Draft Summary of 2004 Award Entries and Recipients: Presidential Green Chemistry Challenge Awards Program

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Note: This document does not contain the summaries of the award-winning technologies. These summaries are posted on EPA's green chemistry website at www.epa.gov/greenchemistry/.

Entries from Academia

In-Situ Generation of H_2O_2 in CO_2 for Green Oxidations

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

We have demonstrated the use of CO_2 as the sole solvent for the generation of propylene oxide (PO) from hydrogen, oxygen, and propylene via the in-situ generation of H_2O_2. CO_2 can solubilize large quantities of gases, is immune to oxidative degradation and provides a non-flammable environment in which to mix H_2 and O_2. Our results to date show that the use of CO_2 as the sole solvent in the reaction produces 90%+ selectivity to PO. We subsequently used the in-situ generation of H_2O_2 to oxidize benzene to phenol. This technology could result in highly intensified processes for the synthesis of H_2O_2, PO, phenol, and other commodities. The chlorohydrin process for PO creates approximately 500 million gallons of salt-contaminated wastewater from US production alone, while the DOE has estimated that a one-step phenol synthesis could save 65 trillion BTU/year and eliminate 50 billion pounds of waste. H_2O_2 could be used to reduce the waste generated by these processes, yet H_2O_2 production using the anthraquinone route absorbs trillions of BTU needlessly and creates numerous waste streams. Demonstration that in-situ generation of H_2O_2 in CO_2 supports subsequent oxidations with reasonable conversion and selectivity opens the door for more intensified, greener oxidation processes.

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

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

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

Developing Highly Efficient C-H Activation of Hydrocarbons
Robert G. Bergman, Department of Chemistry,
University of California at Berkeley

The preparation of high-valued organic chemicals often involves lengthy, multi-step synthetic sequences. These typically require large amounts of various chemical reagents, such as oxidizing and reducing agents, drying agents, and organic solvents for the performance of the reactions. Large amounts of organic solvent are also often required for the separation of the desired products from one another, especially when chromatography is employed. The most effective way to solve this problem is to drastically reduce the the number of chemical steps required in these synthetic sequences. Bergman has demonstrated that the employment of C-H activation reactions within synthetic sequences provides important progress toward this goal. Within the last two decades, the Bergman group has pioneered the direct activation of C-H bonds in organic molecules that are found in locations remote from other functional groups. Due to this pioneering work these C-H activation reactions are now being used successfully in the synthesis of various chemicals and pharmaceutical products. Ultimately this should have a profound impact on various fields and sectors of chemical manufacturing and production. Bergman's studies of the mechanism of C-H activation have also provided a substantial amount of fundamental information about this important process, such as the factors that promote highly activation of different types of C-H bonds in hydrocarbons.

Cost Effective Green Chemistry Approaches to Pharmaceuticals:
Microwave Techniques & "Grindstone Chemistry" for Solventless Reactions and Less Pollution
Dr. Ajay K. Bose, Professor of Chemistry,
Department of Chemistry & Chemical Biology, Stevens Institute of Technology

The advent of new reagents, new catalysts, and new techniques of energy transfer to chemical reactants has made it possible to make traditional organic synthesis more environmentally benign. A very unusual new technique is "Grindstone Chemistry" for conducting many reactions on a large scale – without solvent and at room temperature – by just grinding together reactants (solid/solid; solid/liquid; liquid/liquid with sea sand added). Microwave irradiation of reagents – with or without solvents – greatly enhances a wide variety of synthetic reactions in several ways: by reducing the reaction time, by ensuring high yield and less chemical waste (i.e., reduction of pollution at the source). In our laboratories microwave reactions are conducted in open systems by using moderately high boiling solvents (dimethylformamide, etc.) or no solvents if one of the reagents is a liquid. The microwave energy is controlled to keep the reaction from boiling; thus, no reflux condenser is needed. This open system is free from the risk of explosion observed sometimes in sealed systems and is user friendly. We have improved upon several classical organic reactions described in *"Organic Syntheses"* – the established guide book for synthetic chemists. To illustrate our approach to green chemistry, we have devised an eco-friendly alternative synthesis of DAPSONE – a widely used anti-leprosy drug that also helps some AIDS patients, We have used microwave irradiation to accelerate enzymatic cleavage of proteins and devised rapid analysis of peptides including cyclic peptides – reactions of value for drug development. The use of the combination of microwaves and Grindstone Chemistry techniques will allow pharmaceutical companies to be more efficient, more eco-friendly and more competitive.

Water Immiscible Room Temperature Ionic Liquids as Green Solvents for Extraction and *In-Situ* Photolytic Destruction of Environmental Organic Contaminants

Dionysios D. Dionysiou, Ph.D., Assistant Professor of Environmental Engineering and Science, Department of Civil and Environmental Engineering, University of Cincinnati

The technology described herein concerns an innovative Green Chemistry and Engineering technology dealing with the use of a new generation of "Green Solvents" to solve environmental problems combined with the application of a novel and environmentally friendly method to achieve recyclability and sustainability of the solvents. These solvents concern a new generation of materials known as *Room Temperature Ionic Liquids* (RTILs). These are currently considered as "*Neoteric Green Solvents*" and have great potential to replace volatile organic solvents (VOCs) in chemical and engineering processes. VOCs are currently used extensively and are the source of major environmental pollution problems. Water immiscible RTIL solvents have been employed in this study considering removal by extraction of organic contaminants from polluted environments such as contaminated soils and dredged sediments. The novel method investigated in this project concerns the use of ultraviolet (UV) radiation to destroy extracted organic contaminants *in-situ* in the ionic liquid phase with simultaneous regeneration of the ionic liquid. This approach ensures purification, recyclability, and sustainability of the ionic liquid solvents. Alternatively, the photodegradation method can be utilized to destroy organic contaminants that are present in RTILs as undesirable byproducts in various chemical reactions utilizing RTILs as the solvent media. Finally the photodegradation method can be utilized to eliminate organic impurities present in the RTILs after their manufacturing for the production of extremely clean RTILs, which are required in electrochemical processes and liquid batteries.

Antibody Catalysis

Dr. Kim D. Janda and Dr. Richard A. Lerner, The Scripps Research Institute

A meritorious goal is the production of novel protein catalysts applicable in organic synthesis that can be generated in real time versus hundreds of thousands of years of evolution. Enzymes, in an over-simplified view, are merely catalytic cores embedded in a protein scaffold. It has been demonstrated that a scaffold can be made; the challenge then lies in creating a core with the correct arrangement of amino acid residues and/or cofactors to effect catalysis. Catalytic antibodies meet these goals and challenges. Catalytic antibodies can be procured via animal or *in vitro* systems in a matter of weeks to a few months. By using such systems, antibodies can be tailored to catalyze the reaction of choice by the designer. Many of the reactions catalyzed by antibodies proceed with high rates and regio- and enantioselectivity. In addition, catalytic antibodies have been made that catalyze disfavored chemical transformations and even reactions in which there are no enzyme counterparts known. Antibody catalysis has also shown great potential in the treatment of both cancer and cocaine addiction. In summary, catalytic antibodies are unique in that they can catalyze both important chemical transformations as well as aid in human health problems.

Catalytic C-C Bond Forming Hydrogenations: Atom Economy and the Reductive Coupling of Basic Chemical Feedstocks
Michael J. Krische, Associate Professor of Chemistry, University of Texas at Austin

Elemental hydrogen is the cleanest and most cost-effective chemical reductant available to humankind. However, use of hydrogen as a terminal reductant in catalytic C-C bond formation is presently restricted to processes involving migratory insertion of carbon monoxide, e.g. alkene hydroformylation and related Fischer-Tropsch type reactions. Recently, the first catalytic system to enable electrophilic trapping of the organometallic intermediates obtained transiently in the course of catalytic hydrogenation was developed in our lab. Through implementation of cationic Rh-based catalyst systems, the hydrogen-mediated reductive coupling of enones, dienes and diynes to carbonyl partners has been achieved. In all cases, hydrogenation-induced C-C bond formation occurs in a completely atom-economical fashion, i.e., stoichiometric byproducts are not formed. These results support the feasibility of developing a broad new family of catalytic C-C bond formations. Under the aegis of the EPA-Presidential Green Chemistry Challenge Awards Program, it is our goal to extend this fundamentally new pattern of reactivity to encompass the reductive coupling of basic chemical feedstocks.

Developing Direct Catalytic Addition of Alkynes to Aldehydes and Imines in Water and Under Solventless Conditions
Chao-Jun Li, Department of Chemistry, Tulane University

Optically active propargyl amines and alcohols are important synthetic intermediates for the synthesis of various nitrogen- and oxygen-containing compounds and are components of bioactive compounds or pharmaceutical agents. The resulting alkynyl additional derivatives can undergo further transformations and are versatile synthetic tools. However, these compounds are often prepared in at least three steps: (1) synthesis of a highly reactive organo-metallic reagent such as the BuLi from organic halide and a highly reactive metal such as lithium (although such reagents have been commercialized); (2) converting of alkynes to alkynilides; (3) reaction of alkynilides with aldehydes or imines. All three steps generates stoichiometric amount of waste, as well as requires inert atmosphere and anhydrous organic solvents. Within the last several years, we have developed various *catalytic direct addition of alkynes to aldehyde and imines in water and under solventless conditions*. We have also developed the first direct catalytic enantioselective three-component-addition of alkdehyde, alkyne, and amine in water and under solventless conditions.

Development of Environmentally Benign Low VOCs Manufacturing Processes for Functional Materials: Towards Elimination of Transition Metals from Materials Made by Atom Transfer Radical Polymerization (ATRP)
Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

ATRP is a transition metal mediated controlled polymerization process for radically polymerizable monomers discovered in our laboratories in 1995. The process has been actively incorporated into many industrial research programs for the preparation of polymers targeting a broad spectrum of applications. Since 1995 we have led efforts to develop more active catalyst systems, targeted at reducing the levels of metals in the ATRP systems. We have also led the development of environmentally benign procedures for preparation of many functional ("green") materials via ATRP. However, the most active catalysts could not be used in many systems due to the need to balance the activity of the catalyst and

the number of moles of initiator that had to be added the system in order to prepare low molecular weight functional oligomers of commercial importance. Systems employing hybrid catalysts and SR&NI overcome this limitation. We are now in the position to apply our expanded understanding of ATRP catalysis to the development of a continuous bulk ATRP process. The combined process will fully control the activity of the hybrid catalyst over extended time periods and allow recycling all catalyst residues present in the process effluent back to reactor feed streams, thereby demonstrating elimination of all hazardous substances from the products produced by ATRP and from industrial production waste streams.

Achievement of "Substantially Zero" Atmospheric Emission from Stationary Power Plants and Disposal Plants
Dr. E. Bruce Nauman, Director, Chemistry Department, Rensselaer Polytech

Problems in the combustion of fossil fuels in energy conversion systems from stationary sources have resulted in pollutants detrimental to downstream effects to our environment. An opportunity exists for the reduction and substantial elimination of all hazardous and toxic atmospheric pollutants from stationary combustors, utility plants and solid, toxic and hazardous waste incinerators. An innovative approach to this problem is, "Containment i.e. Encapsulation" of off-gas emission, essentially providing multi-flue treatment chambers, providing a means to chemically convert, and separate off-gas components through the incorporation of molecular sieves, reactors and ceramic membrane filters. The end result will be by-product production, cogeneration of electricity, reduced solid waste residue, and "substantially zero" release of pollutants to the atmosphere. This DVD will define the innovative encapsulation and the "Containment" concept. It will provide flow chart diagrams, mathematical model calculations of mass/energy balances and their anticipated effect(s). The text will entail by-product of gas synthesis and anticipated approaches to renewable sources of energy. It will also provide chemistry models of catalytic absorption and adsorption mechanisms as a means for reduction and substantial approach to reducing ozone depletion of the atmosphere and acid rain effects on the environment.

Tandem Reactions, Cascade Sequences and Biomimetic Strategies in Chemical Synthesis
K.C. Nicolaou, Professor of Chemistry, University of California, San Diego

Tandem reactions, cascade sequences and biomimetic strategies are being increasingly applied to the construction of natural and designed molecules. Such processes, in which ideally a single event triggers the conversion of a starting material to a product which then becomes a substrate for the next reaction until termination leads to a stable final product, are highly desirable not only due to their elegance, but also because of their efficiency and economy in terms of reagent consumption and purification. Often, these multistep, one-pot procedures are accompanied by dramatic increases in molecular complexity and impressive selectivity. The discovery of new molecular diversity from Nature and the demand for more efficient and environmentally benign chemical processes dictates and invites the further development of such synthetic strategies and tactics as we move into a new age of chemical synthesis and green chemistry. The nominated work responds to these needs through the design and development of biomimetic cascade sequences, photo-induced reactions and other alternative, tandem-type synthetic pathways for the construction of molecular complexity. Central to a number of these cascade technologies is the venerable Diels-Alder reaction. Often requiring only thermal- or photo-initiation, this reaction delivers its downstream products with ideal (100%) atom economy.

Mill Designed Biobleaching Technologies
Dr. A.J. Ragauskas, Associate Professor,
School of Chemistry and Biochemistry, Georgia Institute of Technology

The research studies undertaken in this program are directed at utilizing the catalytic oxidative properties of laccase, an oxoreductase enzyme found in several natural systems, to improve the physical properties of lignocellulosic pulps in an enhanced environmentally green manner. As such, our research studies have defined the fundamental chemical pathways involved when laccase and/or laccase-mediator systems (LMS) are employed with lignocellulosic materials. In addition, during these studies we have discovered several novel reactions, including the unique chemical reactivity of LMS with lignin, its ability to be used as an oxidative bleaching system for recycled fiber, a previously unrecognized benefit as a pretreatment for kraft pulping technologies, and as a surface activation technology yielding pulp fibers with substantially improved physical properties. The benefits of these discoveries are anticipated to yield novel methods of eliminating hazardous chlorinated chemical wastes, enhanced usage of recycled paper, improved pulping/ bleaching efficiencies thereby reducing the need for virgin wood resources, and improved physical paper properties thereby reducing the power consumption associated with the production of high-value paper.

Ionic Liquids Enabling Sustainable Technologies: Utilizing Biorenewable Cellulose Rather than Synthetic Polymers for New Advanced Materials
Dr. Robin D. Rogers, Professor of Chemistry,
Department of Chemistry and Center for Green Manufacturing, The University of Alabama

This nomination illustrates the use of ionic liquids (ILs) as non-volatile solvents for the direct co-dissolution and/or suspension of cellulose and active ingredients which can be easily reconstituted in a variety of forms to yield advanced composites integrating particulates, complexants, colorimetric or biological receptors, etc. The ability to easily modify the properties of cellulose into new biorenewable or biocompatable advanced materials will lessen or replace the current dependence on the world's diminishing petroleum feedstocks used to make new polymers and composites. By using ILs to directly dissolve cellulose (and active ingredients which can be used to non-covalently modify the properties of this polymer) one can effectively utilize the full complexity of Mother Nature's natural polymer. While this will lead to the commensurate reduction/elimination of environmentally undesirable solvents, feedstocks, and processes used to make synthetic polymers, it will also allow us to reexamine the current strategy of breaking cellulose down into monomers which are then re-polymerized to form synthetic polymers. This research has achieved the following: (1) rapid, efficient direct dissolution of cellulose, (2) introduction of functional additives, allowing one to easily tune the properties of the final product, (3) simple product generation, and (4) recovery and recycling of the IL.

A Systematic Methodology for the Design and Identification of Environmentally Benign Refrigerants
Nikolaos V. Sahinidis, Professor, Department of Chemical and Biomolecular Engineering
School of Chemical Sciences, University of Illinois at Urbana

Hydrofluorocarbon emissions from the refrigeration and air conditioning sector in the U.S. currently amount to approximately 13 million metric tons of carbon equivalent and are expected to grow to 38 million tons by 2010. Retail food refrigeration accounts for 25% of these emissions: a typical supermarket leaks about 1 ton of refrigerant every year. The fundamental scientific goal of the

nominated project is to reduce these major sources of environmental pollution by designing environmentally benign refrigerants. Using his pioneering optimization methods, Professor Sahinidis has invented a powerful way to search the astronomically large space of possible compounds and identify the entire set of compounds that are potentially suitable automotive refrigerants. By extending this approach to secondary refrigerants, the Sahinidis team has identified over 3,000 potential secondary refrigerants. These secondary refrigeration fluids have an estimated potential of reducing supermarket refrigerant leaks by 90%. This project has yielded a large number of chemical structures that are entirely novel: some of them appear in databases but were never used as refrigerants while others do not even appear in databases of chemicals. Furthermore, the nominated methodology is applicable to the design of a very broad spectrum of compounds, including pharmaceuticals and industrial solvents. Because it produces the entire set of possible compounds that satisfy physical property requirements, this methodology enables the use of environmental criteria to design novel compounds that are environmentally benign.

Development of Totally-Organic Wood Preservatives
to Replace the Relatively New Copper-Rich Systems
Dr. Tor P. Schultz, Professor of Forest Products and
Adjunct Professor of Chemistry, Mississippi State University

Wood deterioration due to decay fungi and termites costs U.S. homeowners an estimated $5 billion per year. This economic loss can be avoided by using lumber treated with various biocides when constructing homes, outdoor decks, etc. Starting in 2004, lumber for residential construction will be treated with the relatively new copper-rich preservatives ACQ, CA and possibly others, with the older chromated copper arsenate (CCA) only permitted for industrial applications. While ACQ and CA do not contain the arsenic or chromium present in CCA, copper-rich systems have their own environmental concerns such as leaching of copper into aquatic environments. In addition, disposal of any metal-treated lumber will likely face future restrictions. Consequently, totally-organic preservatives may be mandated; this is already occurring in some European countries. However, most organic biocides being considered may have their own environmental concerns and any totally-organic system will be very expensive compared to ACQ and CA.

Wood-decaying fungi utilize free radicals generated by metals to degrade wood. Utilizing this basic knowledge, we have found that the combination of various commercial organic biocides with non-biocidal metal chelating and/or antioxidant additives increased the activity by 2- to 3-fold for all commercial organic biocides examined. Many of the additives we examined are relatively benign (i.e., approved as food additives) and inexpensive. Consequently, greatly reduced levels of relatively expensive biocides are required, resulting in a more economical and benign, yet still effective, totally-organic wood preservative systems.

From Waste-to-Energy: Catalytic Steam Gasification of Poultry Litter
Atul C. Sheth, Professor and Program Chair, Chemical Engineering,
University of Tennessee Space Institute

UTSI's poultry litter gasification concept is based on the Exxon's Catalytic Coal Gasification Process. In this concept, poultry waste or any other animal waste is mixed with the other biomass waste and suitable source of additional potassium. The resulting mixture is gasified in "as-is" or slurry form at 1300-1500 °F and at 50-150 psi pressure in a suitable gasifier. The steam for gasification can be produced externally and supplied to the gasifier or can be produced in-situ from the wet/slurried

feedstock. Depending upon the pressure, the resulting fuel gas will be rich in CH_4 or in CO and H_2 and after separating from the solid/char residue can be used as a fuel for heating purpose or to produce electricity. The solid/char residue is significantly small in volume (by a factor of 5 to 10) than the starting waste, and therefore, can be used in cement/concrete manufacturing or as fertilizer to provide concentrated source of K and P-bearing salts. Potassium present in poultry and certain animal wastes such as from swine, cows, horses, and sheep can provide the necessary catalyst. If necessary, additional supplemental potassium can be obtained from other cheap sources such as langbeinite and feldspar.

Entries from Small Businesses

Reducing Nitrates in Buzzards Bay with the Production of Organic Gem® Fertilizer from New Bedford's Fish Processing Wastes
Advanced Marine Technologies

AMT's Organic Gem® fertilizer is manufactured in New Bedford, Massachusetts using approximately 7% of the typically 50 million annual pounds of fresh fish scraps. Organic Gem® (OG), certified by OMRI, was first made from the byproduct of their nutraceutical extraction of marine cartilage. They have developed a unique Enzymatic Digestion Engine (EDE) using proprietary enzymes that accelerate optimal digestive conditions. The EDE strictly controls factors that could potentially denature enzymes and proteins. It is a fast, "cold" process that delivers a low-odor, efficiently absorbed fertilizer to increase plant yield and pest resistance. Presently, its markets include golf courses, turf farms, vineyards, hops, fruit trees, potatoes, cranberries, home gardens and other crops. In New Bedford, the increased manufacture and use of OG delivers a triple economic/environmental impact by decreasing quantities and costs of illegal fish wastes going to landfill; reducing nitrate discharges from the wastewater treatment plant into Buzzards Bay, a prime recreation area; and minimizing agricultural runoff of nitrates from petrochemical-based fertilizers. With its use of an innovative processor supply chain approach, AMT anticipates servicing 100% of the local wastes within the decade. Its plans call for new EDE installations to bring cost savings to other processors and environmental benefits to other ports.

Non Chromate Chemical Conversion Alternative Coating
C.H. Thompson Co. Inc.

The chemicals that we displaced were Chromic Acid, CAS # 133-82-0, and Potassium Ferricyanide CAS# 13746-665-2. These Components are 54% of traditional process solutions. They are on the EPA list of hazardous or toxic chemicals and chrome and cyanide are listed materials for effluent limitation in the categorical pretreatment standard. We replaced them with a product containing Potassium Permanganate ($KMnO_4$) CAS# 7764-7, a very powerful oxidizer. KMnO4 will oxidize both iron and manganese in the metal ores to convert ferrous (2+) into the ferric (3+) state, and 2+ manganese into the 4+ state, to generate the permanganate ion MnO_4, and manganese dioxide MnO_2. This liberates nascent (elemental) oxygen molecules. The stoichemetric amount of $KmnO_4$ required to oxidize 1 mg of iron is 0.91 mg $KMnO_4$. To oxidize 1 mg of manganese requires 1.92 mg of $KMnO_4$. It then reduces these items to insoluble oxides, which are easily removed by filtration. The actual amount of $KMnO_4$ needed has been found by us to be less then indicated by stoichimetry. It is thought that this is because of the catalytic influence of $KMnO_4$ on the reactions. Heat, pH. and process temperatures are integral to the process. Process solutions function best in the range of 130-140 degrees F. and with pH. between the 7.0 and 8.0 range. Processing time varies from 7-15 minutes depending on the amount of oxidation required, with the resultant oxidation ranging from between a medium gold-brown (7-10 minutes) to a dark gold-brown (10-15 minutes). Rinsing is accomplished in de-ionized water.

Thermal Conversion Process Utilizing Renewable Feedstocks
Changing World Technologies, Inc.

Changing World Technologies, Inc. (CWT) has successfully developed and patented a Thermal Conversion Process (TCP) that converts renewable feedstocks into clean fuels and specialty chemicals for industrial and commercial use. The basic technology emulates the Earth's natural geological and geothermal processes that convert organic material into fossil fuels under conditions of heat and pressure. The CWT-TCP accelerates these natural processes using basic physics, chemistry, and process technology in a completely enclosed circulating system thereby reducing the bioremediation process from millions of years to mere hours. The design of the system ensures that there is no odor, dust, fumes, smoke, gas, or excessive noise in the system. The process yields product streams that include: a clean fuel gas, a light organic liquid, and a solid product that can be used as a fuel, fertilizer or filter.

The TCP has been extensively researched and developed and is in the process of being demonstrated in a commercial environment. Prior to 1999 several versions of the technology were designed and tested on various organic and inorganic feedstocks. In December 1999, CWT opened a pilot plant at the Philadelphia Naval Business Center. The facility conducts testing and collects data using various equipment including: Parr Bomb batch reactors, a 1 ton-per-day continuous flow unit and a 7-1/2 ton-per-day process unit. Research is also performed using another Parr Bomb batch reactor located at Hofstra University. Tests were performed on turkey offal and grease, as well as agricultural mixed wastes. These test runs provided a basis for ascertaining operating parameters and procedures as well as insight into system adjustments and response resulting in several process improvements in the last four years. This work helped build a foundation for the design of the first commercial-scale facility.

In 2003, a 200 ton-per-day commercial demonstration plant located in Carthage, MO was completed through a joint venture with ConAgra Foods, Inc. The plant is designed to operate fully on renewable turkey offal feedstock from a nearby processing plant. Operation of the plant is intended to exhibit the viability of the process and provide additional data necessary for the design and construction of a mixed waste agricultural feedstock demonstration plant.

In the fourth quarter of 2003, CWT commenced planning and design of a 378 ton-per-day commercial-scale demonstration biorefinery. The plant will operate on an expanded agricultural mixed waste feedstock, including beef and poultry waste, animal offal, poultry litter, animal/ vegetable-derived greases and wastewater sludges, and beef paunch and mortality. The project will concentrate on process integration and system monitoring, while providing the information and data necessary to develop critical equipment guarantees required for commercialization.

The SEGC 114 Standard and the Chemistry of the Sustainable Earth™ Line of Green Cleaning Products
Coastwide Laboratories

Many commercial cleaning chemicals contribute significantly to the pollution of our air, water, and soil. Toxic ingredients in these chemicals also threaten the health and safety of those exposed to their fumes and residues. A new scientific standard has been developed by Coastwide Laboratories to provide cleaning chemicals that will better protect the natural environment and the health and safety of those exposed to the products. The new standard, called SEGC 114, is based on three rigorous sets of criteria: the cleaning chemical must (a) satisfy a set of nine strict pass-fail requirements; (b) conform to a set of 22 environmental, health, and safety attributes; and (c) score well under the Indiana Relative Chemical Hazard scoring system.

In 2003, Coastwide Laboratories introduced the first green cleaning chemicals to receive third-party certification as fully meeting the requirements of the SEGC 114 standard. Called the Sustainable Earth™ product line, these green cleaning chemicals have been formulated with innovative chemistries to preserve the natural environment and to protect the health and safety of those exposed to the chemicals. The resulting products represent a major improvement in pollution prevention and source reduction over the "conventional" cleaning products now in widespread use.

Environmental Advantages Offered by Boric Acid-Mediated Amidation Between a Carboxylic Acid and an Amine to Form a Carboxamide, a Basic Unit of Peptides and Proteins: A Practical Alternative Green Synthetic Pathway to Carboxamides for Use as an Oral Delivery Agent for Macromolecular and Protein Drugs
Emisphere Technologies, Inc.

A practical and environmentally friendly alternative synthetic pathway has been developed to accomplish the direct amidation between a carboxylic acid and an amine to form a carboxamide using a catalytic amount of boric acid as the mediator. Boric acid is a "green" catalyst. It is nontoxic, environmentally safe, renewable and inexpensive. Carboxamides generate great interest within the synthetic organic chemistry community, and the research directed to their formation is actively pursued. The chemistry of amide bond formation is a vital chemical transformation in organic chemistry. Amide bonds are responsible for linking amino acids to form proteins. Currently, the uses of carboxamides as delivery agents for the delivery of protein and macromolecular drugs in a wide range of settings are being sought and discovered. The amidation mediator, boric acid, has many promising and beneficial properties. The conventional methods reported in the literature for making carboxamides require the use of environmentally harmful reagents and generate hazardous wastes. This boric acid-mediated amidation employs only environmentally benign reagents and generates no by-products. This new alternative green synthetic pathway, using only a catalytic amount of boric acid, guarantees uncontaminated waste flow, thus assuring significantly reduced impacts on human health and the environment relative to the current state of art.

Utilization of Neutral Cleaners for Reducing Environmental and Health Impacts
Environmentally Sensitive Solutions, Inc.

ESS neutral pH aqueous cleaners have replaced the environmental and safety hazards of solvent and aqueous alkaline cleaners in many industrial applications. Unlike alkaline cleaners that are comprised mostly of high pH inorganic ingredients, ESS neutral biodegradeable cleaners are completely organic, comprising of highly specialized detergents and wetting agents. The pH of ESS neutral products is 7.0-7.9. The neutral pH of ESS cleaners makes them noncorrosive, enhancing worker safety while reducing mechanical wear and environmental impact. Unlike alkaline cleaners, there are no chelators in ESS neutral cleaners that can contribute to high heavy metals in wastewater.

The cleaning mechanism is very different between alkaline and neutral cleaners. Alkaline cleaners tend to saponify and emulsify process soils during the cleaning. This soap/soil interaction makes it difficult to remove oils from solution and leads to short wash bath life and water contamination. Thus, much wastewater can be generated. These hazardous cleaners historically leach heavy metals into solution to produce regulated waste.

ESS solutions wet the process soil so there is no strong soap/soil interaction. This allows oils to split out of solution for easy recovery. With the oils removed, the wash bath life lasts longer and wastewater generation is significantly reduced.

Reactin Series™ AS Copolymers: Specialty Reactive Aspartic Acid Copolymers
Folia, Inc.

Reactin Series™ AS Copolymers are synthesized by the polymerization of an intimate mixture of aspartic acid and monosodium aspartate. The intimate mixture is obtained by dissolving diammonium aspartate and monosodium aspartate in water at greater than 70% wt solids and removing the water and copolymerizing the monomers sequentially at > 200C in a continuous reactor designed for high viscosity handling and solid phase polymerization. The copolymers are designated and patented in the molar ratio range of A (for aspartate) and S (for succinimide) from 1:10 and 10:1. The copolymers presently available are in the molecular weight, Mn, range of 1500 to 2000. They are derivatized to the extent desired by reacting the succinimide functionality with suitable nucleophiles such as amines and alkoxides under mild conditions in aqueous media or in neat reactions. Selection of the nucleophile structure and composition dictates copolymer properties that may be obtained and, hence, suitable applications.

Mycopesticides & Mycoattractants
Fungi Perfecti, LLC

A patent has been awarded, with more pending, 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. Since spores of certain entomopathogenic fungi repel termites and ants, widespread commercialization by the pesticide industry has been limited. The novelty of this patent is the discovery by applicant that ants and flies are attracted to entomopathogenic fungi in their mycelial state, prior to sporulation. Cultures of fungi can be isolated from naturally infected insects, and through a selection process can be cultured in the laboratory to create strains that delay spore production for several weeks. The pre-sporulating entomopathogenic mycelia emit powerful attractants and feeding stimulants, drawing select pests to a chosen locus, from where they then spread the infectious fungi throughout the targeted nest and ultimately to the queen. In choice tests, termites prefer the pre-sporulating mycelium of *Metarhizium anisopliae* to wood as food. Research shows that diverse insect species share specific affinities to these fungi in their pre-sporulating state. This discovery may well lead to novel methods for controlling insect pests worldwide. This mycotechnology is economical, scaleable, and utilizes cell culture methods currently in practice.

Evapo-Rust™ Iron Oxide Specific, PH neutral, Chelation
Harris Labs

The submitted chemistry is an industrial replacement product for corrosion control and iron preparation. Current use, low-cost, chemistries are now becoming a major disposal cost and environmental issue. To date, the use of corrosion removal solvents has been limited to strong acids and caustics. The process is generally destructive to the material being treated and strips paint, plastic, plating, and dissolves softer metals. This leaves waste contaminated with heavy metals, and an assortment of paint, grease, oil, and so on. The treated part may have changes in hardness, thickness, and

surface and have flash corrosion problems as well. By selective chelation, Evapo-Rust™ removes the iron oxide into solution. As the operational pH is 6.1, the solution is never hazardous to handle, store or dispose of in neat form. Vat operators do not need PPE with this chemistry, making this an excellent home-use safety product as well. Evapo-Rust™ will replace toxic, caustic, fume & vapor producing processes with a targeted process that only removes the problem rust. Waste generated by Evapo-Rust™ has potential use as lawn and garden fertilizer. Dewatering of the waste yields a solid that is non-hazardous, non-reactive and safe for disposal.

Ecological Paint
Innovative Formulation Company

Ecological Paint was developed as a safe alternative to all other existing paints which do not comply with 29 CFR 1910-1200 and contain hazardous substances listed in Prop 65. It was developed for chemically sensitive people and those who suffer long term exposure such as the professional painter. The paint contains no known carcinogens, neurotoxins, is zero VOC and has no hazardous metals, formaldehydes, leads, mercury, chrome, ethylene glycol, phthalates, benzenes, HAPS or APES. It has virtually no odor and is hypo allergenic. It sacrifices no performance in achieving this and outperforms other paints in many areas such as coverage, hide and application ease. It has no blocking or adhesion problems normally associated with low or zero VOC products. It is a multi-shelled acrilated nano polymer that is 100 percent acrylic. In addition, the unique formulation and pigmenting allow significant energy savings during warmer months by shifting the heat spectrum off the paint without affecting the visible color. It can do this with any color, even the darker color spectrum.

George Forman's Knockout Household Cleaner: A Dynamic Cleaning Experience
In a Colloidal Format With Pollution Prevention Qualities
The Knockout Group

"Knockout" brand multipurpose cleaner has been developed and commercialized over the past five years as Earthday Products and their grand rollout of the current identical product under the banner of "Knock Out Products" will occur in January 2004.This mixture of chemicals is non-toxic, biodegradable and for general use around the home or office.The unique mixture of existing safe chemicals, timing and sequencing of mixing and the built in unique safety of the mix, which contains 98% water will forever prevent pollution due to the extremely small amount of active ingredient necessary to make the product effective.Water is the customers' preferred medium,and it is an excellent solvent and carrier for small amounts of emulsifiers for general cleaning.Currently cleaners contain harsh chemicals with an extremely low or high pH, that are highly bleaching or oxidizing or that create non-degradable by-products in the environment once the product is used.The "Knockout" brand of household cleaners are 100% biodegradable, cause less chemical to be used initially and creates no toxic by-products.

New Green Technology for Eliminating Hydrogen Sulfide
in Petroleum Industry Aqueous Systems
The LATA Group, Inc.

LATA's Bio-Competitive Exclusion (BCX) technology is designed to attack the source of H_2S, i.e., the reduction of 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

formulae (named Max-Well 2000) that target and directly manipulate the indigenous microflora of hydrocarbon-bearing reservoirs and a wide variety of surface systems.

The introduction of low concentrations of Max-Well 2000 formulae act as alternate electron acceptors for targeted denitrifying bacteria (DNB) that flourish and out-compete SRB for essential growth nutrients needed to reduce sulfate to sulfide. Other formulae components are toxic to SRB and react chemically with existing H_2S to form soluble, non-hazardous sulfate (SO_4). Certain *Thiobaccillus* species—when stimulated by Max-Well product—will also attack and degrade existing H_2S. The end result is the production of non-hazardous nitrogen gas, elimination of existing H_2S in the system, and continuous blocking of hydrogen sulfide production.

Development of Novel Liquid Crystal Polymers
LCP Tech Holdings LLC

A new class of liquid crystal polymers which have a backbone chain of either polyiminoborane (-BH-NH-BH-NH- or $[BNH_2]_x$) or polyaminoborane (-BH_2-NH_2-BH_2-NH_2- or $[BNH_4]_x$) or polyborozine ($[B_3N_3H_6]_x$) have been invented and some of their applications demonstrated over the past three years. These polymers almost align, when present at an interface, and their angle of alignment mainly depends on the side chains, which are polymethylsiloxane polymers. Depending on this angle of alignment (2), quantified by an order parameter (S), where S is defined as 1/3 (3cos$_2$2 -1), the interfacial properties of the liquid crystal polymer can be manipulated. A PCT application[1] defining this new composition of matter was filed August 12, 2003, and all claims were approved without dispute. U.S. EPA funded TechSolve, Cincinnati, OH, to conduct toxicological testing, and determination of characteristics for use as “green” metal working fluids. Results of these studies have been published as an interactive CD (EPA/600/C-03/063), which have concluded that these polymers are environmentally benign and exhibit superior metal working fluid characteristics. LCP Tech, a small business company, was created to commercialize these polymers as metal working fluids, and pursue other applications, such as fire retardants, fuel cells, and intelligent membranes.[1]

[1]Liquid Crystal Polymer Technology and Applications, Ferguson, D. and R. Govind, PCT Application filed August 12, 2002.

Production of Eco-Friendly, Sustainable PHA Plastics Using Biotechnology
Metabolix, Inc.

Bio-based products generally, and products of transgenic microbes specifically, have played a small role in the chemical industry compared with traditional catalytic processing of petroleum and natural gas despite the enormous diversity and efficiency of enzyme catalyzed chemistries that can be harnessed in biological systems. An increasing role for enzymatic transformations in the chemical industry (especially in the areas of industrial enzymes, amino acids, and vitamins) is now possible. Metabolix has overcome several key disadvantages which have limited the use of microbial systems in industrial chemical production. Such disadvantages include complicated organisms evolving to propagate and survive rather than to produce a certain chemical from a cheap feedstock as well as undesirable reactions that waste feedstock and increase reaction time, energy requirements, and the production of greenhouse gasses such as CO_2.

It is in catabolic pathways that the key aspect of metabolism responsible for these inefficiencies in many fermentation processes which could produce industriallyuseful materials from renewable resources resides. Metabolix has developed microbial system sin which these pathways have been altered, enhancing productivity for the production of PHAs and creating a new platform for the

sustainable production of new, green, high performing chemicals and plastics from agricultural raw materials.

Environmentally Friendly Aircraft Deicing Fluid
METSS Corporation

METSS ADF-2 represents a new class of aircraft deicing fluid designed as an environmentally friendly alternative to traditional ethylene and propylene glycol based fluids used for such applications.METSS ADF-2 is composed primarily of food-grade materials derived from abundant and renewable agricultural feedstocks that are both economical and readily available.Unlike ethylene glycol-based fluids, METSS ADF-2-2 is nontoxic and non-hazardous to plant and animal life. It contains no phosphates or urea that tend to promote eutrophication of natural waterways that may subsequently lead to fish-kills. METSS ADF-2 biodegrades readily and completely to carbon dioxide and water.Compared to propylene glycol, METSS ADF-2 has a lower Biological Oxygen Demand (BOD) and biodegrades at a slower rate. Commercial airports and military bases are increasingly concerned about the quality of storm water runoff and the effect of deicing chemicals on receiving waters. If storm water drains directly from runways and taxiways into a body of water, discharge permits require regular monitoring of runoff to determine several properties including BOD and contaminants. Due to its low BOD, the use of METSS ADF-2 can assist airport managers in achieving environmental compliance. METSS ADF-2 meets all requirements of the SAE AMS 1424D for aircraft deicing fluids.

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

Water disinfection using chlorine gas has saved countless lives in the United States and the world in the past 100 years. Chlorine gas as a hazardous material is pervasive in our communities and around the world. On-site generation of chlorine-based mixed-oxidants using low cost sodium chloride brine is demonstrated to be superior to chlorine gas for disinfection, including inactivation of water-borne pathogens immune to chlorine gas disinfection, and the process eliminates all of the hazards associated with chlorine disinfection. The technology is scalable for individual use to large municipalities and offers significant chemistry benefits for microflocculation in water clarification processes, chlorine disinfection by-product reduction, taste and odor elimination, chlorine residual maintenance in water distribution systems and biofilm elimination.

Natural Adhesive Polymer
Montana Biotech SE, Inc.

Most adhesives are derived from petrochemicals; some include toxic solvents. Over 5.6 billion pounds of adhesives are used in the US across most industrial sectors - in everything from book bindings to automobiles. Not only are many adhesives harmful to both users and the environment, but the heavy dependence on a petroleum-based feedstock can result in dramatic price increases as seen over the past year.

A search for a more environmentally friendly adhesive screened natural products made by microorganisms. The polysaccharide levan, was found to have good adhesive properties. Although long known, levan had not previously been recognized as having adhesive properties and it had not been

commercially available in more than gram quantities. A method was developed for producing levan by large scale fermentation.

Levan successfully addresses three critical criteria: (1) *Safety*: levan is a polyfructose that is non-cytotoxic and biodegradable; it is safe for both users and the environment. (2) *Sustainability*: levan is derived from a renewable resource, sugar. (3) *Security*: sugar is obtained from sugar beets and sugar cane, both produced in the US and many regions around the world.

MYCELX Technology
(Synthesis and Use of Curable Viscoelastic Polymeric Surface-active Agent in Removal of Organic Pollutants from Aqueous and Airborne Influent Streams)
MYCELX Technologies Corp.

MYCELX technology utilizes biomimetic pathways in order to produce MYCELX chemistry, which is the reaction product of drying oils and methacrylate polymers. MYCELX chemistry can be considered one of the first commercially available products utilizing self-assembling synthetic pathways similar to the manner in which biological systems synthesize compounds. The combination of the properties of bio-molecules and synthetic acrylates results in the novel properties of MYCELX, which are not possessed by conventional synthetic polymers. MYCELX chemistry possesses the following combination of novel properties: broad affinity, curability and viscoelasticity. Affinity refers to the ability of MYCELX infused substrates to bind together and immobilize disparate phases of organic compounds without future separation or desorption. The curability of the compound allows the material to be cured into practically any filter substrate and cured dry with full transfer of properties. Viscoelasticity allows MYCELX infused filters to capture and immobilize organic compounds to filter saturation without any additional differential pressure across the filter. MYCELX infused filters are able to remove emulsified organic compounds (i.e., Naval and Marine bilge water), PCBs and other persistent organic pollutants, oil mists from air and tramp oils in less than one second contact time without desorption.

Reducing Domestic Petroleum Consumption by Twenty-five Percent
PanTerra Technologies, Incorporated

By lowering the friction between moving surfaces in any energy-consuming device, the amount of energy required is significantly lowered. By providing a very low coefficient of friction, the amount of wear on moving parts is also lowered; therefore, any motor, tool, or surface can be operated faster, with less energy or wear than at any other time known to mankind. This is accomplished using physical properties rather than chemical interactions, thereby reducing emissions.

PreKote™ Surface Pretreatment
Pantheon Chemical

Hexavalent chrome (Cr+6) is the industry standard for corrosion protection on aluminum substrates prior to painting. Cr+6 is toxic, hazardous and its discontinued use is an EPA pollution prevention priority through the 1993 Executive Order 12856, as well as being placed on the European list of non-allowable materials spearheaded by the ELV directive. As an aluminum pre-paint pretreatment process, the U.S.A.F. determined that PreKote SP is the only proven replacement for Cr+6. Its use significantly decreases operational costs, eliminates heavy metal waste streams, replaces toxic acids and solvents,

simplifies and reduces process procedures and steps, improves worker safety, health, and morale, provides superior performance, and is environmentally compliant. Unlike Cr+6, PreKote SP's performance is not completely devoted to traditional corrosion inhibition. Rather, it imparts specific, intentional surface properties to the substrate allowing the creation of an intimate, conformal, and improved adhesive bond between the substrate and its intended polymeric coating or adhesive. PreKote SP is compatible with most paint and adhesive systems for use on ferrous and non-ferrous metals, anodized and phosphated surfaces, many plastics and composite materials. Market sectors that can benefit from PreKote SP technology in the elimination of Cr+6 include transportation, infrastructure, government, utilities, manufacturing and production.

Demonstration of a Home Energy Station for Production of Electricity, Heat, and Hydrogen
Plug Power Inc.

Development of the hydrogen economy is driven by its potential economic, environmental, and security benefits. Displacement of fossil fuels for transportation applications will result in reduced emissions, improved air quality, and reduced energy consumption. However, emergence of the use of hydrogen as a fuel for transportation applications is hindered by the chicken-and-egg emergence of hydrogen-powered vehicles and a hydrogen delivery infrastructure.

Plug Power Inc. of Latham, New York, has teamed up with Honda R&D Co., Ltd., to develop, install, and demonstrate a Home Energy Station. This fuel cell-powered system converts natural gas to electricity to power a home, thermal energy for space and water heating, and hydrogen. The hydrogen is compressed and stored, and can be delivered to a fuel cell-powered vehicle. The Home Energy Station changes the refueling paradigm from central facilities to clean, on-site fuel generation.

By using catalytic and electrochemical processes, the Home Energy Station reduces atmospheric emissions and produces energy at higher efficiencies than traditional central generating stations. The Home Energy Station produces clean, reliable energy on-site, representing a significant milestone along the path to a hydrogen economy.

Zero-to-Landfill Fuel Cell Systems
Plug Power Inc.

Plug Power produces fuel cell-based products that are environmentally friendly; however, the concepts of sustainability do not end with this contribution. Plug Power is striving to ensure that the product lifecycle is effectively managed and to achieve minimal waste generation from its operation and maintenance. The goal is zero-to-landfill, meaning that no part of either the product, its operation, or its maintenance finds its way to the trash.

During 2003, Plug Power was able to reduce the fraction of its GenSys^{TM} systems that are thrown away to 10% by weight. This achievement is due in part to efforts to recycle or reuse fuel cell stack plates. The plates represented the largest item, by weight, being sent to landfills at the beginning of 2003. Recycling and reuse methods were developed and proven in the laboratory; both are now being scaled up to support production volumes.

Cleaning Water with Electricity
Powell Water Systems Inc.

Nature has been using electricity to purify water in the forms ranging from lightning to ultraviolet light throughout recorded history. Electricity's effectiveness to make contaminants separable from water was patented in 1906 by Dietrich. The process has been adapted to reduce the electrical consumption by 97%, increase chamber flow capacity one hundred times, and use inexpensive metal blades to provide coagulation nuclei. The improvements have been documented in patents pending, United States Patent 6,488,835 issued December 3, 2002, and United States Patent 6,139,710 issued October 31, 2000. The technology has allowed AWES to obtain permitting in compliance with EPA's Centralized Waste Treatment (CWT) Point Source Category wastewater regulations; Joe's Plating to reduce fresh plating rinse water use from 600 gallons per day to 60 gallons per month through water reclamation; and Hyannis Car Wash to recycle car wash water, increasing the throughput of their reverse osmosis unit by 50%.

ElectroBrom Biocide System
ProChemTech International, Inc.

The ElectroBrom Biocide System uses a novel, low cost electrolytic cell, based upon impregnated electrolytic graphite, to economically produce a biocidal hypobromite solution on demand and on-site, from a nonhazardous aqueous precursor solution equimolar in bromide and chloride anions. Electrolysis of an equimolar bromide-chloride solution provides for maximum production of the desired hypobromite ion, which has a substantially higher biocidal efficiency in the alkaline cooling waters commonly encountered today than chlorine based biocides. Due to the reasonable cost of the technology, it can be used to cost effectively provide the continuous halogenation recommended by OSHA and CTI for control of Legionnaires' Disease. This technology can eliminate the transport, handling, and discharge of up to 40 million lbs/yr of toxic, hazardous chemicals used for biological control in an estimated 300,000 cooling towers located throughout our towns and neighborhoods.

ChemBond™ EC: An Alternate Printed Circuit Board Oxide Process
RD Chemical Company

Multiple layer printed circuit boards (PCB) require an oxide layer on the Copper circuitry on the internal layers (innerlayers) to promote bonding of the layers of the PCB. This is done conventionally today using a process, which generates one gallon of spent oxide producing solution per 25 square feet (2.5 square meters) of PCB innerlayer. This spent solution must be treated to remove the dissolved Copper in it, which averages 25 grams per liter, before it can be disposed of. This process of Copper removal is difficult, and made yet more difficult because the technology to treat these solutions use an organic precipitant which is interfered with by the concurrent Hydrogen Peroxide in the spent waste.

ChemBond™ EC technology avoids all of this by creating a spent oxide producing solution which is readily and economically recycled. Further this process uses atmospheric Oxygen instead of Hydrogen Peroxide, and thus is much lower in cost, and avoids the environmental impact of Hydrogen Peroxide production. The new process is environmentally more benign, economically more attractive, easier to run and control, and produces superior results, over existing technology.

RYNEX® Dry Cleaning Solvent
Rynex Holdings, Ltd.

Rynex Holdings, Ltd. developed, demonstrated and implemented an environmentally safe and effective dry cleaning solvent that is economical and infinitely recyclable. The RYNEX® dry cleaning solvent is composed of an oxygenated surfactant, specifically Dipropylene glycol t-butyl ether (DPTB) and water. This patented technology brings forth new properties that allow for the effective removal of water and oil soluble stains without damage to delicate fibers that can occur with other cleaning methods. RYNEX® is a complete solvent with no hazardous air or water pollutants and has the advantage of behaving like a single molecule. The performance is better than any other solvent available to the dry cleaning industry today. RYNEX® properties include: low volatility, non-flammability, non-carcinogenic and non-persistent in the environment. It has the ability to separate and float on water allowing dirt, grease and soil to be easily removed. RYNEX® cleans water-soluble and fatty acid stains using the same molecule providing, effective detergency and compatibility with existing dry cleaning equipment. It has superior cleaning abilities and does not cause shrinkage to fabrics or cause dyes to bleed with respect to all types of dyes. Enhancements include greater optical brightness in garments and the clothes are softer to the hand.

A New Polymer Coating for Increasing Phosphorous Use Efficiency and Reducing Environmental Impact
Specialty Fertilizer Products

Historically, there has been a problem associated with phosphorous (P) fertilization of crops. Once the fertilizer P is applied to the soil, fixation reactions occur that reduce the P nutrient use efficiency (NUE) by 75-95%. This reduction in efficiency has required farmers to use larger amounts of this essential nutrient to achieve higher crop yields. Poorer NUE of P has led to a build up of residual P in soils which has environmental consequences.

Large sediment loads from soil erosion of land where large amounts of P have been applied, have introduced P into run off waters that have contributed to eutrophication of inland and coastal waterways. In order to improve the efficiency of soil applied P, slow the accumulation of P in agricultural lands and at the same time provide the P needed for higher crop yields, newly patented biodegradable dicarboxylic anionic co-polymers utilized with P fertilizers will lessen or eliminate fixation of P and thereby increase NUE of P fertilizers.

The high cation exchange capacity of these patented anionic diacarboxylic co-polymers when used as coatings on granular P fertilizer interferes with the normal soil P fixation reactions, which allows more applied P fertilizer to remain in solution.

Finessing Carbon Dioxide with Free-Flowing Sulfur
Daniel G. Stecher

Project disclosures teach various multimillion-ton and terawatt hour scale cross-sector environmental benefits when sulfur is combined with liquid sulfur dioxide or anhydrous ammonia without discernable nitrides to form novel mixtures transportable through long-distance pipelines avoiding corrosion, precipitation and clogging of prior art. This is due to unexpected unusual solubility vs. temperature relationships of sulfur in these alternate solvents. Huge-scale carbonless industrial reductants including hydrogen sulfide, ammonia, sulfur dioxide, and sulfur can now be used to make electricity, sulfates, phosphates, gypsum, or hydrogen at very advantageous locations without cartage or greenhouse gas

source pollution. Growing massive problematic excess elemental sulfur inventories can be deposited underground or retrieved and transported without weathering and atmospheric exposure reducing sulfur particulate, run-off and oxides source pollution. Currently wasted hydrogen in hydrogen sulfide reserves can be conserved at much higher practical yields at remote huge-scale sources by known more selective reactions avoiding wasteful Claus processing. Substantially more mineral hydrogen values can be recovered as molecular hydrogen rather than wastewater when processed to provide co-product liquid sulfur dioxide for transport duty. Each ton of conserved molecular hydrogen can be used to avoid about six to ten tons of carbon dioxide pollution from current hydrocarbon reforming.

Natural Plant Hormone Therapy Boosts the Crop Plants "Immune System" Against Insects, Thus Greatly Reducing the Need for Poisonous Pesticides

Stoller Enterprises, Inc.

Insect resistance by plants given a Natural Plant Hormone Therapy is designed to manage the hormonal balance in crop plants, the hormones that are present in plants naturally, to strengthen the crop's natural abilities to counteract insect attack. Validation from universities in the USA and South America is continuously being acquired indicating that auxin indeed gives the plant resistance to an increasing number of kinds of insects, to date including nematodes in plant roots, thrips, white flies, spider mites, aphids and leafminers.

Three important aspects to the use of natural hormones to strengthen the plant's immune system against insects are (1) Economic, (2) Social Benefit and (3) Humanitarian Issues.

Economic Benefit

Not only does Natural Hormone Therapy kill insects but it also strengthens the natural tendency of a crop to produce great yield and quality. The plant with the Natural Plant Hormone Therapy grows in a more vigorous and healthy manner than one that has succumbed to stress and is susceptible to insect attack.

Social Benefit

Consumers do not wish to eat crops or produce sprayed with poisons. The Natural Plant Hormone Therapy strengthens the natural plant's immune system so that it can overcome insect attack. It is this natural immune system that has let the plant evolve over the eons of time without being killed to extinction by insects.

Humanitarian Benefit

Genetic mutations, sterility, acute and chronic health situations are common among agricultural workers using poisonous pesticides. The value in human life lost or affected can be staggering. Natural Plant Hormone Therapy means that the natural hormones that are in the vegetables we eat, in the fruit we eat, and in the grain we eat are able in appropriate amounts to enhance the crops resistance to insects. It means than under times of stress, exogenous applications of the natural hormones can strengthen and help the plant overcome insect attacks. It means that the risk from poisonous pesticides for people and animals is lessened or eliminated compared to those crops treated with poisons. It means that agricultural workers who now have to apply deadly insecticides can be spared repeated exposure to toxic poisons. Natural Plant Hormone Therapy is a revolutionary approach to strengthen the crop plants natural abilities to resist pests and stress.

Waste Minimization and Pollution Prevention Programs for the Production of Films & Chemicals in the Graphic Arts Industry
Ulano Corporation

By replacing hazardous solvent-based coating solutions with non-hazardous water-based emulsions in its film coating operation at Site I, Ulano reduced hazardous waste from 50,000 pounds in 1988 to 200 pounds in 2003 (a 99.6% decrease). By recycling organic solvent blends from tank and pipe rinsings instead of disposing of them in its blending operation at Site II, Ulano reduced hazardous waste from 102,000 pounds in 1988 to 5400 pounds in 2003 (a 94.7% decrease). By redesigning coating cement formulas, Ulano reduced toluene processed during production at Site I, from 68,000 pounds in 1991 to 8800 pounds in 2003 (an 87.1% decrease}. During the same period, toluene released to the environment was reduced from 2000 pounds to 393 pounds (an 80.4% decrease).

Environmental and Economic Benefits of Ulano's Green Chemistry Program: Dramatically reduced hazardous waste, reduced disposal costs, reduced raw material costs, reduced emissions to the environment, and dramatically improved both worker and environmental safety.

Electro-Chemistry
Water Tectonics, Inc.

Electro-coagulation has the capacity to treat emulsified oils, contaminants, metals, submicron particles, and bacteria. When contaminated water passes through the EC system, the fluid and suspended particles are charged using variable current (the colloidal particles in stormwater, primarily negatively charged, are combined with a positive charge from the cell plates, initiating the coagulation process). The particles agglomerate into larger particles and per Stoke's Law, no longer remain static or suspended, but begin to settle. Depending upon the type of particle, it either rises to the surface or falls. The water is then pumped to a settling pond or tank. Stormwater is continuously discharged as controlled by real-time turbidity and pH monitoring. Turbidity reductions from> 2500 NTU to < 5 NTU has been achieved consistently and reduction of phosphorus, heavy metals, and pesticides also were accomplished on recent projects. Efficiencies of the integrated EC system are greatly enhanced due to patent pending automated computerized control of current based upon conductivity of the fluid and particles. Coupled with a sensing system operating in real-time and compensating for variations in the storm water composition and conductivity, we created remote, pond level controls activating the sequencing pumps and the EC system operations. These combined controls with the addition of wireless remote monitoring allow for 24 hour a day—7 days a week operations. This has a dramatic effect upon reducing operational labor costs and monitoring expense. The integrated EC system automation has resulted in the achievement of performance allowing approval of continuous processing and discharge. In-situ toxic testing and bio-assays are performed in the realtime venue all integrated with the overall operations monitoring and discharging of fluids.

Meta-Tec™ Low VOC One Component Cross-Linking Adhesive
W.F. Taylor Co., Inc.

Traditional flooring adhesive chemistry (defined as one- or two-part reactive systems that are urethane, epoxy, solvent, or water-based) includes various industrial solvents and consumes non-renewable resources. The manufacturing and application processes of these adhesives can also create large amounts of hazardous waste by-products and emissions. It is estimated that a minimum of over 23 million pounds of VOCs are released to the environment annually. Meta-Tec™ technology is a unique

class of adhesive chemistry properly designated as a low VOC reactive, one-part, self cross-linking adhesive. While these adhesives have performance characteristics previously exhibited only by reactive systems such as urethanes and epoxies, they contain very low VOCs and emphasize greater use of renewable resources. With the high volume of adhesives used throughout the flooring industry, the ability of Taylor's Meta-Tec™ technology to eliminate the risks associated with volatile hazardous chemicals through reduction of VOCs promises to have a significant positive impact upon the environment and on human health.

WT-HSC13 High Strength, Low VOC Adhesive
Westech Aerosol Corporation

Westech's WT-HSC13 high strength canister adhesive has been carefully formulated to limit volatile organic compounds (VOCs), resulting in a dramatic reduction in toxicity and air pollutants. WT-HSC13 contains no chlorinated or cancer causing solvents (like methylene chloride, a.k.a. dichloromethane). Although a link between cancer and methylene chloride has not been conclusively proven, it is a concern in some geographical areas. In consideration of this, Dr. Carnahan has excluded it from the formula. Most air quality management groups in California now require a VOC level less than 250 grams per liter in an effort to reduce air pollution. The South Coast Air Quality Management District (SCAQMD) for Los Angeles, Orange County, Riverside and San Bernardino takes this a step further by requiring the VOC level to be less than 80 grams per liter. WT-HSC13 is the only solvent-based canister adhesive on the market that complies with this regulation. This new technology in chemistry provides a much needed solvent-based adhesive that is strong, affordable, environmentally safe and adheres to even the strictest regulations with regard to emissions/pollutants.

Aqua Form™, a Water Based, Odorless, Non-Emissive, Non-Styrenated Bonding/Laminating Resin for Structural/Advanced Composites
Zeller International

Aqua Form™ is a self cross linking air drying water based non-emissive polymer which dries/ hardens at room temperature. Aqua Form functions as a wetting agent/binder for numerous forms of pre-sized or gray goods-unprepped non-sized textiles, Fiberglas and carbon fiber reinforcement. Aqua Form is used for durable dimensional shapes without post fume or offgassing. It is a translucent light emitting air/heat cure dispersion used for architectural, decorative, sculptural constructions, light fixtures, panels, free form abstract shapes, scenery, graphics/signage, displays, parade float figures.

Aqua Form wets out, mat/veil cloth, burlap, canvas, non-wovens, Kevlar™, Spectrafiber™, woven roving, Dynel, graphite, carbons, polyester, and numerous E-glass Fiberglas cloths. Aqua Form accepts pigments, dyes, and fillers for viscous gels, Gesso's, putties, and modeling pastes. It is suitable for interior/exterior applications, cleans up with tap water, and is used in small confined areas for vapor/odor free repairs, restoration, stiffening, lining, and structural reinforcement.

Aqua Form is a user friendly planet kind "0" VOC consolidating binder for strong impact resistant composites. Aqua Form is for chemically sensitive individuals. Aqua Form can be painted/overcoated with solvent or water based lacquers, coatings, varnishes, epoxy finishes for wet/damp environments such as foliage, props, rain forest, swamp, scenic settings.

New Biomass Catalytic Reforming Process for SOFC Power Generation
Zivatech

This nominated technology is based on the analysis, testing and evaluation of a new reforming process for conversion of biomass and other secondary, waste streams into a syngas outlet stream rich in hydrogen gas for powering a directly interconnected solid oxide fuel cell. These waste sources are rich in methane and carbon dioxide and the new process is using an effective catalytic reformer to convert those efficiently in a syngas outlet stream. The stream is used as feed into the anode of an integrated fuel cell of a solid oxide structure. Conversion of the above waste source streams to synthesis gas for use in SOFC based electricity generation systems is of increasing importance to both commercial and remote residential energy consumers from an energetic, economic, and clean energy point of view. The use of renewable waste biogas resources is of increased interest to the clean and highly efficient energy generation market. In addition, the designed innovative conversion process of carbon dioxide rich methane gas inside an in-situ reactor, via the developed reaction and catalysis system is under increased consideration in current and future industrial efforts and is considered an additional benefit of this proposed work.

Entries from Industry and Government

All-Acrylic Binders for Low VOC Architectural Coatings
BASF Corporation

Various regulations require solvent level reduction in paints and coatings in an effort to reduce the VOCs that lead to smog creation. One obstacle to meeting these regulations is the latex binder itself, which has traditionally required a coalescing solvent for adequate film formation. Binders soft enough to form a film in the absence of solvent result in tacky, non-durable films. Strategies for increasing film hardness such as, crosslinking, blending or special additives are too complex and costly for most applications. Alternatively, using non-volatile plasticizers in place of solvents adds cost and complication since the plasticizer remains in the film rendering it still too soft. Acronal Optive™ multiphase latex technology from BASF is the first robust and economically viable all-acrylic solution to this conundrum. Multiphase latex technology combines the benefits of a hard, durable polymer and a soft, film-forming polymer into the same latex particle. By using this technology, a paint formulator can reduce VOCs and still achieve the excellent film formation and durability previously accomplished only by incorporating odorous, toxic and environmentally harmful solvents. BASF conducted an eco-efficiency analysis, which demonstrated that Acronal Optive™ multiphase latex technology significantly reduces VOC emissions and the risk potential associated with handling the solvents and solvent-laden paints that lead to VOC.

Environmentally Friendly Bio-Based Plasticizers for Polyvinyl Chloride Resin
Battelle Memorial Institute

There is a strong interest in finding alternative PVC plasticizers that are economically competitive and equivalent or better in performance to DOP with no health and environmental concerns. Over 2 billion pounds per year of DOP plasticizer are used in the U.S. to process polyvinyl chloride resins to make flexible and semi-rigid extruded articles such as films, tubes, blood bags, toys, etc. Although DOP and other petroleum-derived synthetic plasticizers have good performance in the processing of PVC articles, they suffer from two deficiencies, namely, potential health and environmental concerns, and high levels of volatility and exudation. There seems to be continued controversy over the use of DOP emphasizing the need for viable alternatives (*Chemical Week*, p.43, Sep 18, 2002; *Modern Plastics*, p.38 September 2003; *Plastics Engineering*, p.42, April 2003). A recent German risk-assessment study shows that intake of DOP could be much higher than the accepted level of 50 :g/kg body weight per day (*Modern Plastics*, p. 16, November 2003).

Successful development and commercialization of soybean oil-derived plasticizer technology will address a major need in the large and growing PVC industry, namely, a cost effective plasticizer that is less volatile and safe, and does not have the health concerns associated with DOP. Replacing even a part of the 2 billion pounds per year U.S. market for DOP with a bio-based product derived from soybean oil offers significant energy savings with reduced carbon dioxide emission.

Substitution with Carbon Dioxide Eliminates Major Use of Sulfuric Acid
Crane & Company, Inc.

Crane & Company Inc. reduced the use of sulfuric acid by approximately 697,000 lbs and sodium hypochlorite by 576,000 lbs between 1999 and 2000, a combined reduction of about 46%. The company

achieved these reductions by modifying the process chemistry for the re-pulping of off-specification papers. The sulfuric acid was replaced with an innovative liquid carbon dioxide system and the sodium hypochlorite was reduced by specifying cleaner raw materials, and by controlling the temperature and pH of the process.

Cylinderized Phosphine Fumigants as Safer, More Environmentally Friendly Alternatives to Traditional Stored Product Fumigants Such as Methyl Bromide and Metallic Phosphides
Cytec Industries Incorporated

Cytec Industries has developed and commercialized new technology for the stored product fumigation market. Traditional fumigants such as methyl bromide and metallic phosphides have significant safety and environmental shortcomings in their use, application and disposal. Cytec's cylinderized phosphine products address these issues to provide products which result in less worker exposure reduced environmental impact and which are inherently safer.

n-Alkyl Propionate Ester Solvents
The Dow Chemical Company

Union Carbide Corporation, A Subsidiary of The Dow Chemical Company manufactures a family of three n-alkyl propionate ester solvents under the UCAR trademark. These solvents, consisting of n-propyl propionate, n-butyl propionate and n-pentyl propionate, are quickly replacing other solvents as more environmentally friendly alternatives due to their non-HAP (Hazardous Air Pollutant) status by the US Environmental Protection Agency (EPA), superior solvency, low ozone-forming potential and low odor.

Dow BioProducts Ltd. WOODSTALK™ Strawboard
Dow BioProducts Ltd.

Dow BioProducts has implemented a revolutionary process for the manufacturing of fiberboards using 100% waste straw as the fiber raw material. After the harvesting of wheat grain, the remaining stalks are typically burned in the fields or plowed into the topsoil. Historically, field burning has been the preferred method of disposal. However, CO and CO_2 emissions from open air field burning can be significant, especially in the wheat belt areas of Kansas, Iowa and Manitoba. Smoke from these burning fields poses visibility and health concerns. With the WOODSTALK™ process, straw that would have been considered waste and burned in the fields is collected in a second harvest and manufactured into a fiberboard composite panel. WOODSTALK™ fiberboard competes head-to-head with traditional fiberboards made from wood particles (i.e., particleboard, medium density fiberboard, and plywood). In addition, WOODSTALK™ fiberboard does not use formaldehyde-based resins and thereby has substantially less of the aldehyde emissions that can impact indoor air quality as that found in traditional wood-based composite panels. Hence, the WOODSTALK™ process uses waste from a renewable resource, reduces CO and CO_2 emissions associated with the wheat harvest, and substantially reduces aldehyde emissions that are a growing issue with indoor wood-based composite panels. Dow BioProducts does this today while being competitive with traditional indoor wood-based fiberboard products.

Commercial Manufacturing Process for Indoxacarb
E.I. DuPont de Nemours & Co., Inc.

The basic synthesis route for indoxacarb manufacture was selected in 1994. The first scaled up version of the process produced the racemic compound DPX-JW062. This initial process required five reaction steps, utilized highly hazardous materials, produced a racemic product, generated a substantial amount of organic and aqueous wastes, and required four different organic solvents which necessitated numerous isolations, solvent exchanges and dryings. Further process development efforts proceeded with many opportunities to apply the principles of green chemistry in the commercial process. The commercial process started up in January, 2000. The discovery of new catalytic asymmetric oxidation chemistry and new synthetic strategies, the use of a single reaction solvent and single recrystallization solvent both co-products of the process, and meticulous process development and simplification resulted in the production of enantiomerically enriched DPX-MP062, a greater than 90% reduction in overall waste, and a substantial improvement in overall yield. This effort enabled DuPont to take indoxacarb, a significant new insecticide, into commercialization.

Enzyme-Based Technology for Decontamination of Organophosphorus Nerve Agents
Edgewood Chemical Biological Center

The most significant advancements in the research, development and implementation efforts on the nominated technology took place within the US during the past five years. The research and development aspects of the technology culminated with three US patents: #5,028,927, 27 Jul 1999; #6,080,566, 27 Jun 2000; and #6,469,145, 22 Oct 2002. Over the same period, there have been five open literature publications, nearly thirty government publications and approximately thirty technical presentations. In regards to implementation, a patent license agreement will be signed with Genencor International, Inc., in Jan 2004 for the large-scale production of two nerve agent detoxifying enzymes. Commercial products based on these enzymes will begin to be marketed by mid 2004.

Low Temperature, Lead-Free Interconnect for Electronic Circuit Assemblers
Emerson & Cuming

Tin/lead eutectic solder is currently the most common method used to attach electronic components on circuit boards. Lead, however, is a known toxin. Because of concern over lead leaching into the environment, Europe recently passed legislation requiring the mandatory recycling of consumer electronics containing lead by 2006. This has prompted electronic circuit assemblers to seek an alternative attachment solution. Conductive adhesives have also been used for years in some applications, but their use has been limited to the attachment of noble metal (palladium/silver, silver and gold) terminated components on both ceramic hybrid boards and flexible polyester circuits. Our recent development of novel and patented chemistry has allowed us to achieve stable contact resistance and stable adhesion under damp heat and high temperature aging conditions with non-noble metal (tin, tin/lead, and copper) finishes. Stability with these finishes was not possible in the past. This stability was achieved by preventing the occurrence of galvanic corrosion on these less expensive, non-noble metal finishes. The incorporation of a corrosion inhibitor in our adhesive formulation prevents oxidation of the tin on the component under extreme environmental conditions and leads to stable performance over time.

Metal, Phenol and Ash-Free Antiwear Hydraulic Additive Providing Performance Previously Only Achieved by Use of Zinc Containing Additives
Ethyl Petroleum Additives Inc.

The use of heavy metals in lubricants presents environmental concerns primarily due to zinc contamination coming from hydraulic oils. The global antiwear hydraulic lubricant market consists of approximately 980 million gallons, roughly 95% of which is based on lubricants containing Zinc Dialkyl Dithiophosphate (ZDDP) as the antiwear additive and only approximately 5%, based on lubricants containing the less toxic, environmentally friendly, ashless antiwear additive technology. Of the lubricants using the ashless additive technology, the majority of the fluids are based on conventional mineral oils with globally, only approximately 3% based on biodegradable fluids. The slow growth in the use of antiwear hydraulic fluids based on ashless technology is due, in part, to problems in the field, where performance equivalent to fluids based on ZDDPs has not been achieved. This is especially true for biodegradable hydraulic fluids. In this work we have identified an additive technology that is not only ashless, but also phenol free which when used in mineral oils gives performance equivalent if not better than that of ZDDP based fluids. This is the first ashless mineral oil based technology to be tested and approved against new, more severe requirements from original equipment manufacturers (OEMs). Also this ashless additive technology, along with boosters in biodegradable oils, is the first to be approved against new specifications, designed specifically for environmentally friendly fluids.

RPS Technology: Breakthrough Technology for Water-Based Paints, Coatings, Adhesives and Sealants
The Goodyear Tire & Rubber Company

RPS Technology utilizes an innovative and very general approach for producing cured polymer films from polymer latex containing small amounts of metastable organosilicon compounds. These organosilicon compounds are incorporated into the polymer latex via conventional emulsion polymerization, which produces a water-based product suitable for use in a wide range of coatings and adhesives applications. After the latex is applied to a substrate, evaporation of its water triggers a chemical reaction that produces reactive silanol (i.e., Si-OH) groups. These groups react rapidly to produce cured films with excellent solvent resistance, good mechanical strength and superb adhesion to a wide variety of surfaces.

The human health and environmental benefits of RPS Technology are potentially enormous because the technology should be generally applicable for the production of water-based paints, coatings and adhesives. In addition to improving the performance of existing water-based products, RPS Technology provides excellent opportunities for creating water-based products that match or exceed the high performance of solventbased products. Broad implementation of RPS Technology would: (1) represent a huge source reduction in VOCs; (2) improve the health of workers currently exposed to solvent-based paints, coatings and adhesives; and (3) reduce waste associated with the use of solvent-based products with limited pot-life.

Using Chemistry and Engineering Technology to Reduce Volatile Organic Compound Emissions and Eliminate Hazardous Process Waste Generation in the Printing Industry
Highland Supply Corporation

HSC reduced VOC emissions and eliminated hazardous air pollutants (HAPs) and hazardous process waste by switching from solvent based printing inks to water based printing inks.

In 1988, the executive management of HSC accelerated its efforts to develop a viable water based ink system and issued a corporate policy which directed the reduction of VOC emissions and HAPs which are harmful to human health and the environment. The company researched installing air pollution control equipment but chose to replace its solvent based ink system with cleaner water based system. Further investigation revealed that commercially available water based inks contained approximately 20% VOCs by weight. HSC elected to develop an in-house water based ink system to obtain greater reductions in VOC content and higher print quality.

Today, HSC's water based ink system contains less than 0.70% VOCs by weight. HSC continues to aggressively search for components that will lower this percentage. The company has developed ways to recycle all of its water based inks in-house by reformulating excess inks into useful ones. HSC thoroughly reviews product information and controls all items which enter all of its facilities based on strict environmental, health and safety criteria.

ECONEA®028: Designing and Developing a Metal-Free, Environmentally Safe, and Effective Antifoulant for Use Against Hard Fouling Marine Organisms
Janssen Pharmaceutica Inc.

ECONEA®028 is the trade name for a new, non-metal compound developed and tested by Janssen to replace copper compounds now used to control hard fouling organisms on underwater surfaces. Paint containing 3-6% ECONEA®028 provided excellent hard fouling control on numerous test panels on commercial and military vessels. Once released at the surface of the paint into the environment, ECONEA®028 is transformed rapidly into less toxic degradation products that pose minimal risk to aquatic life at predicted environmental concentrations. ECONEA®028 degrades rapidly in seawater by hydrolysis, and in sediment by anaerobic and aerobic metabolism (half-lives of 3 hours, < 1 hour, and < 1 day, respectively). Environmental modeling indicates that ECONEA®028 can remedy an existing environmental problem in San Diego Bay (SDB), where copper levels exceed clean water standards. Elimination of copper from U.S.Navy antifouling paints, by combining ECONEA® for hard fouling with an existing antifoulant for soft fouling, potentially can reduce copper loading in SDB by over 7,000 Kg per year from hull leachate. The combined copper burden in aquatic ecosystems of four military ports can be reduced by over 25,000 Kg annually using this technology, with potentially over 98,000 kg copper annually by conversion of the entire military fleet.

Novel Cleaning System Using less Toxic and Safer Chemicals
JohnsonDiversey, Inc.

This technology is based on peroxygen chemistry in developing more efficient cleaners and germicides with safer and more environmentally preferable chemicals. The application is the cleaning and sanitization of ultrafiltration (UF) polyethersulfone(PES) 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 small amount of non-ionic surfactants. The acid cleaners typically consist of high levels of a blend of phosphoric/nitric acid. The current sanitizer used is sodium hypochlorite solutions at the 200 ppm level. This new technology yields safer cleaners by formulating at a more neutral pH. The use of hydrogen peroxide provides a good bleach alternative that sanitizes more gently than chlorinated alkaline sanitizers. The overall benefits are to clean and sanitize effectively using less toxic chemicals than current alternatives and safer with regards to human health and environment. Also,

this technology has a great economic impact by performing the cleaning and sanitization at lower temperatures resulting in energy savings, plant down time reduction, decrease water and wastewater usage and improve the long-term stability of the UF membrane.

Formamide Replacement in Genetic Sequencing
Los Alamos National Laboratory

The process to determine a nucleotide sequence for a segment of DNA requires multiple steps and chemicals. Formamide was used in the past to resuspend DNA after it had been denatured prior to sequencing. However, formamide is a hazardous chemical with an unpleasant scent that could potentially harm a fetus according to its Material Safety Data Sheet. Researchers at the Los Alamos National Laboratory searched for a non-hazardous replacement for formamide to reduce potential adverse exposure to employees. The research team discovered that a water-based solution gave even better results than formamide for resuspending DNA during the sequencing process. The water-based solution is called Tris-EDTA (TE), and it is easy to mix in any biochemistry laboratory. Formamide was the only hazardous chemical associated with genetic sequencing, so eliminating formamide substantially reduces the amount of hazardous waste and paperwork involved with operations. Total annual savings on reduced waste disposal, procurement costs of distilled formamide, and labor are approximately $78,000.

Equinox™: A Greener Approach to Microbiological Control
Lonza Inc.

Sodium hypochlorite is a well-known inexpensive papermaking slimicide. Far more hypochlorite is currently used to control slime in papermaking as compared to any other chemical. Unfortunately, hypochlorite is highly reactive towards organic papermaking furnish components. Such reactions reduce the efficiency of hypochlorite treatments, resulting in increased use of chlorine, which leads to increased AOX production.

Equinox™ technology was designed by Lonza Inc. as an environmentally sensible chlorine stabilizer. The technology is based on the unique properties of 5, 5-dimethylhydantoin (DMH) to stabilize hypochlorite systems and enhance hypochlorite bactericidal efficiency. Implementation of non-toxic Equinox™ chemistry eliminates the practice of excessive feed of chlorine and results in a dramatically reduced production of unwanted toxic by-products. Lower chlorine usage means lower amounts of AOX compounds ultimately being released in discharge waters.

Equinox™ was developed, tested and proven as a safe and effective chlorine stabilizer for papermaking industry. Equinox™ can be successfully used in any industrial water with high organic content where common chlorine is utilized as a biocide, sanitizer or disinfectant.

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

Many important principles of green chemistry, such as reduction in the use of raw materials, energy consumption, environmental impact and safety hazards, were used as guidelines in the discovery, development and implementation of a new manufacturing process for aprepitant. This compound is the active pharmaceutical ingredient of Emend®, a break-through new medication for the treatment of

chemotherapy-induced nausea and vomiting. A first generation process envisioned for manufacturing aprepitant relied on significant improvements to the discovery synthesis. However, to achieve more than incremental progress towards the green principles outlined above, researchers at Merck set out to discover a completely new synthetic route. Using cutting-edge technology for each of the steps, aprepitant could be synthesized in half the number of chemical steps with a near doubling of the overall yield, compared to the first generation process. This not only reduced the total amount of required raw materials as well as the amount of waste produced by nearly 80%, but also eliminated several severe operational hazards associated with the first generation process. The innovative aspects of Merck's new synthesis for this important molecule have been recognized by the scientific community in the form of several patents, peer-reviewed journal publications, and numerous invited lectures.

Development of Nike Footwear Outsole Rubber as Environmentally Preferred Material
Nike Global Footwear

One of Nike's long-term, corporate environmental goals is to eliminate all substances that are known or suspected to be harmful to human health or the health of biological or ecological systems from its products. To move towards this corporate goal, Nike's footwear organization began an effort to work to eliminate many of the toxic substances from the process of manufacturing footwear rubber outsoles which are common to the athletic footwear manufacturing industry. Nike developed the optimization of rubber outsole project with the following general strategies: selection of a Toxic Chemical Assessment Protocol which identified ingredients to work to avoid, assessment of certain of Nike's rubber formulations against the Protocol, testing and commercialization. The project resulted in a new environmentally preferred outsole rubber that provides a substitution for a traditional Nike rubber formulation (Formula A). A representative sample of the new environmentally preferred rubber contains 96% fewer toxics by weight than the original formulation and costs no more than the traditional rubber.

Through internal incentives and executive reviews, Nike rewards teams that use materials like the environmentally preferred rubber. Nike began using the environmentally preferred rubber in soccer and casual sporting shoes and now footwear development groups in the outdoor, training, running, basketball, Jordan and women's groups have used or have designs in place that will use the Environmentally Preferred Rubber. In one of Nike's most recent production seasons, approximately 7% of Nike's total rubber usage was in the environmentally preferred rubber.

The Development of Green and Practical Processes
Utilizing Dialkyl Carbonates as Alkylating Reagents
Novartis Pharmaceuticals Corporation

In the last five years, Novartis' green chemistry project has developed an environmentally friendly methylation process which employs 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) or 1,4-diazabicyclo[2.2.2]octane (DABCO) as novel catalysts for promoting methylation reactions of phenols, indoles, benzimidazoles, and carboxylic acids with dimethyl carbonate under mild conditions in nearly quantitative yields. Similarly, a novel and green process for the benzylation of nitrogen, oxygen, and sulfur atoms with dibenzyl carbonate was developed by employing catalytic amounts of DABCO or DBU. Additional rate enhancement was accomplished by applying either microwave irradiation or an ionic liquid. By combining DBU or DABCO, microwave irradiation, and ionic liquid, very slow alkylation reactions that previously took up to several days can be performed efficiently in high yields within minutes. Novartis' technology avoids the use of toxic or carcinogenic reagents such as methyl iodide, dimethyl sulfate, benzyl chloride, or benzyl bromide. It also eliminates the need of stoichiometric

amount of base if applicable substrates contain no acidic protons. The novel technology has the benefit of rapid reaction times, ease of operation, use of readily available catalysts and ionic liquids. This should make this newly developed chemistry of great benefit to humans and the environment.

AquaSentinel
Oak Ridge National Laboratory

The AquaSentinel is a revolutionary advance in the protection of primary-source water supplies. It uses the natural processes of photosynthesis combined with state-of-the-art optoelectric instrumentation to provide continuous, unattended protection of all surface-exposed primary source drinking water supplies. Algae grow in all water that is exposed to light. The detection system, invented at Oak Ridge National Laboratory, measures characteristics of photosynthesis, using fluorescence induction curves as a real-time tool to detect the exposure of these microscopic algae to toxic agents. The detection system provides a field-deployable instrument, around-the-clock monitoring of drinking water, and an early warning alert for chemical attacks or toxic spills. Water supplies are vulnerable to attacks that can render the water hazardous or deadly if consumed. However, current methods for testing water safety are cumbersome and often require several hours for test results. The AquaSentinel is designed to help water industry professionals deal with the current challenges of water security and protect the public from exposure to toxic agents.

Green Chemistry in the Redesign of the Celecoxib Process
Pfizer Global Research and Development

The celecoxib manufacturing process was redesigned with Green Chemistry objectives as part of the project's primary goals and resulted in dramatic environmental and worker safety improvements in the manufacture of the active ingredient in the medicine Celebrex®. These improvements followed the elucidation of two unprecedented reaction mechanisms responsible for the formation of isomeric impurities whose presence required a subsequent recrystallization with its concomitant yield loss and resource expenditure. Application of this new mechanistic understanding provided a significant increase in the process efficiency with respect to raw materials, solvents, energy and waste.

The environmental and safety improvements were significant. In total, 5200 metric tons/year of organic solvents were eliminated. THF and 35% HCl (212 metric tons/year) were completely removed. Organic solvent washes during isolation were partially replaced by water. Additionally, raw material input was reduced by over 150 metric tons/year. By eliminating the recrystallization, and judicial utilization of the heats of reaction and other temperature parameters, in excess of 4 billion BTUs/year were saved. Worker safety was improved by reducing the number of unit operations require per batch and by improving the process payload (product produced/reactor volume) resulting in the need for fewer batches to fulfill demand.

A Green Process for the Synthesis of Quinapril Hydrochloride
Pfizer Global Research and Development

Green chemistry objectives were emphasized in the redesign of the quinapril HCl process. The resulting process employs more efficient chemical transformations with dramatic environmental and worker safety improvements for manufacture of the active ingredient in the important cardiovascular medicine Accupril™. Process yields have increased by 30%. The use of methylene chloride and the

highly toxic sensitizer dicyclohexylcarbodiimide have been eliminated. Process throughput has quadrupled and operations that caused yield loss due to the intermolecular cyclization of quinapril HCl have been minimized. Overall improvements resulted in the elimination of the isolation of one intermediate, two drying steps and a hydrogenation step.

The environmental and safety improvements are dramatic. Use of approximately 30 metric tons/year of dicyclohexylcarbodiimide and the subsequent generation of 30 metric tons/year of solid dicyclohexylurea waste were eliminated. The use of approximately 1100 metric tons/year of methylene chloride was eliminated. The volume of solvent used was dramatically reduced; aqueous and organic wastes were reduced by 90%. The efficient use of raw material, water, and energy was remarkably improved.

The Discovery and Development of an Environmentally Benign Commercial Route to Sildenafil Citrate
Pfizer Global Research and Development

Green Chemistry objectives were emphasized in the Discovery and Development of the commercial route to sildenafil citrate, the active ingredient in the important medicine Viagra™. The commercial synthesis generates only 4 Kg of organic waste per kilogram sildenafil, substantially less than is typical for a pharmaceutical product. The key breakthrough in achieving this exceptional result was the discovery of a new, convergent, synthetic route, which was designed with a clean cyclization reaction as the final step hence eliminating purification operations. Subsequent careful chemical development and diligent solvent recovery optimized the environmental performance.

Achievements include a nine-fold yield increase from the pyrazole (1) to sildenafil citrate. The amount of organic and aqueous waste is reduced 14 and 5 fold eliminating over 4000 tonnes and 3900 tonnes of organic and aqueous waste respectively. A tin chloride (toxic heavy metal) reduction was replaced by an environmentally benign catalytic hydrogenation reaction. Hydrogen peroxide (a worker safety issue) was eliminated. Three chemical steps were combined, using a single solvent that was recovered. In eight chemical steps there is no reaction that requires a work-up involving extraction, again leading to low organic waste. Many technological achievements were implemented at the outset of commercial manufacture.

Self-Assembled Monolayers on Mesoporous Silica Technology: A Powerful Novel Adsorbent for Mercury Removal from Waste Streams
Pacific Northwest National Laboratory

Scientists at the Pacific Northwest National Laboratory have patented a simple, inexpensive, and easy-to-use technology that quickly absorbs mercury from low-volume waste streams. Scientists are exploring its use for soil and water cleanup where mercury contamination is prevalent, and for mercury removal in radiological hazardous waste. Called thiol-self-assembled monolayers on mesoporous silica (thiol-SAMMS), this technology is a new class of high-performance nanoporous sorbent material for mercury (a highly toxic heavy metal) that overcomes the deficiencies of conventional mercury-removal processes. Thiol-SAMMS works by integrating a nanoporous substrate with an innovative method for attaching monolayers, or single layers of densely packed molecules, to the pore surfaces throughout the substrate. The monolayers can be tailored to seek out and absorb not only mercury but also silver, cadmium, copper, and lead. Thiol-SAMMS absorbs and encapsulates large quantities of mercury without creating secondary waste and can be disposed of as *nonhazardous* waste. During testing, scientists found that the mercury adsorbed remains in the spent thiol-SAMMS and passes stringent U.S.

Environmental Protection Agency requirements (TCLP test) for safe land disposal. The use of thiol-SAMMS will result in significant cost savings to users who must treat and dispose of mercury-contaminated material using costly conventional treatment and disposal processes.

PURE PERFORMANCE ™ "Zero" VOC Latex Coating
PPG Architectural Finishes, Inc.

Pure Performance™ was developed to address the growing need for premium paint with environmentally preferred characteristics. Pure Performance™ is unique because it offers the traditional features of premium paints such as durability, hiding and touch-up while also adding the additional benefits of zero VOC, minimal odor, and mildew resistance on the paint film. Pure Performance™ paint primarily utilizes vinyl acetate-ethylene (VAE) polymer emulsions. The VAE polymer emulsion improves water resistance and provides added durability. In addition, the polymer "self-coalesces" or melts together when drying without the need for coalescing solvents. Because this product does not require solvents, VOC (volatile organic compound) emissions and the odors associated with the solvents are eliminated.

Oxygen-Enhanced Combustion (OEC) for NOx Control
Praxair, Inc.

Praxair's Oxygen-Enhanced Combustion technology for NO_x control represents a unique combination of reduced NO_x emissions and enhanced combustion. In OEC, a small portion of the combustion air in a staged combustion system is replaced with oxygen, which increases the local temperature under fuel-rich conditions. These higher flame temperatures enhance reactions, converting NO_x to N_2 in the flame zone. As demonstrated in scales ranging from laboratory-scale furnaces to a nominal 125 MW power plant, oxygen-enhanced staged combustion significantly reduces NO_x emissions without added operational problems commonly associated with staged combustion.

By minimizing NO_x formation in the combustion zone, OEC reduces or eliminates the need for post-combustion cleanup technologies that utilize ammonia, such as SCR. By minimizing the need for SCR systems, Praxair's OEC technology also minimizes the requirement for the production, transportation, and storage of ammonia. Given the hazardous nature of ammonia, minimizing its use reduces the potential for harm to both plant personnel and the public. Replacing ammonia with oxygen also reduces atmospheric emissions of ammonia, thereby reducing the associated respiratory health impacts. Further, since ammonia production requires the use of natural gas, minimizing its use also helps preserve this important natural resource.

Invention and Commercialization of Environmentally Friendly Acrylic Thermosets
Rohm and Haas Company

Thermosetting binders are used ubiquitously in composite building and construction materials such as fiberglass insulation, ceiling tiles, air filters, and particleboard. Far and away the most common thermosetting resins used in industry are century-old formaldehyde-based resin systems, including phenol-formaldehyde (PF), urea-formaldehyde (UF), and melamine-formaldehyde (MF). Unfortunately, the inherent reactivity which makes these systems excellent binders also makes them extremely dangerous to human beings. Acrylic Thermoset technology offers a green chemistry solution to the myriad of problems associated with formaldehyde-based resins. The patented technology consists of an

acrylic polymer based resin with a polyol crosslinker and phosphorous-containing catalyst. This novel technology is ideal as a green chemistry solution because it is simple, safe and completely removes phenol and formaldehyde from the equation. Because the reactivity of the system comes from the catalyst, acrylic thermosets are completely non-toxic and stable at ambient conditions. The only byproduct of cure is water and the resin does not contain formaldehyde or formaldehyde producing chemicals. Used in the place of formaldehyde resin systems, acrylic thermosets offer comparable or superior properties at a competitive cost. Acrylic thermosets have already been adopted commercially in applications such as home building insulation, ceiling tile, and appliance insulation.

Greenlist™: Informed Choices for our Environment
SC Johnson

The Greenlist™ process is an environmental classification system based on four to seven specific criteria for chemicals within functional material categories. These include surfactants, solvents, propellants, insecticides, resins, packaging, chelants, antimicrobials/preservatives, fragrance raw materials, waxes and candle fuels, thickeners and future categories such as colorants, and inks. The criteria, which are selected to be meaningful and discriminating within the function groups, include: biodegradability, aquatic toxicity, human toxicity, EU environmental hazard classification, preferred source/supply, vapor pressure, octanol/water coefficient, and other criteria appropriate for the functional material categories.

The environmental classification (EC) score for each raw material is based on the mean of the scores for each criterion appropriate to the category: Best (3), Better (2), Acceptable (1) and Restricted Use Materials or RUMs (0). The final EC score is lowered in some cases to account for "other significant concerns" including: EPA/UN classifications - PBT/POP, endocrine disrupters, carcinogenicity, reproductive toxicity, and other “chemicals of concern” lists.

Product formulators may access the EC score of each chemical via our global databases. Formulators have a goal to use “Better” or “Best” chemicals in product development. By measuring its progress, the company is institutionalizing sustainability and improving its environmental footprint.

Uniseal Inc. reformulated the primer portion of the lamination process in their closed cell sponge rubber (Foam) division in an effort to reduce the use / release of hazardous air pollutants (HAPs). The primary goal was to eliminate Trichloroethylene from the process. The lamination process involves running closed cell sponge rubber through custom-designed lamination machines, which apply primer and pressure-sensitive adhesive to the foam. Uniseal began by trialing the replacement of Silaprene Adhesive with the 3M Primer already in use. The Silaprene Adhesive was also a contributor to their HAP emissions, with a composition of 20% HAPs (Toluene, CAS# 108-88-3). The reason Uniseal began with the replacement / elimination of Silaprene Adhesive is because the Silaprene Adhesive is carried by trichloroethylene. A small-scale trial conduted by hand indicated that both types of foam can be laminated with the same primer. The primary ingredient in the 3M primer already in use is cyclohexane, and was already being used in this combination on one type of foam, so that became the replacement chemical. Efficiency and quality problems soon surfaced because the cyclohexane was not flashing off quickly enough. Next, the trial went to acetate, which also did not flash off quickly enough. Uniseal then decided to try using acetone, which is working rather well. The workability of the acetone is a benefit not only in that it is not a hazardous air pollutant, and not a regulated VOC, but it is also not an ozone precursor.

Environmentally Friendly Water Treatments for Control of Corrosion, Scale and Bioactivity in Heating and Cooling Systems
U.S. Army Engineer Research and Development Center

The U.S. Army Corps of Engineers Engineer Research and Development Center (U.S. Army ERDC) led a research team composed of Federal Government, academic, and private industry researchers to develop a green approach to water treatment for control of corrosion, scale deposit, and microbiological growth for heating systems (boilers and condensate lines) and cooling systems (cooling towers). The project objectives included development, field demonstration and evaluation of three green chemical formulations, as well as state-of-the-art automated equipment to minimize the hazards of chemical handling. U.S. Army ERDC teamed with the Garratt-Callahan Chemical Company; Trevino Mechanical, a small business mechanical sub-contactor; SurTech Corporation to perform the field demonstrations, and the Illinois State Water Survey for verification of field data. The water treatment formulae were applied and their performance monitored at three military installations for a period of two years.