

Draft Summary of 2002 Award Entries: Presidential Green Chemistry Challenge Awards Program

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Entries from Academia

Environmentally Benign Preparation and Polymerization of Phosphazene Polymers

**Dr. Christopher W. Allen, University of Vermont;
Idaho National Engineering and Environmental Laboratory**

Our newly developed, innovative, polymer synthetic method eliminates use of all halogenated hydrocarbon solvents in the synthesis of polyphosphazenes. This synthetic breakthrough offers significant environmental benefit in the preparation of these important inorganic polymers. Polyphosphazenes – one of the most versatile classes of inorganic polymers known -- are unique in their broad spectrum of properties and related commercial applications. For example, they offer the chemist great flexibility in tuning the polymer physical properties. In addition, polyphosphazenes are well known for their stability when exposed to heat, radiation, and chemicals. The synthesis of polyphosphazenes can occur by three routes: (1) traditional ring-opening synthesis (2) living polymerization, which proceeds through formation of a silylphosphoranimine, and (3) the “DeJaeger” method. Each of these three types of synthesis has advantages and disadvantages. All of them, however, as now practiced by industry, require high-boiling halogenated solvents both for thermal control and dispersal. Our approach eliminates use of all halogenated hydrocarbon solvents and produces phosphoryl chloride, a byproduct chemical having commodity uses within the chemical industry.

A Novel Additive System for Time-Controlled Degradation of Polypropylene

Dr. Dianne Allen

Iron(III)dimethyldithiocarbamate (FeDMC) and Nickel(II)di-n-butylthiocarbamate (NiDBC) have been used in agricultural applications for their ability to create time-controlled degradation of both polyethylene and polypropylene upon exposure to sunlight. Polymers containing these additives in concentrations ranging from 0.001% to 0.5% by weight demonstrated a period of mechanical stability followed by a period of rapid degradation. However, the system has not been widely recognized as FeDMC decomposes at 180°C, significantly below the standard processing temperature for polyolefins. Experiments were carried out using Iron(III)Acetylacetonate (FeAcAc) in place of the dithiocarbamate as part of the iron/nickel system in isotactic polypropylene. FeAcAc is stable under all standard processing temperatures. A mixture of the additives and polypropylene pellets was extruded and melt pressed to create films. Spectroscopic and mechanical properties of the films were observed during lab exposure to ultraviolet light to follow the degradative process. Similar controllable degradative behavior was noted, indicating that this new additive system should be extendable to other polyolefins and should perform in all ways like the previous system except that it may now be processed under standard conditions, making time-controlled degradation much more accessible to industry.

Production of H₂O₂ from H₂ and O₂ in CO₂ and its Application to the Direct Synthesis of Propylene Oxide from Propylene

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

Hydrogen peroxide is generally considered to be a green oxidant, as it is relatively non-toxic and breaks down in the environment to non-toxic byproducts. However, the current method for production, the sequential hydrogenation and oxidation of an alkyl anthraquinone, is capital-intensive, produces significant volumes of waste, and consumes sizeable quantities of energy during the purification and

concentration of the product. There has been great interest in the direct synthesis of H_2O_2 from O_2 and H_2 , yet processes developed to date have been unable to resolve the safety vs. productivity dilemma to the point where scale-up has been advisable. We have designed CO_2 -soluble catalysts, and have successfully generated H_2O_2 from H_2 and O_2 in carbon dioxide/water mixtures. The use of CO_2 as solvent allows for use of reasonable concentrations of H_2 and O_2 without danger of explosion, and homogeneous catalysis eliminates diffusional limitations to reaction. We have also recently demonstrated that the safe and rapid production of H_2O_2 directly from H_2 and O_2 in CO_2 allows for the economical direct synthesis of propylene oxide (PO) from propylene. The current process for PO production is neither atom- nor energy-efficient, and hence a direct epoxidation route has been highly sought after.

An Innovative Replacement for Chromium for Aluminum Coatings Dr. John N. Crisp, University of New Orleans Lakefront Campus

An environmentally benign substitute for Chromium has been discovered which provides excellent corrosion resistance for aluminum surfaces. The material can be formulated both for pigment and conversion coating applications. The material has undergone extensive laboratory tests and demonstrated good adhesion and good corrosion resistance. The material has been patented.

The fundamental goal of this project was to find the pigments that could satisfactorily be substituted for environmentally hazardous chromium coatings in use. From the many possibilities that exist, experimental data led to a successful first formula. Since the lithium salts passivate aluminum, they can serve as viable substitutes for chromium in corrosion preventive systems. Also, they can be used in small quantities as a pigment substitute. Aluminum-lithium provided a base for minimal amounts of corrosion inhibitors as nanostructural cores or bases of other systems.

The results of independent laboratory testing confirmed the effective corrosion protection. Although the steel panels corroded seriously, the aluminum panels only had a few pits, as evidenced by the white powder on the surface. The scribes which exposed bare aluminum did not corrode or undercut, and no blisters on the coating were discovered. Closer inspection showed the pits were caused by lumps of pigment which, after being replaced with preheated and screened pigment, had no corrosion. In addition, the top coated primer had no corrosion, even in the scribe to bare metal. The large unfiltered particles caused a circumstance of pitting corrosion which was reduced by the lithium molybdate passivator, but could be eliminated entirely by screening the lumps out prior to painting.

The mechanism of corrosion protection appeared to be a combination of galvanic action by the lithium and passivation by the reaction products. The inhibitor was a complete success on aluminum. In the case of the four steel panels, the galvanic action probably inhibited corrosion, but the reaction products promoted corrosion on cold rolled steel. The technique of corrosion protection by nanostructural inhibitors is still possible, but the sacrificing pigment must not generate a compound which promotes corrosion. Lithium does not function on steel as it does on aluminum. However, it appears that steel substrates may also be protected by similar lithium systems.

Investigations into the mechanism of corrosion protection by the aluminum-lithium pigment revealed another interesting technique. Water slurries of aluminum-lithium pigments were rubbed on the aluminum panels for one-half hour with a subsequent water rinse. The panel developed a permanent corrosion resistant film and a good base for topcoat application. This was consistent with the results using an aluminum lithium pigment in a paint. It was also considered a unique adhesive and showed possibilities as a sealant.

In addition a chemical film which involves precipitation of lithium, molybdate, and cerium on aluminum alloy surface has been found. The film can be formed by both immersion and brushing at room temperature. Different aluminum alloys, including both low copper content and high copper

content, were treated with the chemical film and were tested according ASTM B117. Corrosion resistance of the alloys was greatly enhanced by the chemical film. The chemical film also shows good adhesion to top paint.

Synthesis and Photopolymerization of Monomers Derived from Biorenewable Sources
Professor James V. Crivello, New York Center for Polymer Synthesis,
Rensselaer Polytechnic Institute

Plant derived unsaturated vegetable oils can be readily epoxidized using a novel catalytic method and employing a high yield, solvent-free process to give the corresponding epoxidized triglycerides. Alternatively, naturally occurring epoxidized glycerides can be used as directly obtained from their plant sources. The addition of an onium salt cationic photoinitiator renders these materials photopolymerizable. Further, the use of photosensitizers allows the cationic photopolymerization to be carried out using ambient sunlight. The UV cure of the epoxidized vegetable oils takes place rapidly, with low energy, in the absence of solvents and without any air or water polluting organic volatile emissions. Furthermore, these materials are completely nontoxic. Currently, the epoxidized oils are employed in a wide variety of industrial coating, printing ink and adhesive applications. In addition, we have demonstrated the practical use of these materials as reinforced composites that can be used for such structural, load bearing applications as building and roofing panels, pipe and conduit, boats and for casts and splints. Since a wide variety of unsaturated vegetable oils are available with different structures, a correspondingly large number of materials with specifically tailored properties can be generated to fit specific applications. This technology has the multiple advantages of being very simple, broadly applicable and completely environmentally benign.

Unsaturated vegetable oils produced by American agriculture are an inexpensive and biorenewable resource that are currently in abundant supply. These materials can be converted, using a simple, efficient and nonpolluting process to epoxidized vegetable oils that can be directly used to make polymers. The process used to make polymers involves exposing the epoxidized vegetable oils to either ultraviolet or visible light. A catalyst called a photoinitiator is added to the epoxidized vegetable oil for this purpose. No solvents are employed in the polymerization process that requires a very short time exposure to light and uses no polluting solvents. This technology is already in use for the high-speed fabrication of decorative and protective coatings, printing inks and for adhesives. Work is currently progressing which shows that the technology has particular advantage in such structural applications as housing, boats and sewerage/water delivery systems. Thus, applications of this simple technology range from those employed in the developed as well as the developing world.

Environmentally Benign Lithography for Semiconductor Manufacturing
Dr. Joseph M. DeSimone, University of Carolina, Chapel Hill

Revolutionary processes for high-performance and environmentally-benign patterning of semiconductors are the focus of a collaborative research effort. The technical motivation for this work is the integration of new processes and materials that eliminate environmentally undesirable wet processes used in today's fabrication facilities. The primary goal is to replace conventional processes with superior, "dry" CVD methods and CO₂-based processes. Secondary goals go beyond environmental advantages and address critical challenges facing the microelectronics industry:

1. The high surface tensions and viscosities of organic solvents and water used for current deposition and removal processes damage next-generation < 100-nm-sized structures;

2. The high viscosity of conventionally used solvents makes it challenging to spin uniform, thin films onto large, next-generation >500 mm wafers—the low viscosity of CO₂ allows the deposition of thin films with fewer defects and greater uniformity;
3. The polymers needed for state-of-the-art lithography (157 nm), antireflective coatings, and low-k dielectrics are insoluble in most traditional solvents—novel CVD based processes and liquid CO₂ spin-coating and free-meniscus coating methods eliminate this problem;
4. Solvents and water used today in manufacturing do not lend themselves to integrated “cluster tool” approaches, necessitating expensive clean room facilities—these integrated systems reduce the amount of clean room facilities needed.

Solvent Selection and Recycling: A Multiobjective Optimization Framework under Uncertainty Dr. Urmila Diwekar, Carnegie Mellon University

The research presents a new, efficient, and integrated framework for computer aided green process design that combines chemical synthesis, process synthesis, and process design. Even when multiple and conflicting objectives are present, the framework uses efficient optimization methods to provide cost effective, environmentally friendly, designs and explicitly identifies the trade-offs involved.

Uncertainties inherent in group contribution methods for chemical synthesis and in environmental impact assessments are quantified, characterized, and included in the design process. The framework has wide applicability for designing greener and profitable processes, environmental control technologies, and power plants. It can also be used for effective environmental management and operations, including nuclear waste disposal and fuel cell power plants. We present here two case studies addressing steady state separation system design for continuous production, and synthesis of solvent selection and recycling for batch processing, respectively. Promising solvents, configurations, and designs are found for both cases. This is the first framework that considers chemical synthesis, process synthesis, and design under uncertainty together in the face of multiple and conflicting objectives encountered in environmentally friendly technology design. This approach identifies optimal solutions two or more orders of magnitude faster than state-of-the-art conventional methods.

Supercritical Fluid Spray Application Process for Adhesives and Primers Dr. Marc Donohue, Johns Hopkins University

The objective of this project is to develop low/no-VOC (volatile organic compound), non-structural adhesives to substitute for the current high-VOC, non-structural adhesives used in military applications by substituting supercritical carbon dioxide for conventional VOC solvents and carriers. It is estimated that 8.5 billion pounds of synthetic polymer adhesives are used annually, of which approximately 55 percent are VOCs. While the total DoD usage is not known, it is estimated that approximately 173,000 pounds of VOCs are released annually by Air Force aircraft operations. VOCs commonly used in applying adhesives include aromatics (e.g., toluene), ketones (e.g., acetone, methyl ethyl ketone), and others (e.g., methanol, chloroform) which negatively impact worker health and safety, adversely affect environmental standards, are ozone depleting, and result in increased hazardous material management costs including permitting and installation of sophisticated emission control equipment.

Conceptually, the UNICARB process is straightforward in that a concentrated solution of polymeric material (in this case the adhesive and adhesive primers), and other additives are mixed in situ with high-pressure (in the range of 1000 psi to 2000 psi) carbon dioxide and then sprayed. In practice, the process is complicated in that one is mixing an incompressible, highly viscous material (polymeric material and solvents) with a highly compressible fluid of very low viscosity (supercritical carbon

dioxide). The solvents are mixtures of fast and slow evaporating VOCs which are chosen specifically for their ability to dissolve the polymeric material, reduce viscosity, and aid in atomization and droplet coalescence on the substrate. In the supercritical spray process, supercritical carbon dioxide replaces that fraction of the organic solvent that is needed to give the viscosity reduction necessary for spray atomization. This is also the solvent that is the primary contributor to the high VOC emissions.

For a polymeric material to be adapted to the UNICARB process, the phase behavior of that particular polymeric material (the adhesive in this case) with carbon dioxide has to be known. Mixtures of high-pressure carbon dioxide with the adhesive concentrate must exist as a single phase at elevated pressures for the UNICARB process to work. To date, little is known of the phase behavior of polymer-solvent-carbon dioxide mixtures, and determining the underlying thermodynamic and rheological behavior is an arduous trial and error process. Additionally, precipitation of solids in solution has been encountered and needs to be avoided when using this process.

This project will adapt the UNICARB spray application process to adhesives in two ways: (1) a continuous process for use in a manufacturing setting, and (2) a portable hand held batch process for use in small jobs or repair scenarios. Each of these processes requires its own unique set of phase diagrams given that the portable device operates in dynamic conditions (the materials and pressures of the system are changing with time), whereas the continuous spray operation operates in a steady state mode (the system pressure and material compositions remain constant with time). Therefore, for each adhesive adapted to the UNICARB process, two different types of phase diagrams will need to be generated.

Two adhesive systems, acrylic and neoprene, to date have been selected for study. We have completed examination of the neoprene system. The work using the neoprene has progressed slowly, due predominately to the crosslinked nature of the polymer and its resistance to dissolving in many solvents. When processed in industrial adhesives, neoprenes are exposed to very high shear, a process we wanted to avoid since it also reduces the molecular weight of the polymer that may change its properties for the purpose of this investigation. To date, we have completed carbon dioxide concentration at 9, 20, 30, 35 weight percent in toluene at temperatures of 45, 50, 60, and 70 EC. Equilibrium pressures for the phase boundaries ranged from 700 to 1300 psi.

We have completed the automation of the data acquisition process by including an automated piston controller and modifying the automated data collection computer. These changes will make it possible to increase our testing speed and accuracy by limiting the opportunity for human error.

We have found unforeseen behavior in both systems that requires further investigation. In both the acrylic and neoprene systems, the phase transition measured dynamically occurs at a higher pressure than when measured statically. The presupposition was that the dynamic transition would occur at lower pressures than static due to the time lag for separation of the solvent and polymer. We have found the opposite to be the case and that the dynamic transition found above the static phase boundary reverts back to single phase when allowed to equilibrate. A possible explanation for this phenomenon is the difference between random and nonrandom behavior and that the system in question is showing nonrandom behavior. This finding, once verified, holds important possibilities for understanding phase transitions in multicomponent systems. Our results for the neoprene system with 25% carbon dioxide show a 300 to 400 psi difference between the lower static and higher dynamic results. This is seen from 40EC to 70EC.

Development of Extraordinarily Active Biocatalysts for Highly Selective and Efficient Synthesis of Chemicals and Pharmaceuticals

Dr. Jonathan S. Dordick, Department of Chemical Engineering, Rensselaer Polytechnic Institute

Enzymes occupy a unique position in synthetic chemistry because of their exquisite selectivities and high catalytic rates under ambient reaction conditions. Nevertheless, to be used more routinely, enzymes must function in environments that are appropriate for synthesis; key among these is nonaqueous media. Unfortunately, enzymes are poorly active in organic solvents, and this has limited their synthetic and commercial viability, particularly in large-scale processing. Furthermore, the low activity of enzymes in organic media necessitates large reactor volumes and large quantities of solvent in current commercial applications of nonaqueous biocatalysis. By elucidating the mechanisms that underlie the low activity of native enzymes in dehydrated environments, we have developed methods to dramatically activate a wide variety of commercially relevant enzymes in organic solvents. In particular, by engineering the microenvironment of the biocatalyst through lyophilization in the presence of simple salts, we have opened the door for the application of enzymes in many new processes. New enzymatic processes will offer all the benefits of biocatalysis including high activity and specificity, reduced byproduct formation, and environmentally-friendly processing, and thus will provide a green alternative to less efficient synthetic schemes. This technical achievement is particularly relevant for green processing in the chemical, food, and pharmaceutical industries.

Alternative Solvent Systems for Benign Reactions

Professor Charles A. Eckert, School of Chemical Engineering, Georgia Institute of Technology

Many common solvents used in the chemical industry bring with them both environmental and economic concerns. These range from the potential toxicity to challenges mass transfer, solvent removal, or catalyst recovery. Professors Eckert and Liotta have applied nontraditional solvents to a variety of reaction processes, and have shown both the environmental and economic advantages. Most of these projects were sponsored or cosponsored by industrial partners who have implemented their advances to the benefit of both the industry and of society.

Examples are shown here of the use of benign supercritical CO₂ to tune reaction rates and products, but also for improved mass transfer and ease of solvent removal. Very hot water, 250-300°C provides a natural acid or base catalyst which eliminates neutralization and salt disposal, but also leads to ease of downstream separation. Examples of benign and novel synthetic processes include Friedel-Crafts reactions; aldol, Dieckmann, and Knoevenagel condensations; and ester and ether hydrolyses. Gas-expanded liquids are tunable solvents for facile separations, such as chiral separations. Biphasic fluoruous systems and ionic liquids permit virtually quantitative separation of very expensive or very toxic catalysts for recovery and recycling.

Professors Eckert and Liotta have formulated an outstanding research partnership. By a synergistic combination of chemistry and engineering, they explore interdisciplinary areas of science and technology. Because they show the economic benefit of their environmental improvements, the results have been implemented.

Recycling of Cross-Linked Materials Via "High-Pressure High-Temperature Sintering": Redefining Thermosets

Professor Richard J. Farris, University of Massachusetts Amherst

In 1844, Charles Goodyear obtained his patent for the sulfur vulcanization of rubber. His invention created one of the most difficult materials to recycle, as it will not dissolve or melt. Today, studies estimate that there are roughly 2 billion scrap tires in U.S. landfills, with this number increasing at a rate of over 273 million per year. Recently, we discovered a technique for recycling vulcanized rubber. In short, commercially available rubber powder can be "sintered" together through the adhesion of rubber particles with only the application of temperature and pressure. The method takes advantage of the sulfur exchange chemistry that occurs at high temperatures. Through this labile bond it is possible to re-link the particles into a new chemical cross-linked network. There are two important reactions that occur in the process: the breaking of bonds (continuous stress relaxation) and the remaking of the bonds (intermittent stress relaxation). High-pressure high-temperature sintering (HPHTS) works for all thermosets in which the intermittent stress relaxation is greater than the continuous. A model has been developed based on these two reactions and it predicts the mechanical properties very well.

Overall, HPHTS transforms a useless scrap material into a valuable feed stock for new rubber parts. We have also discovered additives that can improve the efficiency of this process by slowing down and accelerating certain reactions. Finally, we have proven the mechanism of rubber sintering and have shown how to control the reaction with additives and/or by modifying the chemical structure of rubber.

Effluent-Free and Selective Delignification Using Only Oxygen and Water **Professor Craig L. Hill, Emory University**

A fundamentally new chemistry provides controlled electron-transfer pathways for remarkably selective O₂ oxidation of the lignin in wood fiber or pulp to its natural biosynthetic precursors, CO₂ and H₂O. The CO₂ can, in turn, be reacted with CaO to produce the clay filler normally added to cellulose in papermaking. The high selectivity of this chemistry makes it possible, for the first time, to replace chlorine dioxide, ozone, peroxides, and all such environmentally less attractive, or more energy-intensive or costly oxidants, by O₂. Moreover, the conversion of lignin to its natural precursors (lignin mineralization), makes it possible, for the first time, to completely eliminate the liquid waste (chemically modified lignin fragments) emitted by all existing or proposed delignification processes. These outcomes are achieved in two steps by a new multi-functional oxidant and catalyst system. This system is a thermally equilibrating, and thus inherently stable, aqueous ensemble of polyoxometalate (POM) salts. The ensemble is designed to include key species necessary for anaerobic (and hence, highly-selective) oxidative depolymerization and solubilization of lignin (step 1), for catalytic O₂-mineralization of lignin (step 2), and for maintaining the pH near neutral at all times. In related work, 100% oxygen-atom-efficient catalysts for chemoselective O₂-oxidations have been developed.

Tandem Enzymatic-Electrochemical Methods for Green Manufacturing: Efficient Synthesis of Pharmaceuticals from Aromatic Waste **Professor Tomas Hudlicky, Department of Chemistry, University of Florida**

The projects described within this document are nominated for an academic award under Focus Area I-The use of alternative synthetic pathways for green chemistry. The prevention of pollution at its source is addressed by replacement of currently used methods of oxidation and reduction (all based on metal reagents) with enzymatic and electrochemical techniques (all performed in water, alcohols, or other

environmentally acceptable solvents). The combination of enzymatic transformations with electrochemistry, along with efficient design, yields unprecedented brevity in the attainment of important pharmaceuticals from metabolites of type 1 by oxidative dearomatization, a reaction that has no counterpart in traditional chemistry. Halogenated aromatic compounds, viewed as harmful to the environment, are enzymatically converted to useful synthons and effectively removed from the hazardous waste pool with the added economic benefits of strategic conversion that would not be available through incineration of such compounds, which method would be also a contributor to greenhouse gases. It must be emphasized here that the enzymatic conversion of the toxic aromatic materials takes place in the very first step of the synthetic pathway and that all subsequent synthetic intermediates are harmless. The residual mass from the enzymatic processes is suitable for disposal to municipal sewers, thus further reducing the amount of actual waste. The synthesis of a homochiral cyclitol from halobenzene by several steps involving essentially no reagents serves as one of many illustrations of the technology. This document describes the strategy, the logic, the execution, and the future projection of this program of potentially global impact with attendant benefits to the health and economy of society at large through managed processing of aromatic waste to value-added substances. The length of a synthesis and the weight of all reagents and solvents used play a direct role in the attendant accumulated waste mass for the process. A new definition of efficiency, "Effective Mass Yield," is provided as the ratio of the weight of desired product and the weight of all non-benign mass requiring treatment or disposal that is used in the process. Several syntheses of a cyclitol are compared by this criterion in terms of reduced pollution at the source of manufacturing-this indeed is one of the central themes of our design. These projects have been developed in the last five years, and several patents have already been granted on more efficient synthesis of pharmaceutical entities. Several inositols, manufactured by this method, have been marketed by Aldrich Chemical Company since 1997. Since 1998, several diols of type 1 and certain cyclitol intermediates are also catalog items at Aldrich. The overall strategy of this project takes advantage of the best combinations of enzymatic transformations, electrochemical methods, as well as traditional chemistry to achieve unprecedented efficiency in the syntheses of natural as well as unnatural compounds.

Antibody Catalysis

Professor Kim D. Janda and Professor 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 oversimplified 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 region- 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.

The Application of Ultrasound to Catalyze Reactions in Some Industrial Processes
Dr. Finlay MacRitchie, Department of Grain Science and Industry, Kansas State University

Ultrasound has potential as a safe and clean methodology for catalyzing reactions. It uses high-frequency sound waves to change reaction paths and speed up reactions, thus reducing the need for added chemicals. The methodology has so far not been scaled up for industrial application to any great extent. The present proposal aims to apply ultrasound to three areas that have the potential to lead to industrial processes. These are (i) the modification of wheat gluten to create value-added products (ii) the clarification of fruit juices and (iii) the purification of water. Ultrasound will be used as the central technique to produce value-added products from gluten by enhancing functional properties such as solubility, gelling, foaming and emulsifying properties. For example, it can be used to increase the solubility, making it suitable for use in fortified beverages. Previous methods have used concentrated acids or enzymes but these are not environmentally friendly. Clarification of fruit juices is a problem that presently is mainly tackled by using enzymes. Ultrasound offers the possibility to deal with the problem without additional chemicals. Water contamination by microorganisms or by chemical pollutants such as pesticides, is another problem to which ultrasonics will be applied to replace traditional hazardous chemicals.

Elimination of Transition Metals from Materials Made by Atom Transfer Radical Polymerization and Development of Environmentally Benign Low VOCs Manufacturing Process
Professor Krzysztof Matyjaszewski, Carnegie Mellon University

Atom Transfer Radical Polymerization (ATRP) is a transition metal mediated controlled polymerization process for radically polymerizable monomers discovered at our laboratories in 1995. Since that time we have led efforts to develop more active catalyst systems allowing development of more environmentally benign procedures for preparation of functional materials via ATRP. In the past year we have defined and demonstrated a “hybrid catalyst system” that significantly reduces the transition metal residue in materials prepared by ATRP.

We have verified the use of such “hybrid catalysts” as suitable for the preparation of the full range of materials attainable through controlled radical polymerizations and demonstrated that it should be readily transferable to many industrial sectors. We are now in the position to validate its use in the continuous bulk polymerization of vinyl monomers and apply our understanding of ATRP catalysis to the development of a “truly continuous” bulk ATRP polymerization process by fully controlling the persistent radical effect. Thereafter we can implement some additional ideas for ligand substitution that will allow removal of the final 10ppm of transition metal complex from the final material thereby eliminating all hazardous substances from the products produced by ATRP and from industrial production recycle streams.

Environmentally Friendly Organic Synthesis Using Bismuth Compounds
Professor Ram S. Mohan, Illinois Wesleyan University

Synthetic organic chemistry provides access to literally thousands of useful molecules including life saving drugs differing widely in their structural complexity. Work continues to be done to develop new reagents, catalysts and reactions, which are then used in the assembly of complex target molecules. However, most of these efforts have focused on achieving the synthetic processes in an efficient manner and not enough consideration has been given to the effects that the reagents used in chemical syntheses have on human health and the environment. In 1990, Congress passed the Pollution Prevention Act,

which introduced the concept of pollution prevention through proper waste disposal, waste treatment, source reduction and source prevention. In this regard, bismuth compounds are particularly attractive candidates for use as reagents in synthetic organic chemistry for several reasons: Bismuth is the least toxic of the heavy metals. The biochemistry, toxicology and environmental effects of bismuth compounds have been well documented. The majority of bismuth compounds are relatively non-toxic (e.g., the LD₅₀ (g/kg) of BiOCl is 22 and that of Bi₂O₃ is 5 (compared with a LD₅₀ of 3.75 for NaCl). Bismuth and several of its compounds are commercially available and are relatively inexpensive. This project is aimed at developing new applications of bismuth compounds in organic synthesis.

**Industry-University-Government Partnership for Converting
Regional Wastes into Chemical Products
Dr. Gregory F. Payne, University of Maryland Biotechnology Institute**

A unique partnership in Maryland is demonstrating innovative approaches to simultaneously solve environmental problems and facilitate economic development. This partnership includes two companies (a composting company and a specialty chemical company), a chemical engineering professor, and a technology development specialist from a state economic development office. The goal of this partnership is to convert food and agricultural wastes into chemical products - thereby reducing nutrient addition to the Chesapeake Bay while creating manufacturing industries based on the state's renewable natural resources. Beginning with wastes from Maryland's crab-packing industry, the partners guided research and development, leveraged state and federal resources, and obtained private sector funding to establish a manufacturing operation. The culmination of this partnership is ChitinWorks America, a private company that is converting wastes from Maryland's crab-packing industry into the specialty biopolymer, chitosan. This manufacturing operation meets the state's need to cost-effectively manage nutrient-rich wastes, while sparing the state's crab packing industry the financial burdens associated with landfilling. Additionally, the product of this manufacturing operation is an environmentally-friendly biopolymer for various specialty applications (e.g. oil drilling).

**Low Temperature, Hydrocarbon Hydroxylation: The Key to Greener, Lower Cost Chemistry
for Chemicals, Fuel and Power for the 21st Century
Professor Roy Anthony Periana, Chemistry Department, University of Southern California**

As we enter the 21st century we should pause to consider that our foundational technologies are inherently inefficient. Thus, power production is only 20 - 30% efficient while fuel and basic chemicals are primarily produced from limited petroleum reserves rather than from the vast reserves of underutilized remote natural gas. The development of new, lower-temperature, hydrocarbon processing chemistry could lead to a paradigm shift toward greener technologies. The key to this next generation green chemistry is the development of catalysts that allow the direct conversion of CH bonds to COH bonds at temperatures below 250EC in high yields. With this green chemistry power production could ultimately be carried out with >300% reduction in emissions and remote natural gas and other hydrocarbon feedstocks could be more efficiently converted to fuel and basic chemicals. Such catalysts have been long considered a "Holy Grail" in chemistry. However, the recent work of the PI has provided the first demonstration of the only known catalyst that allows the direct conversion of methane to methanol in >70% yield at 220EC. With this precedent in hand, the paradigm shift to greener, petrochemical processes is well underway.

Catalytic Asymmetric Synthesis Using Feedstocks: Highly Selective Reactions of Ethylene for the Synthesis of Fine Chemicals

Professor T.V. RajanBabu, Department of Chemistry, Ohio State University

In this era of heightened environmental awareness and the ever-increasing demand for higher efficiency from chemical processes, one of the major challenges facing organic synthesis is the selective incorporation of abundantly available carbon, hydrogen, oxygen and nitrogen sources into other common substrates. In this context, we have discovered new, catalytic (0.0035 equiv. catalyst) protocols for nearly quantitative (isolated yields up to 98%) and highly selective (100% regioselectivity, up to 89% enantiomeric excess) codimerization of ethylene and various functionalized vinylarenes (hydrovinylation). These reactions proceed under exceedingly mild conditions (-52 EC, 1 atmosphere of ethylene) and produce highly valuable 3-arylbutenes. This reaction consumes both starting materials and leaves no side products, an ideal criterion for an environmentally friendly process. Since the publication of our original results, other workers have shown that the hydrovinylation reaction can be run in environmentally friendly scCO₂. As a prototypical example of the application of this hydrovinylation chemistry, an enantioselective synthesis of the widely used antiinflammatory agent ibuprofen from 4-bromostyrene and ethylene is highlighted. Several other profen drugs (e.g., naproxen, ketoprofen, flurbiprofen) could also be synthesized by this route. During these investigations we have discovered several new control elements that may have broader applications in the discovery of other highly selective catalytic processes. Examples include, (a) effects of electronic and steric tuning of ligands, (b) the role of hemilabile ligands and highly dissociated counter-ions in enhancing selectivity.

Development of Environmentally-Benign Wood Preservatives to Replace Chromated Copper Arsenate

Professor Tor P. Schultz, Mississippi State University, College of Forest Resources

The dominant wood preservative in the U.S. today is chromated copper arsenate (CCA), with about 50 million lbs. of arsenic and 70 million lbs. of chromium (oxide basis) used yearly. However, environmental concerns with CCA may limit its future use. The heartwood of certain trees are naturally durable, which suggests using this as a model to develop new wood preservatives. Our research showed that heartwood extractives have poor fungicidal activity. However, these extractives also have antioxidant, metal chelating and water repelling properties. In laboratory decay tests, when an antioxidant or metal chelator alone was added to wood no protective effect was observed. When either an antioxidant, metal chelator, or both, were combined with commercial organic biocides, however, an increase in efficacy (synergism) was observed as compared to the biocide alone. The greatest efficacy increase was observed when all three components (biocide, antioxidant, and metal chelator) were present. Furthermore, wood treated with a combination of a water repellent and biocide and subjected to above-ground outdoor exposure gave better protection than the biocide alone. Many of the nonbiocidal additives examined are relatively low cost and benign. Since the mixture is synergistic, less of the expensive organic biocide is required to protect wood.

Ionic Liquids for the Dissolution and Processing of Cellulose

Professor Robin D. Rogers, University of Alabama

Cellulose is the earth's most abundant biorenewable material. It has many important commercial applications in a wide variety of industries. However, there are only a select few solvents capable of dissolving cellulose. With increasing governmental regulations restricting the use of current cellulose

solvents, the need to replace them is becoming more important. The use of ionic liquids as ‘green’ replacements for the traditional organic solvents has been demonstrated. We have investigated the use of ILs for the dissolution of cellulose with the intent of making the process cleaner, more efficient, and with a reduction/elimination of environmentally undesirable systems. It has been found that cellulose can be dissolved in ILs without derivitization at relatively high concentrations, up to 30 wt/wt% is possible. Cellulose can easily be regenerated from the IL solution simply contacting the cellulosic solution with water. This affords one, a simple, environmentally benign system for the processing of cellulose into fibers, monoliths and films. The potential environmental and cost advantages over current processing methodologies, which make use of volatile organic solvents, are countless. Results from regenerated cellulose, as well as important intermolecular forces responsible for the dissolution of cellulose will be presented.

An Environmentally Benign Asymmetric Epoxidation Method
Professor Yian Shi, Department of Chemistry, Colorado State University

Epoxides are very important chiral building blocks for the synthesis of enantiomerically pure complex molecules. The epoxidation of olefins bearing no allylic alcohol group with high enantiomeric excess has been a long-standing problem with major synthetic significance. Recently we have developed a highly enantioselective epoxidation method for *trans*- and trisubstituted olefins using a readily available fructose-derived ketone as catalyst and inexpensive Oxone or H₂O₂ as oxidant. The reaction proceeds via a chiral dioxirane which is generated *in situ* from the chiral ketone and oxidant. High enantioselectivities can be obtained for *trans*- and trisubstituted olefins, hydroxyalkenes, conjugated enynes, conjugated dienes, vinylsilanes, and enol derivatives. Generally the epoxidation reaction is quite mild, rapid, safe, environmentally benign, and operationally simple. All these features demonstrate the strong potential of this epoxidation method for practical use.

A New Environmentally Benign Process for the Conversion of Pulp Mill Waste Streams to Value-Added Chemicals & Energy
Professor Israel E. Wachs, Department of Chemical Engineering, Lehigh University

There are 150 Kraft pulp mills in North America that generate waste streams considered to be among the largest Hazardous Air Pollutants (HAPS). These waste streams are typically concentrated into a condensable stream (40-50% water, 40-50% methanol, ~5% methyl mercaptans, ~5% terpenes [pine-like oils] and small amounts of ammonia) and a non-condensable stream (50% nitrogen, 3% oxygen and 47% H₂S). Methanol is the largest single source of volatile organic compound (VOC) emission and EPA Report #453/R-93-050a places limits on methanol emissions for all pulp mills effective April 15, 2001. Two alternative technologies have been proposed to meet these guidelines: incineration and bioremediation. However, these approaches convert the waste streams to global warming CO₂ and acid rain SO₂/NO_x gases at a significant expense.

The new environmentally benign catalytic oxidation process selectively converts the methanol as well as methyl mercaptans in the condensable stream to valuable formaldehyde (employed in the manufacture of particle boards), produces concentrated SO₂ that is recycled to the pulp digestion step, yields N₂ via the selective catalytic reduction of NH₃ and recovers the terpenes for further use as valuable specialty chemicals. The non-condensable stream is fully oxidized to SO₂, which is also recycled to the pulp digestion step. For North America, this novel catalytic process would eliminate SO₂ emissions by ~13,000 tons/year, reduce CO₂ emissions by ~6,500 tons/year as well as smaller amounts of NO_x emissions. In addition, the exothermic oxidation reactions generate process heat that can be used

elsewhere in the plant and the valuable chemicals can produce revenues of approximately \$1,000,000 per year/plant. Lastly, this environmentally benign process yields valuable chemicals that are produced from renewable resources -- trees rather than fossil fuels.

**Melt Processing for Solvent-Less Manufacture of High Performance Dry Powder Coatings
Dr. Ming-Wan Young and Dr. Marino Xanthos, New Jersey Institute of Technology**

The innovation presented in this nomination, developed at the Polymer Processing Institute at New Jersey Institute of Technology, provides a process to manufacture dry powder coating products without the use of solvent. The necessary performance characteristics for the dry powders are achieved by the use of crosslinkable acrylics or crosslinkable unsaturated polyesters prepared in solventless systems by melt processing. The resulting formulations can be shown to have superior performance characteristics, and have been applied within the last five years to automotive coating operations. The technology extends the benefit of dry powder coating in reduction of solvent use by eliminating the use of solvent in the manufacture of the dry powder in addition to the use of the dry powder. The basic concept of chemical reaction in melts with careful selection and handling of reactants and of careful control of reaction conditions is widely applicable to chemical manufacturing.

Entries from Small Businesses

Tasphox Water Treatment System Aegeans, Inc.

TASPHOX stands for Turbo-aspirated Photochemical Oxidizer an innovative edge photolysis based oxidation water treatment process that generates hydroxyl free radicals using hydrogen peroxide and deep ultraviolet light to destroy organic chemicals and pathogens in aqueous fluids.

Contaminated water is pumped through a two-chambered Peroxide Photolysis Ionizer (PPI) reactor constructed of 316-L stainless steel. Design flow rates from 3.0 to 500.0 gallons per minute are possible. Units linked in parallel can treat millions of gallons of water per day.

The fluid is initially irradiated by high intensity UV light and microwave energy. Then directed in the second chamber to a point where concentrated hydrogen peroxide (up to 50 %) and additional UV light produces the transient univalent OH* radical. This is immediately followed by turbo-aspiration through an eductor jet. The resulting ebullition drives additional oxygen into the fluid and residual gaseous waste products such as carbon dioxide, nitrogen, argon etc. out of solution.

This process can be used to pre-treat any organically contaminated water source for drinking or other potable use. And consequently has wide application in emergency response during natural disasters, terrorist attacks and battlefield water purification.

Bioderived Succinic Acid as a Platform for a Carbohydrate Chemistry Applied CarboChemicals, Inc.

The biologically derived succinic acid process produces succinic acid by fermenting glucose sugar from corn at present and mixed sugars from lignocellulosics in the future. After separation and purification, the succinic acid is a chemical intermediate that is converted into a wide assortment of environmentally friendly products. This process makes a new platform chemical (a versatile dicarboxylic acid) based on renewables in a process that is itself energy efficient and more environmentally friendly than petrochemical-based products. The company, Applied CarboChemicals, Inc, has also developed an attractive suite of environmentally friendly initial market products. These products will compete directly on price and features. These products include a biodegradable deicer, which has low corrosivity and ice-melt properties equivalent to NaCl. There is a family of succinate-esters that functions as a biodegradable, recyclable degreaser for machinery. Another formulation enhances the efficacy of certain herbicides, allowing less to be used on the fields. The process is being actively implemented, with a 150,000 L fermentation demonstration scheduled for early 2002. This platform has developed from an active collaboration by all parties. The combination of biotechnology, efficient separation technology and novel chemical synthesis provides economics enabling commercialization of a broad range of products.

New, Environmentally Protective Aircraft De-Icing Technology Air Force Research Laboratory, Wright Patterson Air Force Base

For flight safety, snow and ice must be removed from airplanes before takeoff. Hot ethylene and propylene glycol, toxic chemicals used to de-ice airplanes at airports, usually run off the airplane onto the pavement and may escape into streams or ground water. Recently ethylene glycol along with other water-soluble organic chemicals such as MTBE have come under increased regulatory scrutiny. When glycol runoff seeps into groundwater, it can contaminate drinking water wells. In surface waters, it can harm wildlife. Some airports are installing multi-million-dollar catch basins to retain and dispose of this glycol runoff. The Air Force Research Laboratory Air Vehicles Directorate (AFRL/VA) and independent inventor, Lee Williams have developed a high efficiency forced air deicer that utilizes compressed air to blow snow and unattached ice off of airplane wings and applies a thin film of hot glycol on the cleaned wing to melt any residual ice. The specialized forced air/glycol application system reduces by 50% to as much as 90% the amount of glycol required to de-ice a jet aircraft. Not only does the technology offer a marked cost savings but also the reduction in glycol use is a tremendous benefit to the environment.

Roach Terminal: A New Generation in Roach Control Cleary Chemical Corporation

The *Nutritional Metabolism Disrupters* (NMD's) in Roach Terminal block the metabolic pathway responsible for the formation of uric acid, a vital nutrient component used in insect metabolism and reproduction. This unique mode of action of the NMD's is highly effective on all growth stages of German cockroaches, even those that have developed resistance to conventional chemical insecticides.

Active Ingredients - Roach Terminal contains 2% NMD (1% Oxypurinol and 1% Xanthine) as the active ingredient. Xanthine occurs naturally and is commonly found in many foods such as potatoes and coffee. Oxypurinol is similar to allopurinol, which is currently used to treat humans for gout. The 98% inert ingredients consist of food components designed to be highly attractive to foraging cockroaches. The bait material is secured in a self-contained child resistant bait station similar to current commercial bait products.

Mode of Action – In cockroach physiology, uric acid is the nutritional storage molecule used in most facets of metabolism and reproduction. During the growth and molt cycles, insects draw heavily on their metabolic reserves to achieve the rapid growth of cells necessary for the development of internal and external organs and a new larger exoskeleton. In reproduction, the male provides large quantities of uric acid to the female during mating for use in egg production. The female then combines this “paternal investment” with her own stores of uric acid for egg development and transfers a supply of uric acid to the eggs for use during embryogenesis.

The purine metabolic pathway is central to all these processes. Upon ingestion by insects, the NMD contained in Roach Terminal inhibits the enzyme, xanthine oxidase, which regulates the production of uric acid in this pathway, eliminating synthesis of uric acid. Previous uric acid stores are rapidly depleted and since no new uric acid is produced, the effects on cockroach populations are highly detrimental.

Biodegradable Packaging Film Incorporating Corrosion Inhibitors Cortec Corporation

Biodegradable packaging films useful in protecting metallic articles in corrosive atmospheres have been prepared and evaluated. Incorporating volatile corrosion inhibitors in film-forming biodegradable polyester resins improves the corrosion resistance of the films to equal conventional polyethylene packages. These new films not only pass the recently approved ATSM standard and the proposed CEN standard for biodegradability and compostability, but also proved a “green alternative” to polyethylene.

EcoFuel - A Safe and Effective Canned Heat Alternative DynynStyl Inc.

DynynStyl developed a new canned heat product, EcoFuel, that offers major safety and environmental benefits. EcoFuel is designed to greatly reduce the safety hazards associated with “Sterno”™ type fuels. DynynStyl worked with a new concept of delivery that eliminates danger both in use and disposal. EcoFuel is non-flammable, non-explosive and spill resistant. The odorless and consistent combustion controlled with a dual aperture lid produces a regulated burn time and temperature as a 5 hour Cooker or 10 hour Warmer. The rapid light ignitor permits easy lighting and relighting until the fuel is completely consumed. All components are 100% biodegradable except the inert fiber.

EcoFuel has effectively proven a major reduction of risk due to fires, explosion, flash back, and spontaneous combustion in military and institutional markets. The elimination of personal injury and damages associated with low flash point fuels has received approvals and endorsements from fire and safety professionals. EcoFuel’s high flash point does not require special storage, handling or transportation.

The reusability and ability for complete consumption of EcoFuel provides a solution to the vast volume of unburned fuels left by conventional canned heat products. Also reduced are the secondary waste stream of packaging materials and the energy for manufacturing and transportation. One can of EcoFuel replaces five cans of “Sterno”™.

EarthShell Packaging: Designed with the Environment in Mind EarthShell Corporation

EarthShell composite material is made from common raw materials and has unique environmental attributes, comparable performance characteristics and is competitively priced with conventional paper and plastic packaging. EarthShell Packaging was developed over many years using a Life Cycle Inventory and in consultation with leading environmental experts to reduce the environmental burdens of rigid food service packaging through the careful selection of raw materials, processes and suppliers. EarthShell Packaging substantially reduces risk to wildlife compared to polystyrene foam packaging because it biodegrades when exposed to moisture in nature, physically disintegrates in water when crushed or broken and can be composted in a commercial facility (where available) or in your backyard.

The EarthShell Packaging composite material is made by combining starch, limestone, fiber and water to form a batter. The batter is placed into heated molds and baked for about a minute. The water turns to steam and forms and sets the product. The products are then coated with biodegradable coatings, printed and boxed. The use of advanced particle-packing technology allows the addition of large

amounts of limestone (CaCO_3) reducing the overall cost while maintaining the strength and other properties. Over 130 patents speak to the unique nature of the EarthShell technology.

**Environmental and Economic Advantages Offered by Boric Acid-Mediated Amidation Between a Carboxylic Acid and an Amine to Form a Carboxamide, a Basic Unit of Proteins
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. Carboxamides generate great interest within the synthetic organic chemistry community, and 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 macromolecular drugs in a wide range of settings are being sought and discovered. The amidation mediator, boric acid, has many promising and beneficial properties. It is nontoxic, stable, environmentally safe, renewable and inexpensive. 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 a significantly reduced impacts on human health and the environment relative to the current state of art.

**Totally Degradable Plastic Additives (TDPA™)
EPI Environmental Plastics Inc.**

In order to be considered environmentally degradable, a plastic must disintegrate by some mechanism to lower molecular weight fragments that are susceptible to microbial attack and, ultimately, elimination as biomass, gaseous byproducts, and water. Polyolefins are usually regarded as environmentally inert. To make them environmentally degradable, mechanisms must be identified to convert these hydrophobic and high molecular weight plastics into water-wettable, friable fragments of very low molecular weight to render them microbially susceptible. It is well established that abiotic oxidative degradation of polyolefin films produces oxidized molecular fragments of very low molecular weight in the range of a few hundred to a few thousand Daltons (Profs. A-C. Albertsson, C. David, and others). Such fragments are substantially biodegradable as measured by carbon dioxide evolution in a variety of aerobic environments.

EPI developed and introduced TDPA™ additives for use at low levels (< 10 weight percent), to specifically promote polyolefin oxidative degradation in the presence of heat and/or near-UV light. Adjusting the components in TDPA™ additives and the blend proportions with polyolefin, controls the rate and time for polyolefins to degrade to low molecular weight fragments and hence biodegrade. This control permits use in a wide range of applications and disposal sites.

**The EVANS DE-TOX™ Process for the Detoxification of Ethylene Glycol
Evans Cooling Systems, Inc.**

Approximately 4,500 humans are poisoned and 90,000 domestic animals die annually in the USA by the ingestion of ethylene glycol (EG). EG is not toxic until it becomes metabolized by alcohol

dehydrogenase (ADH) to glycoaldehyde and then metabolized further to other toxic metabolites. The inventors discovered that propylene glycol (PG), when mixed with EG, acts as an ADH inhibitor, preventing the metabolism of EG and preventing the toxic metabolites that are the essence of EG poisoning. Laboratory testing during 2000 and 2001 demonstrated that only a small percentage of PG is needed. By including a minor amount of PG in their EG-based products, producers can manufacture improved low-toxicity products at lower cost than was possible previously. All of the EG poisonings by ingestion are preventable. If the new technology were applied universally to EG-based products, all ingestion-related EG poisonings of humans and animals by these products could stop. Until revealed by Evans Cooling Systems, Inc. in 2001, PG's effect on the toxicity of EG was unknown. The many tests and the development of the theory that PG acts as an ADH inhibitor, so effective as to prevent the poisonous metabolites of EG from being produced, demonstrate scientific merit.

**Research and Development to Commercialize an Innovative Line
of Environmentally Benign Antifouling Paints and Coatings
for the Marine and Aquaculture Industry
Flexabar Corporation**

This on-going R&D project has as its primary goal: to eliminate heavy metal biocides, including copper, preferably in low VOC waterbased antifouling paints and coatings for the aquaculture fish farming industry and in bottom boat paints for pleasure boats. In introducing Aquagard Waterbase Antifouling Bottom Boat Paint to the market, the initial market impression was that the public had to be educated on the merits of waterbase bottom boat paint.

It was recognized that the education of the public to this new waterbase technology was going to take time, much longer than anticipated. The consumers who attended the trade shows were skeptical of waterbase paint "holding up" on the bottom of boats. However, even during the early stages, boat owners - who tried Aquagard - began to have confidence in our product.

Aquagard has gained a small market share in the northeast coast of the United States. The strategy has been to create demand through the marinas (boat dealers) and Aquagard sales representation is continually expanding the dealer base.

This strategy is to create enough demand for the product so that a major distributor will pick up the Aquagard product line. The distributors have been hesitant to carry Aquagard since it would affect their relation with their other paint suppliers. As our sales grow, the distributors are more aware of our presence in the marketplace. We must continually promote and educate the public through trade show advertising and our dealer networks.

The next generation of Aquagard products will continue the growth in the marine marketplace: Aquagard II Waterbase Antifouling Bottom Boat Paint for aluminum outdrives, boats and transducers will not cause electrolysis.

**A Green Revolution with Nanostructured™ Chemicals
Hybrid Plastics**

Hybrid Plastics' has developed and commercialized a revolutionary green building block technology based on POSS™ Nanostructured™ Chemicals. POSS™ can be derived directly from commodity silanes or sand/silica, the most abundant component of the earth's crust. Their nanoscopic size renders them VOC free while their hybrid "organic-inorganic" composition provides them with inherently low flammability and excellent oxidative stability. They dramatically improve the thermal and mechanical properties of traditional polymers while offering turnkey incorporation using existing manufacturing

protocols. They are biocompatible, recyclable as silica, and are competitively priced with traditional performance material technologies.

**Picklex® Process: A Non-Polluting Pretreatment/Conversion Coat
Which Replaces Chromate Conversion Coating and Zinc & Iron Phosphating Treatments
in Powder Coating, Paint and other Organic Finish Applications
ICP**

The Picklex® Process, a proprietary formulation, is an alternative to conventional metal surface pretreatments. It produces significantly less waste than conventional processes and in some cases can accomplish zero discharge. The process accomplishes faster and simpler production without lowering the performance of the final product. A laboratory program was designed to evaluate the Picklex® Process in common, large scale, polluting surface finishing operations against conventional processes, using steel and aluminum panels, measuring product coating properties, process operability, and costs. Over 60 finishing combinations were tested under both “contaminated” and “non-contaminated” conditions with respect to finish adhesion, bending, impact, hardness, and corrosion resistance. Results indicate that Picklex®-pretreated panels performed as well as panels that were conventionally pretreated, and with a simpler process. Picklex® is particularly acceptable for powder coated steel or aluminum. A field study in an actual powder coating shop was conducted to validate the lab results (the results came out much better and cost effective than the lab test). For the powder coating study, the *chromate conversion coating was replaced* for aluminum substrates and the *zinc phosphate coating was replaced* for steel substrates. Picklex® did not generate by-product waste solids, was effective at room temperature, used short processing times, and was easy to use. An engineering assessment indicated that Picklex® has cost advantages as well.

**Fertilizer From Photowaste
Itronics Metallurgical, Inc.**

More than 100 million gallons of photographic wastes are generated in the United States annually. According to U.S. Environmental Protection Agency studies in the early 1990’s, these wastes represented approximately 40 percent of all liquid toxic waste produced by American industry. This waste is a significant environmental hazard to the nation’s bodies of water because photographic wastes contain silver and other heavy metals. Silver is potentially toxic to fish and other aquatic life. The waste, from photo finishers, photo labs and studios, X-ray laboratories, and printers, is dumped into the environment without pre-treatment, although rules are being tightened in many states and municipalities to curtail this or to require more intensive treatment.

Itronics, Inc. is the world’s only fully integrated photochemical recycling company. It provides photochemical waste collection services, recovers and refines silver from the photochemicals, manufactures and blends liquid fertilizers from the processed residual, and sells and distributes lines of liquid fertilizers designed to meet specific plant nutrition needs. Since virtually all the toxic metals have been extracted, the fertilizer manufactured from this clean liquid base, is environmentally beneficial, helping to solve the major national concern of heavy metals from fertilizer contaminating farm fields or bodies of water.

Rhamnolipid Biosurfactant as a Low Toxicity Alternative to Synthetic Surfactants Jeneil Biosurfactant Company

Jeneil Biosurfactant Company's rhamnolipid biosurfactant program has resulted in breakthroughs for producing and making available at commercial scale and low cost a series of low toxicity and environmentally friendly readily biodegradable rhamnolipid biosurfactants. These biosurfactants are useful for numerous and diverse applications requiring surfactants with good emulsification, wetting, detergency or foaming characteristics and are substitutes for more toxic and less environmentally benign synthetic or petroleum-derived surfactants. The technology for producing the rhamnolipid biosurfactants utilizes alternative feedstocks that are renewable and are innocuous as compared to those used for production of synthetic or petroleum-derived surfactants. In comparison, biosurfactants require very small resource input and employ less complex, capital and power intensive processes. In their production and application they avoid the utilization or presentation of hazardous substances into the environment. They are extremely useful in applications where their use will preclude harmful environmental impacts and they are also useful in applications for remediation of environmental pollution conditions. Examples are hydrocarbon or heavy metal removal from soil and crude oil tank cleaning and sludge remediation. In many applications these biosurfactants can be a substitute for or work in combination with and reduce the amount needed of less environmentally friendly synthetic or petroleum-derived surfactants.

Cadmium Replacement in Mechanical Coating Madison Chemical Company

Madison Chemical Company manufactures specialty chemical compounds used in numerous applications throughout general industry, and in the metal manufacturing industry. We custom design our products to meet specific needs. Many times these include elimination of highly toxic materials from a customer's facility. In the mechanical plating industry, platers use powdered metal rotated in a barrel with impact media to mechanically plate parts. Frequently cadmium is the metal of choice in mechanical plating applications, because it adheres to the substrate metal to form a corrosion-resistant coating while giving the coated part a lustrous finish. Cadmium is also highly toxic, a proven carcinogen, and listed under Section 313 of SARA. Chemists at Madison Chemical developed a method of replacing large concentrations of cadmium with trace amounts of nickel in zinc mechanical plating. Zinc and nickel exhibit far less toxicity than cadmium, and our product shows greater corrosion resistance than the cadmium compounds generally used. This formula change was considered unique enough to warrant two U.S. patents.

A Cleaner and More Advanced Method for the Fabrication of Printed Circuit Boards Micro Interconnect Technology

An environmentally cleaner and a more streamlined method for the fabrication of printed circuit boards has been developed. Although the end product looks, feels, and performs the same as conventional boards, the process for manufacturing has been significantly changed and enhanced.

A single solution has been developed to make the holes conductive and ready to electroplate.

An advanced computer/laser imaging system was developed that eliminates the use of conventional photo masks. To clean boards, in preparation for imaging and plating, non-toxic, all aqueous fluids are used that make disposal simple and straightforward. Mask removal uses non-toxic, commercially

available fluids. Etching uses the latest re-usable etching bath with chemistries based solely on replenishment. Here again, no hazardous waste disposal is needed.

A method for accurate placement of solder mask and letter screen has been developed. Non-toxic ancillary chemicals have been developed to facilitate these steps, while retaining a simple all-aqueous developer.

This new process has addressed all steps needed to manufacture boards and implement, wherever possible, aqueous, non-toxic chemicals in contrast with conventional board manufacture.

Since all data is stored in computers, no film is needed. The method reduces labor and shortens the time and cost of production.

Short Perfluoroalkyl Chain, Polymeric Fluorosurfactants as Wetting, Flow and Leveling Agents for Aqueous Coatings Omnova Solutions, Inc.

OMNOVA has substantial business supplying latex resins to the floor care industry. These formulations require fluorosurfactants as wetting, flow and leveling agents for successful application. The fluorosurfactants currently used are typically long perfluoroalkyl chain materials supplied by 3M and others. The prevalent fluorosurfactant for floor polish is Fluorad FC-129 from 3M, which is being removed from the marketplace. Based on data contained in the 3M EPA public docket there are environmental concerns with these materials. The USEPA is now studying the general class of long perfluoroalkyl fluorinated materials for possible adverse environmental and health effects.

Through R&D, OMNOVA has discovered that fluorosurfactants based on short perfluoroalkyl oxetane polymers can replace the longer-chain fluorosurfactants in a number of applications. These Short Perfluoroalkyl Chain, Polymeric Fluorosurfactants have less potential for environmental or health concerns due to a combination of larger molecular size and reduced toxicity of the shorter perfluoroalkyl chain. Two OMNOVA products have been reviewed by US EPA and Low Volume Exemptions have been granted to manufacture these materials. Introduced commercially in 2001, they are incorporated into commercial floor polish formulations. Research continues developing fluorosurfactants for other replacement applications.

Dispersit: A Waterbased Oil Dispersant for Oil Spills in Salt and Fresh Water U.S. Polychemical Corporation

Oil spills in marine environments pose a significant ecological and economic threat. Mechanical recovery methods are ineffective. Petroleum based dispersants, while effective, present their own environmental problems, in addition to, health threats to the user. Other waterbased dispersants, are either ineffective or highly toxic. Dispersit is a breakthrough formula combining effectiveness with safety.

It is an effective and non-toxic oil spill dispersant combining a predominately oil-soluble surfactant with a predominately water-soluble surfactant and a co-solvent for coupling a mixture of the predominately oil-soluble surfactant and the oil spill, with the predominately water-soluble surfactant. Water is included in the combination to help advance the interaction between the predominately oil-soluble surfactant and the predominately water-soluble surfactant, as well as, the co-solvent. The water component also helps reduce the viscosity of the dispersant to allow it to be pumped under pressure. The resulting product performs to a superior degree in both fresh and salt water. It does not pose a threat to human health.

**Integrated Methods for the Control of Aquatic Plants (IMCAP™):
Innovative Chemical and Precision Technologies
SePRO Corporation**

Integrated Methods for the Control of Aquatic Plants (IMCAP) is a set of newly developed and existing chemical and non-chemical technologies that successfully overcomes many challenges to "precision" use of pesticides. IMCAP makes possible planning for and the application of SePRO's top herbicide product, Sonar™ (chemical name fluridone), to aquatic environments within a few parts per billion of target concentration levels. SePRO developed or adapted five major components to create IMCAP: an immunoassay (FasTEST™), two plant bioassays (PlanTEST™ and EffecTEST™), and bathymetric/volumetric and hydroacoustic/remote sensing assessment techniques. All five of these components are supported within a Geographic Information System (GIS)/Global Positioning Satellite (GPS) framework. IMCAP allows Sonar herbicide to be used at concentrations as low as 4% of its maximum approved FIFRA label use rate (e.g., 6 parts per billion (ppb) compared to the label rate of 150 ppb). At these lower application rates, Sonar provides control of some of the most noxious submerged aquatic invasive plant species while minimizing or eliminating harm to desirable native species. IMCAP, therefore, makes possible far more selective use of Sonar against target plant species, while taking advantage of Sonar's other unique environmental properties that make it an attractive aquatic herbicide (e.g., it is nontoxic to animals and algae at its maximum application rates, and it induces the slow death of target vegetation, avoiding hypoxic or anoxic conditions). IMCAP's precision technologies allows up to a 70% reduction in chemical loading under certain treatment conditions. It also permits the wider scale use of Sonar with the resulting protections for animals, algae, native plant populations, drinking water, and recreational water uses, as well as reductions in herbicide costs. IMCAP is a successful system of "precision" technologies. No other manufacturer or user of aquatic herbicides or pesticides in general has developed or applied in a commercial setting a system comparable in scope or scale to IMCAP.

**440-R SMT Detergent Hazardous Solvent Alternative
for Printed Circuit Board Stencil Cleaning
Smart Sonic Corporation**

440-R SMT Detergent uses proprietary acidic surfactants which act to buffer the sodium silicate base to bring the useable concentration of 440-R SMT Detergent to within non-hazardous pH limits (11.0 – 12.0 pH). A purple dye and a mild citrus fragrance are added for identity and quality control purposes and to prevent the possibility of unpleasant odors in the workspace.

The surfactant formulations are critical in that they must not only address the flux contaminant, but must also clean effectively at low temperatures (<110EF). It is established that SMT stencils are heat sensitive. The adhesives used to bond the stencil screen to the frame and to the metal etched foil are heat-cured at approximately 160EF. Hot wash solutions will breakdown the stencil adhesive and cause detachment. Temperature fluctuations also cause expansion and contraction of the various metals used to construct a stencil leading to minor distortion of fine-pitch apertures causing misregistration and production misprint problems.

Care was taken not to introduce any additional hazardous or restricted ingredients into an already hazardous cleaning application. By using only non-hazardous and non-VOC ingredients, 440-R SMT Detergent wastewater qualifies for routine liquid evaporation, eliminating the need for drain discharge and liquid hazardous waste disposal.

Crystal Simple Green Sunshine Makers, Inc.

Invention and commercialization of new safer family of products for use in the industrial marketplace exemplified by “Crystal Simple Green,” the non-toxic, biodegradable degreaser/cleaner.

The use of toxic chemicals in the industrial marketplace exceeds one billion dollars in the United States. These chemical are responsible for environmental and personnel hazards.

Workmen’s compensation claims have skyrocketed due, in part, to the use of acids, high pH solutions, and chlorinated solvents.

Crystal Simple Green utilizes proprietary technology to effectively degrease/clean substrates that are heavily loaded with industrial oils, greases and hydrogenated animal fats. Crystal Simple Green, with a mild 9.35 pH emulsifies, saponifies, and degreases substrates through a process known as micelle creation (Micro Particulate Fractionalization). This unique process breaks oils and greases into small particles, which continues to a molecular level.

Crystal Simple Green is essentially non-toxic, and represents low toxicity hazard to mammals by inhalation, ingestion or topical route of entry. Furthermore, Crystal Simple Green represents no spill hazard and will not be deleterious to microorganisms utilized in the bioremediation process. In fact, Crystal Simple Green has properties that increases the effectiveness of bioremediation.

These attributes, along with Crystal Simple Green’s cleaning efficacy further the use of safer chemical products in the industrial area.

World-wide Elimination or Reduction of Solvent and Chemical Cleaning of Laboratory Glassware Using Thermal Pyrolysis-oxidation Chemistry Tempyrox Company, Inc.

Pyro-clean® technology is a commercial system developed by Tempyrox Company to change the way chemists, technicians, scientists, and laboratory personnel clean their glassware. The technology is designed to eliminate or greatly reduce the current wide spread use of hazardous chemicals and solvents for cleaning of laboratory glassware.

Although sales are in its infancy (about \$ 3,000,000), laboratories adopting Pyro-clean® technology have reported typical reduction of 40% in cleaning solvent use after purchase of the Tempyrox systems. The Federal Highway Administration purchased four units for evaluation by the DOT labs of four different states². After the year long study was done, each state adopted Pyro-clean® technology as the method of choice to reduce solvent usage. Since then, virtually all state DOT labs in the USA (46 out of 50 states) have switched to this new solvent free cleaning technology.

World wide adoption of Pyro-clean® technology for cleaning of lab glassware (where applicable) could significantly impact and reduce use of solvents and chemicals detrimental to human health and the environment.

Treyco Power Plus-One (TPP-1), Microbial Enzymatic Cleaning Solution with High Ph Stability Treyco Supply

The instant invention is directed to a cleaning composition comprising: (a) an enzyme in an amount effective to promote cleaning; (b) viable microorganisms in an amount effective to degrade and promote the degradation of organic materials; (c) a surfactant; and (d) an aqueous carrier; said cleaning composition having at least 95% enzymatic activity at a pH range of from about 5.5 to about 13.5.

The present invention is also directed to a method for cleaning metal parts, glass parts, ceramic parts, or plastic parts having a hard surface, comprising the steps of: (a) treating said metal part with a cleaning composition comprising: (i) at least one enzyme; (ii) at least one viable microorganism; and (iii) a surfactant; wherein said cleaning composition has at least 95% enzymatic activity at a pH range of from about 5.5 to about 13.5; (b) removing residual cleaning composition by treatment with a rinsing agent; and (c) optionally drying said part to completely remove said rinsing agent from the part.

Entries from Industry and Government

Acramite™ — A Novel Product for Control of Spider Mites Crompton Corporation

Acramite™ is a new selective acaricide from a unique class of chemistry with a novel mode of action, which was discovered by Uniroyal Chemical. It is effective on a wide variety of pest mite species while having little impact on beneficial insects and predatory mites. It demonstrates rapid knock down activity on mites while providing long residual plant protection. It is highly compatible with Integrated Pest Management (IPM) programs.

Acramite has a very low acute mammalian toxicity, minimal chronic effects and no adverse reproductive or developmental effects. It poses minimal risk to applicators, handlers, and the general population including children. It has low risk to non-target terrestrial animals and plant species because of its low to moderate toxicity, lack of phytotoxicity, low use rate, and fewer required applications. Residues readily dissipate and do not accumulate. It has minimal risk to aquatic animals and plant species because of its low water solubility, very short half-life in water and soil, and low potential for run-off into aquatic environments.

The entire above mentioned attributes make Acramite one of the safest, most selective acaricides for growers to use to produce high yielding crops in both conventional and IPM programs.

Autothermal Reforming Catalyst for Fuel Cells Argonne National Laboratory

Researchers at Argonne National Laboratory have developed an autothermal reforming catalyst that efficiently reforms various liquid hydrocarbons, such as gasoline, into the hydrogen a fuel cell needs to produce electricity. The unique catalyst is the key to a fuel processor (or reformer) the size of a 1-liter soda bottle that will allow fuel-cell-powered vehicles to operate on conventional fuels, rather than on hydrogen stored onboard, making the vehicles much more attractive to consumers. The catalyst is so efficient that the fuel processor can now be 25 times smaller than any previous types, and therefore less expensive, less of a drain on a vehicle's fuel economy, and easier to integrate into a vehicle. Unlike most conventional catalysts, which are poisoned by sulfur, the Argonne catalyst tolerates the sulfur present in petroleum-derived fuels. The new catalyst could also help make fuel cells more attractive as stationary power sources for homes, commercial buildings, and remote locations. The advantages of using fuel cells in automotive and stationary power applications include their high efficiency and the absence of harmful emissions.

CSSX Process Demonstration Pacific Northwest National Laboratory

A U.S. Department of Energy (DOE) team has successfully demonstrated a new process that will be used to decontaminate 34 million gallons of high-level radioactive waste now stored in underground tanks at the Savannah River Site (SRS). This process, called CSSX, for caustic-side solvent extraction, will separate the radioactive isotope cesium-137 from the extremely alkaline liquid in the tanks.

Although the CSSX process is a waste treatment process, our goals were the same as those used in designing any environmentally benign industrial operation. That is, the goals of CSSX are inherently

green: to eliminate pollution, secondary-waste production, and risk to the environment while processing the waste to the required level.

The demonstration achieved key process goals, which showed that the volume of high-level waste can be reduced 15-fold and the cesium-137 can be removed with decontamination factors of 40,000 or higher. Furthermore, these goals were met using a very low solvent-to-feed ratio, an achievement made possible by using multistage centrifugal contactors and a new, highly selective solvent.

The team is now working to provide research and development results that will assist SRS in designing a facility for the CSSX process.

Deoxo-Fluor Reagent Air Products and Chemicals, Inc.

Deoxofluorination, the conversion of carbon-oxygen to carbon-fluorine bonds for pharma, agro and other chemical synthesis applications, is routinely accomplished at a small scale in the laboratory with DAST [(diethylamino) sulfur trifluoride], usually at near ambient conditions. The thermal instability of DAST has precluded its use at larger scale and at more forcing conditions. Air Products and Chemicals, Inc. undertook a program to render deoxofluorination safer at large industrial scale which led to the discover and development of the Deoxo-Fluor reagent. Extensive thermal analysis by DSC, Radex, ARC, Setaram calorimetry have clearly shown the far superior stability of the Deoxo-Fluor reagent over DAST. *Ab initio* quantum-mechanics calculations on the conformational structures of the reagent have provided a rationalization for this greater thermal stability. The Deoxo-Fluor reagent is effective in the conversion of alcohols to alkyl fluorides, ketones/aldehydes to *gem*-difluorides, and carboxylic acids to CF₃ compounds with, in some cases, superior performance as compared to DAST. Within the past 2 years, Air Products and Chemicals, Inc. has successfully brought the Deoxo-Fluor reagent product from discover to commercial production. Major pharmaceutical companies in the U.S.A., Europe and Japan are currently using the reagent for the synthesis of pharmaceutical products in their development pipeline.

Development of the Aqueous-Coated Photothermographic Material “FUJIMEDICAL Dry Imaging Film” Fuji Photo Film Co., Ltd.

The demand for high quality photothermographic materials used for hard-copying medical image-signals is remarkably growing. Conventional photothermographic system ejects no waste of solutions and material in processing, but this system has the ecotoxic difficulty using an amount of organic solvents for coating the material.

We have developed new ecological and non-harmful photothermographic materials produced using organic silver salt by an “aqueous-coated method”, which is constructed from the aqueous-latex technology and the control technology of thixotropic fluids.

Firstly this technology excludes concerns about explosion of organic solvents in manufacturing, to avoid unnecessary incidental investment. Estimation of world demand for all the photothermographic materials based on this technology suggests that reduction of the organic solvents may reach more than 10,000 tons/year level in the near future. Moreover, the materials manufactured with this technology are free from generation of unpleasant odor caused by organic solvents.

Secondly this technology contributes to reduce the use of silver, the useful raw metal, resulting in 20% reduction of stored amount of silver after diagnosis, compared with that of organic solvent coating.

Furthermore, this technology eases the recycling of polyester base material from used film or machining chip.

**Development of Two Unique Processes for Manufacturing
High-Purity Cyclopentane from Dicyclopentadiene
ExxonMobil Chemical**

The team working in Baytown Texas developed two unique processes for manufacturing high-purity cyclopentane from dicyclopentadiene. Cyclopentane replaces ozone-depleting substances (ODS's) such as CFC-11 or HCFC-141b foaming agents used in the manufacture of rigid polyurethane or polyisocyanurate insulation. Cyclopentane has the necessary physical properties including low vapor thermal conductivity and vapor pressure to make it a viable replacement for ODS's but was not commercially available in sufficient quantity due to lack of an economic manufacturing process. This team's invention (US Patent 5998683) is employed in a manufacturing facility started up in December 1998 located at Sarnia Ontario. That facility was built primarily to support the conversion of US insulation manufacturers from the use of ODS's to the green cyclopentane substitute. US consumption of ODS's in polyurethane and polyisocyanurate insulation amounts to about 100 Mlb/yr, all of which may be replaced by cyclopentane.

**Electrometallurgical Treatment of Nuclear Waste
Argonne National Laboratory**

Researchers at Argonne National Laboratory have developed an electrometallurgical treatment that can effectively separate toxic, hazardous, or radioactive metals from a wide variety of nuclear wastes. The key step in the process involves the fast, compact electrorefining of large quantities of waste material in an electrochemical cell. Argonne researchers have demonstrated this step by the extraction of more than 200 kg of uranium from spent fuel in one month. The uranium product can be stored, recycled, or converted to an oxide for disposal as a low-level waste. The metal residue, fission products, and transuranic elements from the spent fuel can be immobilized in highly stable waste forms for disposal in a geologic repository. Compared with conventional processing, electrometallurgical technology holds promise for significantly reduced costs, greatly decreased volumes of high-level radioactive waste, and negligible volumes of secondary or low-level wastes. This technology could facilitate the environmentally sound processing of most of the more than 2000 metric tons of spent fuel accumulated within the Department of Energy complex. This technology also has potential spin-off applications for industry, such as the treatment of enrichment tailings from nuclear plants and the disposal of nontoxic wastes (e.g., barium-contaminated slats) from industrial processes.

**Electronic and Photonic Polymers from Biocatalysis
U.S. Army Soldier and Biological Chemical Command**

An alternative, biocatalytic approach to new conducting and light-actuated polymers has been developed. In this approach, enzymatic polymerization of anilinic and/or phenolic monomers is carried out in the presence of ionic templates to yield high molecular weight, water-soluble complexes of the polymer and the template used. Here the template provides a unique preferential local environment, which serves to both emulsify the monomer prior to polymerization. Metal-like electrical conductivities,

Non Linear Optical (NLO) activity and optically driven large amplitude surface relief gratings are obtained from these biologically derived polymeric materials. This approach is particularly attractive because it is completely benign, simple (one step), and uses very mild aqueous conditions. In addition, the process is general as numerous ionic templates and derivatized monomers may be interchanged to build in desired functionalization. This process has the potential to revolutionize the use of electronic and photonic polymers since toxic catalysts or solvents are no longer required for the synthesis or processing of these polymers into useable forms. In addition, templates from renewable sources, such as lignins and even DNA can be used. This technology is expected to have wide technological impact towards the development of new electronic and optical devices.

Electrorefining of Spent Nuclear Fuel Argonne National Laboratory

Electricity generation using fossil fuels releases enormous amounts of airborne pollutants that can be avoided through substitution of nuclear power. There is, however, a minimal but non-negligible environmental impact from uranium mining and milling operations. Also, only a limited amount of electric energy can be derived from known uranium resources by using the present nuclear fuel cycle. Electrorefining of spent nuclear fuel addresses these drawbacks, making it an enabling technology for clean electric power generation. A fast reactor fuel cycle incorporating electrorefining would increase the efficiency of uranium usage a hundredfold and would permit reuse of depleted uranium now in waste storage, both of which could defer mining and milling of uranium for more than a millennium.

The electrorefining process recovers uranium and other actinides from spent fuel by electrotransport through a molten salt, which minimizes waste generation by avoiding the use of solvents and reagents. Recovered actinides are returned to the reactor, and fission products are placed directly into two durable waste forms that are suitable for long-term geologic disposal.

Electrorefining of metallic nuclear fuel has been demonstrated at the pilot plant scale and is currently being used to treat DOE's inventory of sodium-bonded spent fuel.

Eliminating Air Pollution (VOC & HAP) at the Source Through the Use of Ultraviolet and Electron Beam Polymerization RADTECH International, North America

Paints, coatings, inks and adhesives have historically been based on the dispersion of polymers in solvents. These were then applied to substrates in thin layers. Commercial products, thus treated, were then subjected to heat to evaporate the solvents and convert the polymers to solids. These solvents, volatile organic compounds (VOC), thus became air pollutants and/or hazardous air pollutants (HAP). As such they reacted with NO_x to generate ground level ozone, a major air pollutant. Minor changes to the polymers used have allowed some VOC reduction, which has been overcome by rising production levels. The emission levels of volatile solvents remain very high.

The candidate technology described herein abolishes solvents completely. Instead, it provides for oligomers that are dissolved in monomers of similar reactivity. This permits the formulation and application of the above listed products, which are then cured by the application of ultraviolet (UV) or electron beam (EB) energy that causes 100% copolymerization of the oligomers with the monomers forming high performance coatings, inks and adhesives. Since no solvents are used, the emissions are nearly zero. Converters to this technology are therefore free of VOC and HAP regulations even if their production increases substantially. Environmental and health benefits are great. This technology is currently in use in a wide variety of industries and is growing at a 10-12% annual rate.

Environmentally Benign Antibacterial Agents
U.S. Department of Agriculture, Southern Regional Research Center

Water-dispersible products were prepared by reaction of readily available, water-soluble reactants (magnesium acetate tetrahydrate and hydrogen peroxide; mole ratios 1:2 to 1:40). These new compositions (magnesium hydroperoxyacetate–HOO-Mg-OAc and magnesium dihydroperoxide–HOO-Mg-OOH) have peroxide contents of 1-35%. Molar amounts of hydrogen peroxide used (70% less) and reaction time (reduced from 90 to 10 minutes) were dramatically reduced by microwave synthesis compared to conventional heating. These new compounds exhibit antibacterial activity against representative gram-positive (*Staphylococcus aureus*) and gram-negative bacterium (*Klebsiella pneumoniae*), are hydrolytically stable at ambient temperatures for at least 60 days and thermally stable below 350EC.

These environmentally benign antibacterial agents (containing only magnesium and peroxide) are affixed as aqueous dispersions to textiles to impart antibacterial activity to natural, synthetic fibers and blends by pad-cure processes (10-17% active ingredients cured at 2-4 min. at 120-150EC). Modified textiles containing bound peroxide (0.1-1.7% by weight) are active against bacteria as low as 0.10% peroxide. Renewable fibers (cotton, others cellulose) have the best affinity for the agents with cotton fabrics retaining their antibacterial activity up to 50 launderings. Marked improvements in fixation and durability of these agents to synthetic fibers have also been recently made by incorporating selected softeners in treating formulations.

Environmentally Benign Enzyme Reactor for Polymer Synthesis
Los Alamos National Laboratory

Most common methods for commercial polymer synthesis are using chemicals to oxidize monomer. During this process, large amount of by-products and waste are generated with the polymer production. There has been great interest in development of alternative pathways to reduce or eliminate waste generation in polymer synthesis, such as using biological route for polyaniline synthesis, with only products of polyaniline and water. However, the current biological techniques using enzyme solution for polymer synthesis suffer from significant limitations. When enzyme is directly used in solution format in the reaction process, it is hard to recover the enzyme from the final products and almost impossible to reuse the expensive enzyme. In this work, we have developed a novel technology for polymer synthesis through biological route, with an example of polyaniline. The technique takes full advantages of the solution enzymatic synthesis method but overcome its limitations by immobilizing the enzyme on a solid support as a catalyst. The stability of the enzyme is significantly increased through the immobilization process. Furthermore, the catalyst enzyme can be easily recovered and reused with the immobilizing technique. Since the solid support is used, it is ideal to fabricate an enzymatic reactor for polymer synthesis. Most importantly, the newly developed technology in this research makes the biological route for polymer synthesis become usable and practical in commercial production process. A patent application for this new technology was filed at USPTO in year 2001.

Environmentally Benign Two Step Synthesis of Fatty Alcohol Mixtures
Using Supercritical Carbon Dioxide (SC-CO₂) and SC-CO₂/Hydrogen Mixtures
National Center for Agricultural Utilization Research

The nominated process differs from reported synthetic methods using utilizing supercritical fluids in that it embodies two distinct sequential reactions to esterify vegetable oils followed by high

temperature/pressure hydrogenation using a chromium-free catalyst. Transesterification is also accomplished with a “green catalyst,” a commercially-available lipase. The hydrogenation of the methylated oil is much more rapid in the supercritical fluid media compared to traditional technology and produces methanol as a product which can be reused as a starting reactant in the initial transesterification step. Fatty alcohols can be produced in over 98% yield with minimal by-products (n-alkanes) via this process. The described synthesis can be accomplished using only two sequential flow reactors to convert a renewable resource, soybean oil, to a mixture enriched to over 90% in steryl alcohol.

Fabricating Computer Chips Without Acids and Solvents — The Enviro Process ULVAC Technologies, Incorporated

The nominated technology eliminates acids and solvents from computer chip manufacturing using a combination of dry gas plasma treatment and DI water rinsing. Front end and back end wafer processing were addressed. The dry plasma chemically treats organic and inorganic wafer surface contaminants rendering them 100% soluble in DI water.

Phase 1, conducted by ULVAC Technologies, was the development of dry plasma processes employing multiple-step gas mixtures with and without halogen species to remove bulk organic contaminants and to render any inorganic residuals soluble in DI water. This work proved on a pilot scale that obtaining acceptably clean wafers and workable devices was feasible.

Phase 2, conducted with the Motorola Corporation, moved this process technology into back-end manufacturing for via veil removal after dry etching of vias. A manufacturing-qualified, robust, reliable, and high yield process for solvent-free back-end processing was developed.

Phase 3, conducted with LSI Logic Corporation, focused on front-end manufacturing, including high-dose ion implantation and poly-gate etching. This resulted in 100% replacement of hazardous hot concentrated sulfuric-acid/hydrogen peroxide ("piranha") solutions with simple DI water rinses for all front-end processing steps.

Nalco ACT – Advanced Condensate Treatment for Boiler Systems ONDEO Nalco Company

The ONDEO Nalco Chemical Company of Naperville, Illinois, a wholly owned subsidiary of Suez, initiated a research program to develop a safer and more environmentally friendly alternative to the use of amines in boiler water treatment as corrosion inhibitors. Nalco in fact did discover an innovative approach to limit boiler condensate corrosion without the use of any nitrogen bearing chemistry. Nalco received a United States patent for this approach in 1998. In 1999, the commercial application program was fully introduced throughout the United States and to the rest of world. During the start of the millennium, those who operate boiler systems have begun to switch from an amine based corrosion inhibition treatment, to the safer Nalco ACT program. The use of the new ACT program is gaining momentum as the operators of boiler systems enjoy excellent corrosion protection while using a more environmentally friendly and safer alternative to amines.

Nitrapyrin, A Unique Compound with Positive Impacts on Water and Air Quality Dow AgroSciences, LLC

Nitrogen fertilizer application is an integral part of corn production in the Midwestern US, but N fertilization is an inefficient process. Approximately 25% of the N fertilizer applied in the Corn Belt each year is lost from the soil by leaching of nitrate-nitrogen or conversion of nitrate-nitrogen to nitrous oxides (N₂O), which are released to the atmosphere. Inefficient N fertilizer utilization is a contributor to human, animal, and environmental health concerns relating to excessive nitrate-N occurrence in water and to N₂O emissions as an agent of global warming. Nitrogen pollution is no longer solely a local or regional concern, it is a problem with global ramifications. These concerns are causing refinement of best management practices for N in ways that conserve fertilizer and restrict N mobilization from agricultural lands.

Nitrapyrin, a product historically used by farmers for agronomic reasons, has the potential to reduce human health and environmental concerns stemming from increased global burdens of industrially fixed N. The conversion of fertilizer and manure N from the stable ammonium form to the nitrate form via the nitrification process results in nitrate that can leach from the soil and can also be converted to N₂O. Nitrapyrin reduces loss of N to the environment by inhibiting nitrification through its specific activity for *Nitrosomonas spp.*, the soil bacteria responsible for initiating the conversion of soil-stable ammonium-N to environmentally-mobile nitrate-N. Nitrapyrin exhibits a low level of toxicity to mammals, avian, and aquatic species. Nitrapyrin has an environmentally benign fate within agroecosystems. It does not leach, bio-accumulate, or persist in the soil, and has little or no impact on beneficial soil organisms.

Patterned Channel-Constrained Process for Additive Electroless Metal Deposition Naval Research Laboratory

Channel-constrained metallization (CCM) is described as a process for the fabrication of patterned metal features useful as etchmasks and electrical interconnects for microelectronics applications. The method creates a reactivity template through patterned exposure and development of a photoresist film to uncover an underlying ligand self-assembled monolayer (SAM) coating the substrate to be plated. A Pd(II) catalyst, selectively and covalently bound to the uncovered ligand sites, initiates additive, patterned electroless (EL) metal deposition of the substrate. Because the photoresist channel walls confine lateral EL metal deposition, the deposited metal film faithfully replicates the pattern of the mask used to expose the photoresist. Adhesion of the EL deposit, which is controlled by the strength of the Pd(II)-ligand bond, is sufficient to pass an ASTM tape peel test even on flat, unroughened surfaces. Consequently, the use of adhesive Sn(II) salts is not required for CCM, avoiding environmental problems associated with the use and disposal of Sn, accelerators, and substrate surface etchants currently employed with standard subtractive EL processes. The additive nature of catalyst and metal deposition characteristic of CCM further minimizes both reagent use and the generation of plating waste relative to subtractive methods, providing additional environmental and cost advantages for the process.

**The Process Greenness Scorecard:
Design for Environmental Health and Safety Through Green Chemistry
Bristol-Myers Squibb Company**

The synthetic and semi-synthetic processes utilized in the manufacture of pharmaceuticals at Bristol-Myers Squibb are chemical-intensive and involve the use of many solvents and reagents. The organic chemistry developed at the earliest phases of research and development is essentially geared to producing complex organic molecules through convenient “building block” chemicals. Many of these building block materials are highly regulated chemicals. Process developers use these chemicals because they are widely available and may accelerate the development process and launch of critical life saving and enhancing drug products.

The Process Greenness Scorecard is a tool that helps Bristol-Myers Squibb research chemists and engineers to identify materials of concern and to evaluate potential substitution with environmentally preferable process materials. In addition, the scorecard enables users to consider process conditions that minimize the impact of using these materials. Controlling the use of reagents and solvents, increasing process yields, and reducing waste streams are a few of the factors measured in the scorecard.

The scorecard encourages early product pipeline work to dramatically improve the environmental impact of commercial-scale pharmaceutical operations. It is a means of driving green chemistry by directly measuring progress in designing processes that reduce hazardous solvent use, waste generation, employee exposure, and process hazards.

**Recovery and Beneficial Use of Sodium Nitrite from a Wastewater Stream
GE Plastics**

Currently, our operation burns ~13,100 tons of a waste stream, containing ~3400 tons of solids, annually. This project will recover the main constituent from that waste stream, namely sodium nitrite, purify it, and market it as a technical grade product. The amount of waste that will then be incinerated will fall to ~2000 tons/year (containing ~400 tons/year of solids). The process will also reduce secondary waste streams, such as NO_x emissions and refractory slag generated by the incinerator, and waste generated by the commercial manufacturing of sodium nitrite, typically from absorption of nitrogen oxides into aqueous sodium carbonate or sodium hydroxide. Finally, the energy requirements to treat the waste will be reduced. The long-term objective of the project is to decommission our incinerator. The waste stream to be recovered represents 75% by weight of the material in the feed to this incinerator.

**The REMEDIA™ Catalytic Filter System:
Dioxin Destroying Filter Media for Industrial Application
W. L. Gore & Associates, Inc.**

Dioxin and Furans, listed among the “Dirty Dozen” persistent organic pollutants (POPs), are one of the most toxic chemical families known to mankind. Recently a novel filter element has been developed that not only controls particulate emissions, via a microporous ePTFE (expanded polytetrafluoroethylene) membrane, but more importantly, catalytically destroys dioxins and furans, via a catalyst/ePTFE-felt substrate. A simple replacement of current filtration media with this catalytic filter can reduce dioxin emissions up to, and in some cases greater than, 99%.

An early implementation of this technology took place in May 1999 at Phoenix Services, a medical waste incinerator in Baltimore, Maryland. Here, dioxin/furan emissions have been reduced by almost two orders of magnitude from historical values and are far below all local, state, and federal regulatory limits. In addition, in the past four years, the nominated technology has been installed in 27 applications worldwide, each with emissions that have been remediated to a level significantly below regulatory limits.

This filter element effectively combines the accepted technologies of catalysis and surface filtration to form a novel product which controls particulate emissions and destroys carcinogenic dioxins and furans. The result is green chemistry producing a safer and healthier environment for the world.

**STABREX[®] Microorganism Control Chemical:
An Environmentally Sensible Chlorine Alternative for Industrial Water Treatment
ONDEO Nalco Company**

Chemical products should be designed to preserve efficacy of function while reducing toxicity, degrade rapidly and innocuously, reduce accident risk, and be made from renewable sources. A chlorine alternative for microbial control is needed: Chlorine gas is dangerous, the liquid is not stable, biofilm control is not adequate, and chlorine disinfection by-products are toxic. STABREX[®] Microorganism Control Chemical overcomes these deficiencies. Comparatively, STABREX is 3-22x less toxic and generates 50% less disinfection by-product. It is 10x less volatile, 50% less reactive, more stable in storage/transport, more effective against biofilms, and easier to handle. These technical attributes result in valuable benefits: Less environmental toxicity, less chemical waste, and lower accident potential. One hundred million pounds of chlorine or its equivalent have been replaced in 4,500 industrial water systems with 25 million fewer pounds of STABREX. Four hundred billion gallons of industrial water have been treated with an inherently less toxic, more effective antimicrobial. This innovation is recognized as original and unique: It is the first biomimetic industrial antimicrobial, having been designed to imitate compounds naturally produced in mammalian immune systems, and it is the first commercially developed stabilized liquid bromine product.

**Use of Stabilized Enzymes to Remove Slime Deposits in the Paper Industry
Buckman Laboratories International, Inc.**

It is indeed rare to have the opportunity to replace toxic materials with *virtually nontoxic* alternative technology. Our nomination for the Presidential Green Chemistry Challenge Award can do exactly that.

The accumulation of polymeric slimy material is a serious operational problem in papermaking systems, and can cause fouling in many other industrial systems as well. In these systems where large amounts of water are used, microorganisms can attach to surfaces and extrude copious amounts of slime exopolymer. This slime, comprised of carbohydrates and protein, can plug and foul machines, reduce heat transfer, and cause many other problems. In the past, the only viable solution was the use of toxic chemicals such as bactericides and fungicides. Over the years safer, less toxic materials have come to be used. But still there are significant risks in handling and transporting the modern microbicides.

This nominated technology utilizes stabilized enzymes to clean surfaces, removing the deposit, thus eliminating the use of some toxic materials currently required. These enzymes are biodegradable, nontoxic, and produced from renewable resources. They do not function by killing microorganisms - they are nontoxic. The enzymes are very effective in removing the accumulation of deposits produced by microorganisms.

The Use of Vitamin C to Neutralize Oxidants Such as Chlorine in Drinking Water Skagit County Public Utility District

The chlorination of public drinking water has proven to be a significant breakthrough in the prevention of disease in humans. However, chlorine, even in minute quantities, is toxic to fish and other aquatic life. The water (and wastewater) industry must use extreme caution when operating their systems so that chlorinous discharges do not adversely impact aquatic life downstream.

Industry has used specific sulfur-based compounds to neutralize chlorine. However, during dosing applications these sulfur-based chemicals can present distinct health hazards to the waterworks operator and/or the fish that happen to occupy nearby streams.

It was discovered that vitamin C in the form of ascorbic acid, is an effective neutralizer of oxidants such as chlorine. Vitamin C is safer than other chemicals that can cause respiratory problems in humans and deplete oxygen levels in the water which fish require. Vitamin C is the only reagent with a NFPA rating of 0,0,0.

Vitamin C is just as effective, and in other ways it is better than all other chlorine neutralizers. However, vitamin C offers a unique advantage. It synergistically boosts the immune system of the effected aquatic life while simultaneously removing toxic disinfectant dangers from their susceptible habitat.

Water Based Synthesis and Purification of Mannich Base Modified Polyphenols Henkel Surface Technologies

Mannich reaction products of polyphenols with formaldehyde solutions and secondary amines produce unique chelating polymers. These have replaced many hexavalent chromium containing treatments and continue as components in new and diverse non-heavy metal containing conversion-coating technologies. Originally, the precursor phenolic polymer was dissolved in an organic solvent before the reaction. Acidification of the newly acquired amine functionality allows dilution with water before application. At this point, the organic solvent component serves no apparent useful purpose. Since phenols can be ionized, and thus be solubilized in water, by a strong base such as sodium hydroxide, a water-based synthesis process was developed. These reactions proceed with paraformaldehyde (eliminates methanol content) and amine at lower temperatures and higher yields than the solvent-based processes. Dilution and acidification, followed by deionization through a strong-acid type cation-exchange column quantitatively removes the sodium, residual amine, monomeric Mannich reaction products (small ethylphenol content from the precursor polymer) and other cationic impurities - resulting in a highly purified 100% aqueous polymer solution. Additional benefits realized include: improved shelf-life and hot/cold stability of the concentrate, elimination of flash points, BOD/COD and residual formaldehyde reductions, and the elimination of worker exposure to organic volatiles during manufacture.