral salts is a major problem in water-bearing systems because scaling reduces the efficiency of heat transfer and interferes with the operational performance of industrial processes. Previous scale inhibitors were either products with poor biodegradability and moderate toxicity but good performance (e.g., polyacrylates) or biodegradable products with limited applicability (e.g., polyaspartates).

Solutia and Cosun (The Netherlands) used inulin, an oligosaccharide harvested from the roots of chicory, to develop carboxymethyl inulin (CMI). CMI is a cost-effective, safe, and

versatile alternative to traditional antiscalants. It combines excellent scale inhibition of various types of scales, particularly sulfate scales, with good biodegradability and very low toxicity. The product can be used in many applications, but is suited especially well for environmentally sensitive areas, such as offshore oil production. For example, CMI is used in the Norwegian offshore oil-drilling sector of the North Sea. CMI also is a suitable replacement for poorly biodegradable scale inhibitors in water and process water treatment, in sugar refining, and in pulp and paper operations. CMI is a candidate to replace polyacrylates as a laundry aid to prevent re-deposition and as a builder component for automatic dishwasher detergent. In addition to CMI, Solutia and Cosun are developing a wider range of inulin-based products with different functionalities.

In 2004, Solutia began marketing CMI (the first inulin derivative) in the United States under the trade name Dequest PB. During 2005, U.S. customers tested the product.

Development of Nike Brand Footwear Outsole Rubber as Environmentally Preferred Material

Nike, Inc.

One of Nike'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 environment. Nike is pursuing the vision of Considered Design, where its goals are to make innovative, performance-quality products that demand less of our natural resources and to incorporate sustainability as a design component from the beginning.

With these ultimate goals, Nike Footwear has demonstrated its industry leadership by successfully eliminating many toxic substances from its rubber outsoles. Nike Footwear redesigned two of its rubber formulations using the Cradle-to-Cradle™ Design Protocol to assess chemicals against 19 human health and environmental criteria. Using this protocol, Nike identified rubber ingredients to be replaced and preferred alternatives to meet its performance requirements. Using more benign accelerators, vegetable oils, and modified processing, Nike created new environmentally preferred rubber for outsoles. The new formulations contain 96 percent fewer toxic substances by weight than the original formulations, provide equal performance, look the same, and cost no more than traditional rubber. To Nike's knowledge, these are the most advanced and sustainable rubber formulations within the footwear industry; they will help initiate collaboration with manufacturers in other industries in the design and use of more sustainable materials. Nike is currently pursuing the establishment of a consortium of companies to pool resources to jointly research, develop, and use preferred chemicals, helping both to improve cost factors and to increase the sustainability of materials that can be used collectively. The goal is to increase the list of chemicals that are tested and categorized as well as to open the protocol to scientific peer review.

In 2005, Nike produced about 170 million pairs of shoes worldwide that contained some of its new rubber formulations, representing approximately 25,000 metric tons of environmentally preferred rubber.

Development of Water-Based Materials for Post-it® Super Sticky Notes

3M Office Supplies Division Laboratory

In the late 1980s, 3M developed a prototype of a new, enhanced Post-it® Notes product for use on vertical and hard-to-stick surfaces. This prototype used solvent-based adhesive formulations. At the same time, 3M launched an initiative to reduce volatile organic compound (VOC) emissions by 90 percent by the year 2000. Rather than install pollution control equipment to control the VOC emissions from the proposed manufacturing process for the

new Post-it® Notes, 3M delayed introducing the product until it could develop a new, water-based adhesive formulation. 3M finally introduced Post-it® Super Sticky Notes in 2003.

The new water-based microsphere materials that 3M uses in its Post-it® Super Sticky Notes yield the desired performance, generate fewer air emissions, have a reduced environmental risk profile, and are less expensive to manufacture than the original, proposed solvent-based formulations. The formulations are trade secrets, but they are based on acrylate polymers. They do not contain any fluorochemicals, alkylphenol ethoxylates, poly(vinyl chloride), phthalates, or heavy metals intentionally added or present as impurities above *de minimus* levels. The new formulations reduce annual VOC emissions by 33,400 pounds (with pollution controls) or 2,170,000 pounds (before pollution controls) and Toxic Release Inventory (TRI) emissions by 20,500 pounds (controlled) or 1,024,000 pounds (before control) compared to the projected emissions of the proposed, solvent-based process. The water-based system eliminates the need for a thermal oxidizer to control VOC emissions, reducing 3M's emissions of CO_2 from fuel combustion. It also increases worker safety and reduces the possibility of fire, chemical release, or explosion. The water-based system also generates significant cost savings.

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. Following its success with Post-it® Super Sticky Notes, 3M added water-based formulations to Post-it® Sticky Picture Paper for printing digital pictures and to other specialty applications in 2005.

Headwaters NanoKinetix, Inc.

Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

Hydrogen peroxide (H_2O_2) is a clean, versatile oxidant with many industrial uses and the potential for many more. Projected global demand for H_2O_2 in 2006 is approximately 1.8 million metric tons. Applications include use in the pulp and paper industry, chemical manufacturing, and laundry products. Demand for H_2O_2 has grown in recent years, but its high production cost makes it more expensive than chlorinated oxidants, which have deleterious environmental impacts. The current H_2O_2 manufacturing process is complex, expensive, and energy intensive. It also requires large amounts of hazardous and toxic chemicals and creates undesirable byproducts that must be kept out of the environment.

Researchers in industry and academia have long sought an inexpensive, commercially viable, and environmentally benign method for synthesizing H_2O_2 directly from hydrogen and oxygen. Several technical challenges (including the potential of hydrogen gas to explode) have kept others from developing a safe, direct synthesis for H_2O_2 in industrial settings.

NxCat catalyst technology is a highly selective, robust nanocatalyst technology that has overcome these challenges through the adroit use of a catalyst with proprietary molecular templates and appropriate substrates. The molecular templates are usually made of organic molecules or polymers with many functional groups that have specific effects on the catalyst, a precisely tailored combination of palladium and platinum in a molar ratio of 50:1. Through the precise control of the size, composition, dispersion characteristics, and stability of the catalytic nanoparticles and the catalyst crystal structure, the NxCat technology achieves up to 100 percent reaction selectivity for H_2O_2. It requires no hazardous materials and produces no byproduct except water.

Headwaters NanoKinetix has tested its technology in partnership with a major H_2O_2 manufacturer and will be demonstrating it on an industrial scale during 2006. The new technology is expected to be ready for market in 2007.

Duraflame® All-Natural Manufactured Firelog

Duraflame, Inc.

Duraflame, Inc. is America's leading marketer of manufactured firelogs. Headquartered in Stockton, CA, 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 (to replace petroleum wax) as a combustible binder. Standard petroleum wax–sawdust firelogs produce approximately only one third of key air pollutants associated with residential wood combustion compared to an equivalent natural wood fire. In contrast, Duraflame's new all-natural firelogs produce approximately one quarter of the emissions of an equivalent natural wood fire. The Duraflame® All-Natural Firelog is now available in supermarkets across the United States and Canada.

Environmentally Advantaged Formulations for Aircraft Ice Control

Foster-Miller, Inc.

During the 1992–1993 deicing season, the 20 largest airports in the United States used over 11 million gallons of aircraft deicing fluids (ADFs). The large quantities of effluents that are released into the environment during aircraft deicing operations have resulted in several reportable incidents of environmental damage in the vicinity of airports throughout the world. This damage is caused by the high biological oxygen demand (BOD) of current ADFs that deplete oxygen levels in receiving waters sufficiently to distress and kill aquatic life. Airports are now required to obtain National Pollutant Discharge Elimination System (NPDES) permits to discharge ADFs into storm water sewers. Regulations under development by the U.S. EPA are expected to be much more restrictive. In addition, treatment costs of current ADFs are between $12 and $20 per gallon of deicing fluid, several times the purchase price of approximately $5 per gallon.

LBOD, Foster-Miller's new ADF formulation, consists of a mixture of triethylene glycol and glycerol. Foster-Miller designed it to have unique BOD characteristics that do not impose an environmental threat: its 5-day BOD is as much as 85 percent lower than that of current ADFs based on propylene glycol.

The new formulation can also be modified to have a high degradation rate with a reduced BOD, making it advantageous for high-volume users with onsite treatment facilities. The flexibility of the new ADF technology provides airport authorities with the option of either treating their waste or discharging it without treatment, depending on their size and situation. In either case, the new technology will substantially reduce life-cycle costs for deicing fluids. The new technology is also expected to expedite the associated environmental permitting process. Foster-Miller's technology is currently being demonstrated at the Niagara Falls Air Reserve Station in Niagara Falls, NY.

Bunge North America and Novozymes North America, Inc.

Enzymatic Degumming of Vegetable Oils: Reducing Environmental Impact and Improving Oil Yield

Typical production of refined, bleached, deodorized vegetable oil, particularly soy oil, involves removing lecithin and phospholipid (the naturally occurring gums) with phosphoric acid and caustic in succession. Centrifugation of the final aqueous-oil mixture removes the aqueous phase along with the gum. The process uses a final pH in excess of 7, which saponifies the oil and generates soapstock (a mixture of fatty acid salts and gums). This soapstock has no value, and it is often sent to landfills.

The new Bunge/Novozymes process uses relatively small amounts of citric acid and caustic along with a phospholipase (Lecitase® Ultra) and about 2 percent water. Lecitase® Ultra cleaves the fatty acid from the 1-position, yielding a *lyso*-phospholipid and a fatty acid. Centrifugation then readily removes the aqueous mixture containing *lyso*-lecithin, which is of value for animal feed. Finally, the deodorization step removes the free fatty acids, which can be used as a valuable coproduct or processed into other products such as biodiesel fuel.

Enzymatic degumming of vegetable oil reduces the phosphorous content of the oil (a measure of residual gums) to below 5 ppm. The process generates less water and soapstock waste and increases oil yield, reducing the environmental impact with respect to traditional processing.

The average annual production of soy oil in the United States is approximately 9.5 million metric tons. Lifecycle analysis shows that if all of this oil were refined using the Bunge/Novozymes enzymatic process, carbon dioxide (CO_2) emissions would be reduced by an amount equal to the average population environmental effects of over 200 million people and energy would be saved by an amount equal to over 2 million barrels of refined gasoline.

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

Enzyme-Based Technology for Decontaminating Toxic Organophosphorus Compounds

The U.S. Army Edgewood Chemical Biological Center (ECBC) has developed and patented a technology that neutralizes 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 deicing 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 United States, is using 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™. Kidde Fire Fighting introduced the first such commercial product, All-Clear™, in August 2005.

Enzymes to Improve Paper Quality, Reduce Energy Use, and Increase Recycling of Paper

Buckman Laboratories International, Inc.

Buzyme® from Buckman Laboratories is a novel enzymatic technology to modify the wood fibers used to manufacture paper. Buzyme® consists of a group of new cellulytic or hemicellulytic enzymes; for each grade of paper, Buckman selects the enzyme from the group that provides optimum results. This enzymatic treatment of the wood fiber reduces the amount of mechanical refining required to reach desired fiber properties. In various commercial applications in paper mills, this invention has given benefits such as increased use of recycled paper, reduced energy needed to produce paper, and improved quality of paper goods made from recycled paper. This technology improves the strength of paper and paperboard, reducing the use of chemicals to improve strength. Less energy is needed to give the required strength to paper products. The technology is already in use successfully in about 10–15 paper machines in North America; these machines produce tissue papers, napkins, corrugated boxes, and other grades of paper. One paper mill that makes dinner napkins was able to use recycled fiber exclusively and save $1 million that it had been spending for virgin wood pulp each year.

Buzyme® products make it possible to recycle more paper, produce paper more efficiently, and manufacture higher quality paper. Enzymes produce several benefits: enzyme biotechnology comes from renewable resources, is safe to use, and is itself completely recyclable. Use of these enzymes reduces requirements for chemicals derived from petroleum feedstocks. These enzymes are nontoxic to human health and the environment. They are produced by fermentation from readily available renewable resources. Although this technology has been studied in laboratories for some years, Buckman has only recently found the keys to make it successful on a full-scale industrial basis.

Flexible NORYL Resins for Wire Coating*

GE Plastics

Poly(vinyl chloride) (PVC) has been widely used in the wire and cable industry as both insulation and jacketing material for decades. The current annual U.S. consumption of PVC for these applications is about 300,000 metric tons. During its product cycle, PVC contributes significantly to ozone depletion, global warming, and the release of cancer-suspect dioxin and phthalate. It releases toxic smoke containing hydrogen chloride and cancer-suspect dioxin during its manufacture and incineration.

GE Plastics has invented and commercialized ten grades of flexible poly(arylene ether) resins that substitute for PVC in coatings and coverings for wire and cable. They market them as Flexible NORYL* resins. GE's Flexible NORYL* resins are based on proprietary compositions containing poly(arylene ether), polyolefin, and a nonhalogenated flame retardant. Flexible NORYL* resins totally eliminate halogenated compounds, heavy metal stabilizers, pigments, and phthalates. Moreover, Flexible NORYL* resins may facilitate the reuse of wire coating to benefit the environment. Wire coatings made with Flexible NORYL* resins have helped the consumer electronics and automotive industries meet stringent environmental initiatives, such as the European Union's ISO 14020 and ISO 14024 and EcoMark in Japan.

For the consumer electronics industry, wire coatings made from Flexible NORYL* resins offer better heat performance, increased flame retardant properties, and lower costs due to reduced weight. In the automotive industry, NORYL* resins can improve vehicle performance by improving abrasion resistance, improving heat performance, and allowing more compact electronics. The light weight of Flexible NORYL* resins and their outstanding abra-

sion resistance enable ultrathin wall wire construction. They may reduce an automobile's wire-resin weight by as much as 25 percent. Flexible NORYL* resins can make a significant contribution to helping global automotive manufacturers meet end-of-life and take-back requirements including the European Union's Restriction of Hazardous Substances and End-of-Life Vehicle directives, Japan's Automobile Recycling Law (2005), and the Japan Automobile Manufacturers Association (JAMA) guidelines.

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

GF-120™ NF Naturalyte™ Fruit Fly Bait

Tephritid fruit flies, including the Mediterranean fruit fly, are important quarantine pests that can devastate fruit and vegetable production and limit the transportation 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 0.5–1.0 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 United States.

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 has redesigned its celecoxib manufacturing process with green chemistry objectives as some of the project's primary goals. The results are 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 increased expense. Celecoxib made by Pfizer's new process is pure enough to permit final isolation directly from the reaction mixture; 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. Compared to its initial process, Pfizer's new process (based on 2003 production volume) reduced total waste (excluding water) from 8.9 million to 2.4 million kilograms per year (waste reduced from 23.4 to 6.3 kilograms per kilogram celecoxib). In total, Pfizer has eliminated 5,200 metric tons per year of organic solvents. Pfizer has also completely removed tetrahydrofuran and 35 percent

hydrochloric acid (212 metric tons per year). Organic solvent washes during isolation have been partially replaced 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 saves over 4 billion Btu 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.

The U.S. FDA has approved Pfizer's improved manufacturing process for celecoxib; more than 50 similar agencies worldwide have also approved the new process. These regulatory authorities now require Pfizer's new process for all commercial pharmaceutical manufacture of celecoxib.

Green Chemistry in the Redesign of the Pregabalin Process

Pfizer Global Research and Development

Pregabalin is the active ingredient in the medicine Lyrica®, which received FDA approval in the United States in December 2004 for the management of neuropathic pain associated with diabetic peripheral neuropathy and posthermetic neuralgia. Pfizer's initial commercial synthesis of pregabalin was launched in late 2005. In this route, Pfizer synthesized the desired chiral molecule as a racemic mixture and resolved it in the final step with stoichiometric amounts of (*S*-)mandelic acid. The resolution was only modestly efficient, and the undesired enantiomer could not be recycled. Nearly 70 percent of all process material, including intermediates, reagents, and solvents, ultimately became waste.

Pfizer's new route to pregabalin uses an innovative biocatalytic route. Pfizer identified the enzyme for its new route by high-throughput screening. The new process uses a relatively inexpensive, food-grade enzyme, operates at high substrate concentrations, eliminates organic solvents from all four reaction steps, and dramatically improves environmental performance and worker safety. At projected peak production, the biocatalytic process will eliminate 5 million gallons of organic solvents annually, including tetrahydrofuran, methanol, and ethanol. Additional gains in process efficiency have also reduced starting material demands and reagent consumption. Based on a projected production of 400 to 500 metric tons per year for pregabalin, the overall annual reduction in reagents and starting materials ranges from 893 to 1,116.3 metric tons. Using its biocatalytic route, Pfizer can recycle the undesired enantiomer of the starting material, increasing the overall yield significantly and reducing the amount of starting materials required. Pfizer believes that pregabalin must be one of very few pharmaceutical agents in which every chemical step in the manufacturing process is performed in water.

Pfizer has successfully demonstrated its new biocatalytic process at production scale and will increase the batch size further in 2006. Because Pfizer implemented its new synthesis soon after FDA approval, it will realize the environmental benefits for almost the entire product lifecycle.

Guar-Based Chemistry Advances Targeted Performance of Crop Sprays by Reducing Drift and Improving Retention

Rhodia Inc.

It is estimated that less than 10 percent of all sprayed pesticides reach their intended targets. A major reason for the off-target movement of pesticides is the drift of the droplets and the inability of the droplets to stick to a leaf or plant surface.

Rhodia uses derivatives of guar, a naturally occurring polysaccharide, to solve this problem. Hydroxypropoxylation (HP) of guar improves its hydration, making it amenable to uses in a wide range of temperatures. Rhodia's technology uses HP-guar to mitigate the effect of drift and improve the retention of pesticide droplets on target surfaces. Guar-based polymers can reduce drift by increasing droplet size and can improve the retention of droplets by providing a "shock absorber" effect. The results of field trials using pesticides corroborate Rhodia's fundamental studies: when guar-based polymers are added to a fungicide against the pathogen Asian soybean rust, both the efficacy and the crop yield increase. Also, results of field tests using an herbicide show that guar-based polymers increase weed kill across the board. More importantly, a very small amount of HP-guar (0.07 percent) can increase efficacy considerably, irrespective of the active ingredient.

Rhodia sells HP-guar for agricultural applications as AgRHO™DR 2000. Farmers currently apply AgRHO™DR 2000 on more than 16 million acres of soybeans in the United States, which represents 15 percent of the total sprayable soybean acreage. Within the next five years, Rhodia expects to apply its technology to other crops covering more than triple the current sprayable acreage.

Rohm and Haas Company and Johns Manville

Invention and Commercialization of Environmentally Smart Thermosetting Binders

Thermosetting binders give shape and strength to nonwoven fibrous materials, including fiberglass insulation. The most common thermosetting binders are formaldehyde based, but concern with formaldehyde's potential as a carcinogen and as an indoor air pollutant has sparked research for safer alternatives. Manufacturing operations and products that rely on formaldehyde-based technologies also require expensive emissions abatement equipment, employee protection measures, special handling, and transport.

In response, Rohm and Haas Company (ROH) has developed and patented Aquaset™ acrylic thermosetting binders, a family of formaldehyde-free, curable, aqueous solutions of poly(acrylic acid), triethanolamine, and sodium hypophosphite (NaHP). Hypophosphite catalysis had been used earlier for esterification in permanent press fabric applications; ROH adapted it to fiberglass insulation to achieve greater network formation and robust physical properties. ROH enhanced reactivity and cross-linking by using NaHP as both an esterification catalyst and a chain-transfer agent. Ultimately, they enhanced the mobility of the polyol within the curing resin, increased the reactivity of primary alcohols such as triethanolamine, and optimized the cure temperatures.

Combining these steps, ROH created a class of acrylic thermosets that is an ideal green chemistry alternative to phenol-formaldehyde resins. The byproduct of cure is water; the technology eliminates formaldehyde wastes, emissions, and exposures. Aquaset™ technology is nonreactive, nonflammable, recyclable, and benign at ambient conditions to ease handling, transport, storage, application, and cleanup.

Johns Manville (JM) has been refining the Aquaset™ technology along with ROH. Since 2002, when it began manufacturing formaldehyde-free fiberglass insulation, JM has converted all of its building insulation products to the Aquaset™ technology, eliminating the emission of more than 200,000 pounds of formaldehyde and one million pounds of ammonia each year. JM has also eliminated more than 180,000 pounds of phenol and 280,000 pounds of methanol emissions per year. JM is now the only manufacturer exempted from the U.S. EPA National Emission Standards for Hazardous Air Pollutants (NESHAP) for Wool Fiberglass Manufacturing.

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. Other projected benefits include a 325-ton reduction in solid waste requiring incineration and a savings of 24,400 megawatts of energy from recycling the two remaining process solvents.

JONCRYL® FLX 5000: A High-Performance, Water-Based Polymer to Facilitate the Conversion from Solvent- to Water-Based Inks in Surface Film Flexible Packaging Printing

Johnson Polymer, LLC

The inks used in the flexible packaging industry must meet extensive performance requirements. They are expected to print well on a variety of flexible substrates and provide good print quality, excellent water and chemical resistance, adhesion, crinkle resistance, and heat resistance. Traditionally, such requirements have demanded that printing inks be solvent-based. Typical solvents are alcohols and acetates. An estimated 135–150 million pounds of solvent-based inks are used each year in the United States for applications on film and laminated flexible packaging. This high-volume use is, however, associated with environmental and handling concerns.

Johnson Polymer has developed a unique, water-based, self-cross-linking polymer system that has enhanced the performance of water-based inks significantly. Specific improvements include water-resistance, crinkle-resistance, and adhesion. At the same time, the new inks maintain the on-press resolubility that is critical for high-quality printed images.

This nomination compares the performance of JONCRYL® FLX 5000, a new self-cross-linking, water-based polymer, to that of traditional water-based polymers; it also compares print trials using water-based inks based on JONCRYL® FLX 5000 to a traditional solvent-based ink.

Johnson Polymer formally introduced JONCRYL® FLX 5000 to the U.S. printing ink manufacturing market in October 2005, culminating a research and development effort in the United States and Europe spanning the previous three to four years. Johnson Polymer has conducted multiple press trials, resulting in ongoing commercial sales in Europe and initial trial sales in the United States.

Merck & Co., Inc.

Kilogram-Scale Purification of Pharmaceutical Candidates and Intermediates Using Preparative Supercritical Fluid Chromatography

Preparative chromatography is increasingly used in the pharmaceutical industry to purify kilogram quantities of developmental compounds for preclinical evaluation. Historically, the industry has carried out these separations by high-performance liquid chromatography (HPLC) using large amounts of petrochemical-derived organic solvents. Merck has recently demonstrated the possibility of performing these separations at the kilogram scale using subcritical or supercritical fluid chromatography (SFC), in which pressurized carbon dioxide (CO_2) replaces the hydrocarbon solvents often used in HPLC.

Using custom-designed preparative SFC equipment prepared in collaboration with several vendors, Merck has recently carried out the first kilogram-scale SFC enantioseparations of pharmaceutical intermediates in the pharmaceutical industry. Merck has reported its results in a recent publication (Welsh, C.J. et al., *LC-GC*, 2005, 16-29). In one example, enantioseparation of 2.5 kilograms of an intermediate was projected to require 36,000 liters of solvent by HPLC versus only 900 liters by SFC. Although this example is extreme, a 10-fold decrease in solvent consumption is typical. Equally important, SFC also produces a corresponding decrease in solvent evaporation, leading to considerable savings in equipment, time, and energy. Further, preparative SFC is generally more productive than HPLC, especially for chiral separations. The SFC advantage can be extreme, as in the case where there was no suitable HPLC purification for a single stereoisomer of a drug candidate intermediate, yet SFC (5 cm i.d. column, 350 g/min, 830 L organic solvent) purified 1.7 kilograms easily in only 72 hours. During 2005, Merck demonstrated preparative SFC using a 15-ton CO_2 bulk tank and custom-built, 3-kilogram-per-minute CO_2 delivery system.

Merck has demonstrated that preparative SFC is not only a more environmentally friendly method for purifying development drugs and intermediates, but is simply better, with greater productivity and cost-effectiveness, both important considerations for large-scale separations to support pharmaceutical manufacturing.

Syngenta

Mesotrione and Callisto® Plant Technology

The mesotrione story began when a U.S. Syngenta scientist noticed that few weeds were growing under a *Callistemon citrinus* (bottle brush) plant. Upon analyzing a soil sample, he discovered that the Callistemon plant secretes an herbicidal compound through its roots, an ability known as allelopathy. Using a combination of infrared spectroscopy, mass spectroscopy, and nuclear magnetic resonance, he identified the structure of the allelopathic compound produced by the bottle brush plant as leptospermone. This allelochemical, leptospermone, presented interesting properties including good foliar activity, soil activity, being tolerated well by corn, and control of a wide range of weeds.

Scientists at Syngenta discovered mesotrione ($C_{14}H_{13}O_7NS$; MW 339.32) by modifying and optimizing the backbone of leptospermone. Mesotrione has the same mode of action as leptospermone, but is 20 times more potent and, thus, more commercially viable. Mesotrione is a member of the triketone group of selective herbicides that act by inhibiting the enzyme *p*-hydoxyphenylpyruvate dioxygenase (HPPD). HPPD is part of the biosynthetic pathway for carotenoid, a precursor of chlorophyll. Thus, inhibition of HPPD causes bleaching followed by necrosis in sensitive plants (i.e., target weeds).

In 2001, U.S. EPA approved mesotrione as a reduced-risk herbicide. Shortly thereafter, Syngenta introduced Callisto®, a mesotrione-containing herbicide for post-emergent weeds.

Callisto® challenged all competitive broadleaf herbicides for use in corn crops: during its first full-season year in 2002, it achieved almost a 25 percent share of the post-emergent, broadleaf weed control market, treating more than four million acres. Syngenta's introductions of two mesotrione formulations for pre-emergent weeds, LUMAX® in 2003 and Lexar® in 2005, added strength to the Callisto Plant Technology family. Today, farmers worldwide recognize mesotrione and Callisto Plant Technology as unique herbicide products that provide important benefits including exceptional crop safety, unprecedented broadleaf weed control, application flexibility, and a 21st-century environmental profile.

New Asymmetric Hydroxylation Technology for the Commercial Manufacture of Indoxacarb

DuPont Company (DuPont Crop Protection)

Indoxacarb is a major new insecticide marketed worldwide by DuPont Crop Protection. The U.S. EPA has designated indoxacarb as both a reduced-risk pesticide and an organophosphate replacement. Indoxacarb is the insecticidally active *S*-form of a racemic pair; the *R*-form is not active.

It is undesirable to manufacture and apply racemic mixtures of pesticides, due both to the environmental burden of the inactive enantiomer and to the waste generated in its production. Recognizing this, scientists at DuPont developed new proprietary technology for the asymmetric synthesis of indoxacarb. The first-generation process used cinchonine to catalyze an asymmetric hydroxylation, affording a 50-percent enantiomerically enriched product. DuPont used this technology for its first commercial production of indoxacarb in January 2000. Then, improving on its earlier technology, DuPont developed a second-generation process that uses proprietary complexes of chiral diamine ligands and zirconium to carry out the critical asymmetric hydroxylation in high yield with high enantiomeric excesses.

Commercial production of the first fully enriched indoxacarb (with over 98 percent enantiomeric excess) began in September 2005. At current production volumes, DuPont's new synthesis of indoxacarb is reducing the total material burden on the environment by hundreds of tons per year over the first-generation process. In the United States, indoxacarb is marketed as DuPont Steward® Insecticide and DuPont Avaunt® Insecticide; it is currently registered in over 70 countries. Worldwide sales were $130 million in 2004 and are expected to reach $150 million in 2005.

Nexterra™ Carpet: Modified PET Carpet Backing

Beaulieu Group, LLC

Carpet tile backings have previously been made of polymers such as Poly(vinyl chloride) (PVC), polyurethane, or mixtures of various thermoplastics that are derived from petrochemicals. The manufacture or disposal of some of these backing materials raises environmental concerns. Further, the energy required for the physical separation of the tile backing and the face fiber (usually by grinding or air elutriation) adds to the cost of recycling current tile backings. Physical separation also leads to impure component streams for recycling.

Beaulieu has developed a modified polyethylene terephthalate (PET) backing system that contains a much lower percentage of products derived from virgin petroleum, requires significantly less energy to produce, and offers new solutions to carpet tile recycling. Beaulieu had already been purchasing postconsumer PET bottles and converting them into carpet fiber. Now, however, Beaulieu is also converting plastic PET bottles into a pliable, flexible carpet tile backing system using a unique transesterification process (patent allowed). This process lowers both the molecular weight and the melting point of the polymer. Beaulieu's

modified PET polymer allows them to use postconsumer ground glass as a filler in their backing. Altogether, their backing system contains 85 percent post-consumer materials and only 15 percent virgin petrochemicals by weight. Traditional carpet tiles have approximately 50 percent virgin petroleum content. The exclusive modified PET backing enables more cost-effective and energy-efficient recycling. The solubility of the polymer in polar solvents allows separation of the carpet tile backing from the face fiber (usually nylon 6 or 6,6). During recycling, Beaulieu uses a glycol monomer bath at 150–180 °C to dissolve the polymer, separating it and the glass from the insoluble face fiber.

Beaulieu launched Nexterra™ carpet tiles in May 2005. The company estimates its 2005 product sales at $1–5 million; Beaulieu is expecting significant sales growth during 2006.

Georgia-Pacific Corporation

Nitamin® Steady-Delivery Fertilizers for Improved Nitrogen Efficiency in Crops

Worldwide, farmers apply approximately 82 million metric tons of nitrogen fertilizer, primarily urea, to cropland annually. Plants are often unable to take up all of the nitrogen released into the soil from urea hydrolysis and salt-based fertilizers such as ammonium nitrate, so the excess nitrogen leaches through the soil and contaminates nearby waterways. Agricultural nitrogen is a major contributor to the increasing nitrate levels in many waterways around the world. These excess nitrates create hypoxic areas in which the levels of dissolved oxygen are too low to support life.

Nitamin® fertilizers provide an economic solution to this problem by slowing the rate at which nitrogen is available to the plant. By reacting urea with ammonia and formaldehyde under specific conditions to form a blend of small urea-formaldehyde polymers and cyclic compounds, Georgia-Pacific can control the rate at which the nitrogen is released to plants. The primary Nitamin® fertilizer product releases nitrogen for approximately 90 days, corresponding well to the requirements of many crops. This controlled delivery allows the plant to use more of the applied nitrogen, resulting in reduced application rates and reduced leaching. Nitamin® fertilizer reduces the amount of nitrogen used by 25 percent (onions and tomatoes) to 55 percent (cabbage); in other studies with potatoes, onions, and tomatoes, Nitamin® fertilizer increased crop yields by 7–54 percent. Based on U.S. figures alone, even a 5 percent reduction in the amount of nitrogen applied to crops could lead to 810 million pounds less nitrogen applied annually. This improved efficiency of nitrogen use coupled with affordability is the highlight of this technology.

Georgia-Pacific first commercialized its technology in January 2004. During 2005, universities and growers ran over 80 trials with different crops to verify the marketability of Nitamin® fertilizer. During spring 2006, Georgia-Pacific will commercialize a liquid Nitamin® fertilizer for use on vegetables.

JohnsonDiversey, Inc.

A Novel Cleaning System Using Less Toxic, Safer Chemicals

The nominated process cleans and sanitizes the poly(ether sulfone) 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 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. Their technology consists of an aqueous solution of hydrogen peroxide, a 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 the environment. This technology has a great economic impact by performing the cleaning and sanitization at lower temperatures; it saves energy by as much as 43 percent, reduces plant downtime by as much as 18 percent, decreases water use by as much as 33 percent, 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 the typical system, JohnsonDiversey has demonstrated average savings of $700,000 per dairy plant per year. As of the end of 2004, JohnsonDiversey had tested and verified its new technology in a pilot plant membrane module for two years.

Oxygen-Enhanced Combustion for NO_X Control

Praxair, Inc.

The abundance of coal and expected high costs for other fossil fuels, such as natural gas, suggest that coal-fired power plants will still be in use 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, oxygen replaces a small portion of the combustion air in a staged combustion system, increasing the local temperature under fuel-rich conditions. These higher flame temperatures convert NO_X to N_2 in the flame zone. In equipment from laboratory-scale furnaces to a nominal 125-megawatt power plant, oxygen-enhanced staged combustion reduces NO_X emissions by as much as 60 percent without the 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. In two industrial boilers at the P.H. Gladfleter Paper Company in Pennsylvania, OEC systems reduced NO_X emissions by over 40 percent.

By minimizing NO_X formation in the combustion zone, OEC reduces or eliminates the need for postcombustion cleanup technologies such as selective catalytic reduction (SCR) that require ammonia. 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. Further, because ammonia production requires natural gas, minimizing ammonia also helps preserve this important natural resource. Making broad assumptions about 600 coal-fired plants in 22 states, Praxair estimates that 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.

LANXESS Corporation

Picaridin: A Safe, Effective, and Environmentally Friendly Insect Repellent that People Will Use

Under a commitment to Responsible Care®, LANXESS Corporation and its parent company, LANXESS Deutschland GmbH (formerly part of Bayer AG), developed, manufacture, and market picaridin, an insect repellent. Picaridin offers a safe, effective, user-friendly, and environmentally responsible alternative to traditional repellents that are based on the widely known and frequently employed active ingredient diethyl-*m*-toluamide (DEET). Unpleasant odors, stickiness, and cautions associated with many formulations of insect repellent too frequently may deter people from using these products, thus leaving themselves unprotected from the risk of bites, infection, and disease.

Picaridin results from scientific innovations that overcome the cosmetic disadvantages that keep people from using insect repellents. The LANXESS active ingredient is marketed globally under the registered trademark BAYREPEL®; generically, it is recognized as picaridin in the United States, where LANXESS introduced it in 2005. Picaridin was developed to increase efficacy against a broad range of insects and to improve cosmetic performance. Its attributes include (1) broad effectiveness against mosquitoes, ticks, sandflies, and horseflies; (2) cosmetic acceptability: gentle on the skin, non-sticky, almost no scent to humans; (3) not damaging to plastics, fibers, coatings, or sealing compounds; (4) can be used during pregnancy and breast-feeding; and (5) safe for children age two and older.

Picaridin is a custom molecule developed under a hypothesis that repellency is triggered by action on specific olfactory receptors of insects. Three-dimensional modeling was used to map a molecule to interact with the insects' receptors. Picaridin undergoes a fast and thorough primary biodegradation, yielding the more stable metabolite, picaridin acid. In tests carried out in Germany, neither groundwater nor tap water contained residues of picaridin or picaridin acid, indicating the complete degradation and removal of the substances by sewage treatment plants and groundwater conditioning systems.

U.S. Department of Energy, Pacific Northwest National Laboratory, operated by Battelle Memorial Institute

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

Mercury contamination has long been recognized as a serious threat to national and global environments. Development of innovative technologies to remove mercury without producing harmful byproducts or secondary waste is critically important to our constantly changing industries and environment.

Thiol self-assembled monolayers on mesoporous silica (thiol-SAMMS) can absorb mercury and other heavy metals 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 U.S. Department of Energy's 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 resid-

ual 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. Steward Advanced Materials in Chattanooga, TN, has licensed the technology and will be manufacturing SAMMS using the PNNL synthesis. Other licenses are pending with an oil- and gas-filtration equipment company for offshore oil and drilling applications and a major oil company.

SONOXIDE Ultrasonic Water Treatment System

Ashland Specialty Chemical Drew Industrial

Both oxidizing and non-oxidizing chemical microbiocides are commonly used to control microorganisms in recirculating cooling water systems. Typically, these chemicals are the most corrosive, hazardous, and toxic portion of the overall water treatment program. This applies to both process and comfort cooling systems.

SONOXIDE ultrasonic treatment eliminates the use of chemical biocides along with their hazards and toxicity. The SONOXIDE system is a self-contained, turnkey unit that requires only plumbing and power for installation to a bypass of a recirculating water system. It controls total bacteria, biofilm, and algae with a unique, patented ultrasonic treatment incorporating low-power, high-frequency ultrasound, and microbubble aeration. The resulting intracellular stress to microorganisms is not immediately fatal; instead, the treated microorganisms circulate throughout the water system and disrupt the balance of the microbiological community, inducing systemwide microbiological control. SONOXIDE treatment reduces both sessile and planktonic organisms throughout the system. Controlling microorganisms maintains the cleanliness of water systems, reduces energy use, extends equipment life, and eliminates handling and disposal of chemical biocides.

Ashland Specialty Chemical first introduced SONOXIDE treatment in Europe in 2003 and in the United States in 2004. Worldwide, SONOXIDE units are successfully treating over 350 recirculating cooling water systems with this technology.

Tide Coldwater®: Energy Conservation through Residential Laundering Innovation and Commercialization

Procter & Gamble Company

Procter & Gamble has recently commercialized a patented, breakthrough chemical innovation in environmentally friendly cleaning technology to provide superior cleaning and significant energy savings in low-temperature (60 °F) wash water. Over 6 million U.S. households have used Tide Coldwater® since its introduction in North America in January 2005.

Tide Coldwater® uses surfactant systems designed to be more hydrophobic than other detergents. The liquid detergent formula uses an optimized combination of alcohol ether sulfate, linear alkyl benzene sulfonate, ethoxylated zwitterionic surfactants, and alkyl amine surfactants. The powder detergent formula is based on high-solubility alkyl sulfate, a proprietary branched surfactant. In combination with a unique bleach activator, builder/chelant, soil suspension, enzymes (protease and amylase), and brightener systems, these proprietary surfactant systems deliver superior cleaning performance in cold water.

Blind consumer tests have shown that Tide Coldwater® provides superior cleaning in cold water relative to detergents formulated for warm and hot water. Without sacrificing performance in stain removal or whitening, consumers can save up to $63 per year in home energy

costs while reducing greenhouse gas emissions from fossil-fueled power plants. Using a peer-reviewed model for residential energy use, Procter & Gamble estimates that Tide Coldwater® will reduce the fraction of residential energy used to heat water by up to 26–36 percent, with an associated reduction in carbon dioxide (CO_2) emissions of up to 1,259 pounds per household per year. The potential benefits of this innovation are significant: if everyone in the United States switched to cold water for laundry, the potential energy savings would be 70–90 billion kilowatt-hours per year, representing up to 3 percent of the nation's energy consumption. These savings are the equivalent of 26–34 million tons of CO_2 per year, representing over 8 percent of the CO_2 reduction target for the United States set in the Kyoto Protocol.

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 has 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 6.1 metric tons of tin–lead eutectic solder; in five years, it should replace 50 metric tons of solder a year.

Ecolab Inc.

Wash 'n Walk™ Floor Care System

Standard industrial floor cleaners are based on heavy-duty alkaline or acid blends of surfactants and water conditioners. They typically require warm water and rinsing after use. Over time, however, lime scale, polymerized grease, and detergent residuals build up, contributing to slippery floors and worker accidents.

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 accumulated grease deposits. Formulated to clean kitchen floors, Wash 'n Walk™ incorporates a patent-pending, low-alkaline 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 using substantially less water; (2) clean grout, reducing the potential for growth of odor-producing bacteria; and (3) extensive removal of

polymerized grease, resulting in a significant increase in the coefficient of friction (i.e., increased slip resistance) of kitchen quarry tile floors and reducing worker accidents. In addition to institutional and industrial floors, Wash 'n Walk™ is suitable for cleaning floors and grout in household kitchens.

Ecolab introduced Wash 'n Walk™ in January 2004; by December 2005, over 50,000 customer sites in North America were using this product. If half of these 50,000 locations employed Wash 'n Walk™ daily, 273 million gallons of water would be saved each year. Ecolab has introduced this product in Canada and will expand to global sales in 2006. Globally, Ecolab estimates that there are over one million potential institutional and industrial users for this technology.

Xerox's Emulsion Aggregation Toner Technology

Xerox Corporation

Toner is the dry ink for laser printers and copiers. Xerox's Emulsion Aggregation (EA) toner technology represents a breakthrough in the chemistry and chemical processing of toner materials. It is a unique, environmentally friendly technology that allows customers to print in color more accurately and affordably. There are over 400 patents protecting this Xerox innovation.

Toners are a mixture of plastic resin, colorant, and other ingredients. The conventional method of making toners uses a top-down approach: a mechanical mechanism physically grinds composite polymeric materials into micron-sized particles, which are then sorted by size. The EA technology uses sophisticated chemical design- and control-based nanotechnology methods to generate toner particles of about 3–5 microns in diameter from nanoscale components in a bottoms-up approach. The process includes a semicontinuous emulsion polymerization in water to generate nanometer-scale polymer particles.

The key advantages of EA technology are its ability to control the size, shape, and structure of the particles. This technology improves print quality, uses less toner, wastes less toner, and decreases energy use, both for manufacturing toner and for using it in printing. Xerox can now produce toner using 25–35 percent less energy per pound of toner. Combined with 40–50 percent less toner needed during printing, EA technology offers an estimated 60–70 percent energy savings per printed page. EA technology produces less waste and increases the life of machine parts. EA is an environmentally friendly, water-based process.

The Xerox Research Centre of Canada and its Xerox partners in the United States and Japan jointly developed this technology. Xerox introduced its EA technology in 2002 in its DocuColor 1632/2240 color copier/printers; currently, several other Xerox products also use this technology. In June 2005, Xerox announced plans to build a second EA toner plant on the company's property in Webster, NY.

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

Rust-Oleum Corporation

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 contains zero volatile organic compounds (VOCs), zero hazardous air pollutants (HAPs), and no odor. As a commercial product line, these coatings are reducing VOC and HAP emissions, which have in return translated into broad-based benefits for end-users (paint applicators, workers, and building occupants) and the macro-scale 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 distributions, and chemical composition without solvents. These compositions, combined with other traditional raw materials for paints and coatings, activate upon the evaporation of water. The principal component of the 2K products is a proprietary, advanced molecular-weight epoxy polymer with a unique distribution of molecular weight; it 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, both patented and trade-secret, have made possible new designs for waterborne resins, coatings, and paint products that meet the demanding performance of institutional and industrial environments, while not contributing any airborne environmental emissions or worker safety issues.

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