Draft Summary of 2003 Award Entries: Presidential Green Chemistry Challenge Awards Program

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

Entries from Academia

A Novel Additive System for Time-Controlled Degradation of Polypropylene
Dr. Dianne Allen

Iron(III)dimethyldithiocarbamate (FeDMC) and Nickel(II)di-n-butyldithiocarbamate (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 180EC, significantly below the standard processing temperature for polyolefins. Experiments were carried out using Iron(III) Acetylacetonate (FeAcAc) in place of the dithocarbamate 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 H_2O_2 from H_2 and O_2 in CO_2 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.

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

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

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 an economically attractive, high yield, solvent-free process to give the corresponding epoxidized triglycerides. Alternatively, naturally occurring epoxidized vegetable oils 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.

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 CO_2-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 CO_2 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 CO_2 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.

Tunable Benign Solvents to Couple Reactions and Separations
Professor Charles A. Eckert, School of Chemical Engineering,
Georgia Institute of Technology

For any chemical process there must be both a reaction and a separation. Conventionally these are often designed separately, but Professors Eckert and Liotta have combined them with a series of novel, benign, tunable solvents to create a paradigm for sustainable development—benign solvents and improved performance.

By a synergistic combination of chemistry and engineering, they have exploited a series of solvents using primarily water and carbon dioxide to alter reaction conditions to increase selectivity, eliminate waste, recycle catalysts, and to achieve facile separations. The fluids involved include supercritical CO_2, nearcritical water, and gas-expanded liquids (with CO_2).

Eckert and Liotta have formulated an outstanding research partnership, both within Georgia Tech and in collaboration with a wide variety of industrial partners. As a result of these interactions, tunable solvent processes with benign solvents have been developed that have the potential of replacing environmentally undesirable solvents and eliminating many hundreds of millions of tons a year of waste.

Further, these processes also offer improved economics for increased competitiveness, and as such are being implanted by the many industrial partners involved in their development.

Direct Biocatalytic Synthesis of Functionalized Catechols:
A Short Route to Combretastatin A-1
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 (all based on metal reagents) with enzymatic techniques (all performed in water). In previous projects we have already proven the value of the enzymatic oxidation in the attainment of important pharmaceuticals from metabolites of aromatic compounds. Halogenated aromatic compounds, viewed in many cases 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. 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 judged suitable for disposal to municipal sewers, thus further reducing the amount of actual waste. The key philosophy of our projects rests on the managed processing of aromatic waste to value-added substances. A new definition of efficiency, "Effective Mass Yield," is provided as the percentage of the weight of desired product in the weight of all non-benign mass requiring treatment or disposal that is used in the manufacturing process.

Antibody Catalysis
Professors Kim D. Janda and Richard A. Lerner, The Scripps Research Institute

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

Antioxidant-Functionalized Polymers

Professor David L. Kaplan, Department of Chemical & Biological Engineering, Tufts University

A bio-catalytic technology was developed for the synthesis of antioxidant functionalized polymers. The process consists of two steps. First, a lipase is used to catalyze the highly selective modification of a vinyl monomer with ascorbic acid. Second, horseradish peroxidase is used to catalyze polymer formation. During this two step enzymatic process the ascorbic acid retains antioxidant activity due to the regioselective nature of the enzymatic coupling process and mild reaction conditions employed by these enzymatic methods. This approach represents a novel green chemistry strategy to functionalized polymers that are otherwise difficult to synthesize and require large amounts of solvents or toxic chemicals to make. Furthermore, this novel approach enhances human heath and the environment by avoiding overuse and overexposure to benzene-derived antioxidants in foods, beverages, and materials in general, and provides for enhanced stability of labile and naturally occurring antioxidants to promote lower concentrations during use.

Photoacylation and Photoalkylation of Quinones

Dr. George A. Kraus, Iowa State University

Dr. Kraus, a professor of chemistry at Iowa State University, has developed the photoacylation and photoalkylation of quinones as an environmentally benign alternative to certain Friedel-Crafts reactions. This reaction can be conducted in supercritical carbon dioxide and is a good example of both atom economy and the more stringent criterion of reaction mass efficiency. Photoacylation produces adducts which have been used in very direct syntheses of benzodiazepines such as valium, natural products such as frenolicin, and antioxidants such as tert-butylhydroquinone. His research (eight publications, two patents, and one patent disclosure) has made available new and direct pathways for the synthesis of commercially important products. His publications have led to a renewed interest in this photochemical reaction.

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.

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

ATRP is a transition metal mediated controlled polymerization process for radically polymerizable monomers discovered at our laboratories in 1995. The process has been actively incorporated into many industrial research programs for the preparation of polymers targeting a broad spectrum of applications. Since 1995 we have led efforts to develop more active catalyst systems, targeted at reducing the levels of metals in the ATRP systems. We have also led the development of environmentally benign procedures for preparation of many functional ("green") materials via ATRP. However, the most active catalysts could not be used in many systems due to the need to balance the activity of the catalyst and the number of moles of initiator that had to be added the system in order to prepare low molecular weight functional oligomers of commercial importance. Systems employing hybrid catalysts and SR&NI overcome this limitation. We are now in the position to apply our expanded understanding of ATRP catalysis to the development of a "continuous" bulk ATRP process. The combined process will fully control the activity of the hybrid catalyst over extended time periods and allow recycling all catalyst residues present in the process effluent back to reactor feed streams, thereby demonstrating elimination of all hazardous substances from the products produced by ATRP and from industrial production waste streams.

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

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

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.

Environmentally Benign Preparation and Polymerization of Phosphazene Polymers

Dr. Eric S. Peterson, Idaho National Engineering and Environmental Laboratory (INEEL) Separations Group

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.

Asymmetric Catalysis in Water: Hydroxyphosphine and Hydroxyphosphinite Ligands for Amino Acid Synthesis

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

A series of chelating *bis*-phosphinite ligands with acid-sensitive protecting groups were prepared from readily available sugars, α,α-trehalose and D-salicin (2-(hydroxymethyl)phenyl β-D-glucopyranoside). Deprotection of the ketal protecting groups in these compounds with acidic resin in methanol eventually gave water-soluble cationic Rh complexes that were competent to effect highly efficient hydrogenation of acetamidoacrylic acid derivatives in organic, aqueous or biphasic media. However, enantioselectivities of these reactions in neat aqueous or biphasic media are generally lower than those observed in organic medium. As a solution to this problem, two different protocols for the preparation of water-soluble, enantiomerically pure polyhydroxy *bis*-phospholanes from D-mannitol are reported. These procedures circumvent two of the commonly encountered limitations in the synthesis of these potentially important ligands: (a) formation of phosphonium salts from the highly basic phosphines under acidic conditions; (b) the need to start with preformed fully protected cationic metal complexes. Cationic Rh-complexes of these ligands have been prepared in a separate step, and they have been found to be excellent catalysts for organic and aqueous phase hydrogenation of dehydroaminoacids. The viability of catalyst recovery has been demonstrated in three different systems, including in two cases where >99% ee can be achieved under recycling conditions (up to six cycles).

Dissolution and Reconstitution of Cellulose without Derivatization or Pretreatment: A "Green" Utilization of Ionic Liquids Where Traditional Solvents Fail

Dr. Robin D. Rogers, Professor of Chemistry, Department of Chemistry and Center for Green Manufacturing, University of Alabama

We have discovered that ionic liquids (ILs) can be used for the dissolution of cellulose which can make such processes cleaner and more efficient with commensurate reduction/elimination of environmentally undesirable solvents. Three main objectives achieved include (1) rapid, efficient dissolution, (2) simple reconstitution, and (3) recovery and recycling of solvent. By understanding the relationship between free chloride activity and cellulose dissolution, we have shown that cellulose can be dissolved *without derivatization* at high concentrations, up to 30 wt/wt% and easily reconstituted into water or other environmentally acceptable solvents. The availability of a wide and varied range of ILs coupled with the current understanding of their solvent properties allows flexibility and control in the processing methodology, with increased solution efficiency and reduction or elimination of the current undesirable solvents. No derivatization, fewer steps, no additives and lower temperatures required to process cellulose with ILs, can provide chemical, waste, and energy savings.

A Systematic Methodology for the Design and Identification of Environmentally Benign Chemicals

Professor Nikolaos V. Sahinidis, School of Chemical Sciences, University of Illinois at Urbana

A major obstacle that stands in the way of designing environmentally sound chemicals is the testing of all possible structural alternatives. The number of possible ways in which atoms or submolecular groups can be combined to form molecules exceeds several trillion even when one restricts attention to small molecules. Using his pioneering optimization methods, Professor Sahinidis has invented a powerful way to search the astronomically large space of possible compounds and identify the entire set of compounds that are potentially suitable refrigerants in an automotive refrigeration cycle. By extending this approach to secondary refrigerants, the Sahinidis team recently identified over 3,000 potential secondary refrigerants. In addition to rediscovering known refrigerants, this methodology yielded a large number of chemical structures that are entirely novel: Some of them appear in databases but were never used as refrigerants while others do not even appear in databases of chemicals.

Professor Sahinidis' approach to molecular design is applicable to a very broad spectrum of compounds, including pharmaceuticals and industrial solvents. Because it produces the entire set of possible compounds that satisfy physical property requirements, this methodology enables the use of environmental criteria to extract those compounds that are environmentally benign.

Development of Relatively Benign Totally-Organic Wood Preservatives To Replace Metal-Based Systems

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

The dominant wood preservative—by far—used in the U.S. is chromated copper arsenate (CCA), with about 50 million lbs. of arsenic and 70 millions lbs. of chromium (oxide basis) used yearly. However, recent public concerns over possible arsenic exposure has led to CCA being restricted starting in 2004. Use of alternate copper:organic systems is expanding, but these copper-rich systems also have environmental and/or disposal concerns and will likely face future restrictions with totally organic preservatives mandated; this trend is already apparent in some European countries. No totally organic wood preservative is currently Standardized by the AWPA (American Wood Preservers' Association) for residential applications, and most organic biocides being considered may have their own environmental concerns and may be much more expensive than CCA or the newer copper:organic systems.

We have studied naturally-durable woods and found that the extractives in durable woods have excellent antioxidant and metal chelating properties but are only weakly fungicidal. Utilizing this concept, we have found that the combination of various organic biocides with non-biocidal metal chelating and/or antioxidant additives gave enhanced protection to wood as compared to the biocide alone. Many of the additives we examined are relatively benign (i.e., approved as food additives) and inexpensive. Consequently, this concept may lead to relatively benign and economical totally organic wood preservatives.

From Waste-to-Energy: Catalytic Steam Gasification of Poultry Litter

Professor Atul C. Sheth, Chemical Engineering, University of Tennessee Space Institute

UTSI's poultry litter gasification concept is based on the Exxon's Catalytic Coal Gasification Process. In this concept, poultry waste or any other animal waste is mixed with the other biomass waste and suitable source of additional potassium. The resulting mixture is gasified in "as-is" or slurry form at 1300-1500°F and at 50-150 psi pressure in a suitable gasifier. The steam for gasification can be produced externally and supplied to the gasifier or can be produced in-situ from the wet/slurried feedstock. Depending upon the pressure, the resulting fuel gas will be rich in CH_4 or in CO and H_2 and after separating from the solid/char residue can be used as a fuel for heating purpose or to produce electricity. The solid/char residue is significantly small in volume (by a factor of 5 to 10) than the starting waste, and therefore, can be used in cement/concrete manufacturing or as fertilizer to provide concentrated source of K and P-bearing salts. Potassium present in poultry and certain animal wastes such as from swine, cows, horses, and sheep can provide the necessary catalyst. If necessary, additional supplemental potassium can be obtained from other cheap sources such as langbeinite and feldspar.

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 H_2O_2 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.

Converting Pollution to Profits: Valuable Chemicals & Energy

Professor Israel E. Wachs, Department of Chemical Engineering, Lehigh University

Sulfur-containing molecules are found in many different industrial sectors and are usually desulfurized by combustion to SO_2 or hydrogenation to H_2S because they are toxic, corrosive, strongly malodorous, involved in the formation of particulates and are responsible for acid rain. H_2S and SO_2 emissions are typically converted to elemental sulfur and gypsum sludge and are disposed in landfills. Clearly, these pollution control approaches don't result in valuable chemical products or energy that generate monetary incentives for industry to minimize environmentally undesirable sulfur emissions.

An alternative approach is to view the S-containing molecules as inexpensive feedstocks for the production of valuable chemical products and energy via new synthetic and selective catalytic reaction chemistry. The oxidation chemistry of S-containing molecules has previously not received much attention because the ultimate goal has been to completely oxidize to SO_2 or elemental sulfur. However, the recent work at Lehigh University has discovered that S-containing molecules can indeed be selectively catalytically oxidized as well as dehydrogenated, via exothermic energy generating pathways, to highly valued chemicals such as H_2, H_2CO, maleic anhydride, phenol, C_2-C_4 olefins and alkanes as well as H_2SO_4. Furthermore, the application of these new synthetic methodologies can also partially displace the energy intensive and polluting synthesis of H_2 (consumes enormous amounts of fuel, generates significant global warming CO_2 and smaller amounts of NOx/SOx emissions), which will become even more important in the coming years. Lastly, these new selective catalytic processes are sustainable in those industries that are based on renewable resources—biomass.

Entries from Small Businesses

Reducing Nitrates in Buzzards Bay with the Production of Organic Gem® Fertilizer from New Bedford's Fish Processing Wastes (An SGNB Project)
Advanced Marine Technologies (AMT) BioProducts Corporation

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

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.

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

There is a strong interest in finding alternative plasticizers for use in the processing of PVC resins that are economically competitive and equivalent in performance to dioctyl phthalate (DOP) with no health and environmental concerns. Over 2 billion pounds per year of DOP plasticizer are used in the US to process polyvinyl chloride resins to make flexible and semi-flexible extruded articles such as films, tubes, blood bags, toys, siding, etc. Although DOP and other petroleum derived synthetic plasticizers have good performance in the processing of PVC articles, they suffer from potential health and environmental concerns. Studies have shown that phthalate plasticizers are suspected endocrine disruptors and are not encouraged in some applications such as toys and medical devices in the US (Chemical Marketer Reporter, p3, February 4, 2002) and are banned in some countries in Europe (Modern Plastics, p14, December 1999).

Successful development and commercialization of soybean oil-derived plasticizer technology (patent pending) will address a major need in the polyvinyl chloride (PVC) industry, namely, a cost effective plasticizer that is safe and does not have the health concerns associated with dioctyl phthalate (DOP). Replacing even a part of the 2 billion pounds per year US market for DOP with a bio-based product derived from soybean oil offers significant energy savings with reduced carbon dioxide emission.

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

The chemicals that we displaced were Chromic Acid, CAS # 133-82-0, and Potassium Ferricyanide CAS# 13746-665-2. These Components are 54% of traditional process solutions. They are on the EPA list of hazardous or toxic chemicals and chrome and cyanide are listed materials for effluent limitation in the categorical pretreatment standard. We replaced them with a product containing Potassium Permanganate (KMnO4) CAS# 7764-7, a very powerful oxidizer. KMn04 will oxidize both iron and manganese to convert ferrous (2+) into the ferric (3+) state, and 2+ manganese into the 4+ state, to format the permanganate ion MnO4, and manganese dioxide MnO2. This liberates nascent (elemental) oxygen molecules. The stoichemetric amount of KmnO4 required to oxidize 1 mg of iron is 0.91 mg KMnO4. To oxidize 1 mg of manganese requires 1.92 mg of KMnO4. It then reduces these items to insoluble oxides, which are easily removed by filtration.

The actual amount of KMn04 needed has been found by us to be less then indicated by stoichimetry. It is thought that this is because of the catalytic influence of KMn04 on the reactions. Heat, pH and process temperatures are integral to the process. Process solutions function best in the range of 130–140 degrees F and with pH between the 7.0 and 8.0 range. Processing time varies from 7–15 minutes depending on the amount of oxidation required, with the resultant oxidation ranging from between a medium gold-brown (7–10 minutes) to a dark gold-brown (10–15 minutes). Rinsing is accomplished in de-ionized water.

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

The Nutritional Metabolism Disrupters (NMDs) 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 NMDs 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.

Zero VOC Protective Coatings for Aerospace Applications
Deft, Inc.

The Zero VOC protective coatings developed by Deft include an epoxy resin based primer and a polyurethane topcoat based on polyester polyol-polyisocyanate resins. Each has a design organic solvent content of zero confirmed through measurements as specified in EPA Method 24. Neither uses exempt solvents to achieve zero VOC. The primer, Aquapox™, was listed as qualified to military waterborne primer specification MIL-PRF-85582, Type I (standard pigments), Class C2 (strontium chromate) on July 11, 2001. It is based on emulsified epoxy resin and polyamine curing agents. Coatings qualified to the specification have an intended use as corrosion inhibiting, chemical resistant coatings for use on most aircraft substrates. The topcoat product line, Defthane® Z-VOC™, is qualified to military specification MIL-PRF-85285, Type III (aircraft and ground support equipment, 50 g/L VOC maximum), Class W (waterborne). It was qualified in July 2002. Coatings qualified to this specification, based on the range of requirements for application, appearance, fluid resistance, corrosion resistance, and weathering resistance, are intended for use in naval aviation environments and other less severe environments.

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

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

Aquagard Waterbase Antifouling Bottom Boat Paint
Flexabar Corporation

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.

Acetylene, A Viable Fuel Alternative for the Internal Combustion Engine
Go-Tec, Inc.

Go-Tec, Inc. has developed an environmentally clean dual and multi-fuel composition for use in an internal combustion engine, comprising acetylene as a primary fuel and a combustible fuel, such as one or more fluids selected from an alcohol such as ethanol, methanol or any other alcohol or alcohols from the group comprising C.sub.1–C.sub.20 carbon chains, ethers such as from the group comprising dimethyl ether, diethyl ether, methyl t-butyl ether, ethyl t-butyl ether, t-amyl methyl ether, di-isopropyl ether and the like, low-molecular-weight esters such as from the group comprising methyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, ethyl malate, butyl malate, and the like, or diesel in the case where the engine is a diesel engine, or other suitable combustible fluid as mineral spirits and the like, as a secondary fuel for operatively preventing early ignition and knock arising from the primary fuel. If additional information is required, refer to U.S. Patent # 6,076,487 & U.S. Patent # 6,287,351.

GreenEarth® Cleaning, Dry Cleaning with Silicone Solvent
GreenEarth® Cleaning, LLC

GreenEarth Cleaning (GEC) is a process that has been patented for use in the drycleaning industry. The process is the use of silicone as a solvent with the preferred being:

Chemical Name	Dectamethylcyclopentasiloxane
Synonyms	D5
CAS Number	541-02-6
Molecular Formula	C10 H30 O5 Si5
Structural Formula	((CH3)2 SiO)5

The physical state of silicone, clear and odorless, produces garments that are clean and without smell. The D5 has a Kari Butnoyl value of < 20 that allows garments to be processed with ornamentation, adhesives, and plasticizers, unlike its counterpart PCE. The surface tension is 18.94 dynes, which results in silicone solvent penetrating textiles more freely and lifting soil more easily from garments.

The water solubility is 17 ppb with a density of .95. Environmentally speaking, this is safer since the silicone solvent is not considered to be a “sinker.” Yet due to silicone’s closeness in density to water it is difficult to separate the two liquids. GEC has developed apparatus patents and techniques to accomplish this separation. Given the characteristics of D5 and the techniques developed, drycleaners are able to accommodate this new process.

The Use of Vitamin C To Neutralize Oxidants Such as Chlorine in Drinking Water Which Is Often Discharged to the Environment

H2OK Engineering

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 operator and/or fish that occupy nearby streams.

It was discovered that vitamin C in the form of ascorbic acid, is an effective and affordable neutralizer of oxidants such as chlorine. Vitamin C is safer than other chemicals which can cause serious respiratory problems in humans and deplete oxygen levels in the water. Vitamin C is the only dechlorination 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 aquatic life while simultaneously removing toxic disinfectant dangers from their fragile habitat.

Both humans and fish benefit from this new technology.

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.

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 at commercial scale and low cost a series of low toxicity and environmentally friendly biodegradable 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, for example, alkylphenol ethoxylates (APEs). The technology for producing rhamnolipid biosurfactants utilizes alternative feedstocks that are renewable and are innocuous as compared to those used for production of synthetic or petroleum-derived surfactants. Further, biosurfactants require smaller resource input and employ less capital and power intensive processes. In their production and application they avoid the presentation of hazardous substances into the environment. They are extremely useful in applications where their use will preclude harmful environmental impacts and are also useful in applications for remediation of pollution. An initial commercial application is as an adjuvant to facilitate delivery of nutrients to crops. Other examples are hydrocarbon or heavy metal removal from soil and crude oil tank cleaning. In many applications biosurfactants are a substitute for or work in combination with and reduce the amount needed of less environmentally friendly synthetic surfactants.

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

Bio-based products generally, and products of transgenic microbes specifically, play a small role in the chemical industry compared with traditional catalytic processing of petroleum and natural gas. This situation persists despite the enormous diversity and efficiency of enzyme catalyzed chemistries harnessed in biological systems, and an increasing role for enzymatic transformations in the chemical industry (especially in the areas of industrial enzymes, amino acids, and vitamins). Several key disadvantages have been mainly responsible for the limited use of microbial systems in industrial chemical production. Microbes are enormously complicated, evolving to propagate and survive, not to produce a certain chemical from a cheap feedstock. As a result, these organisms catalyze undesirable reactions that waste feedstock and increase reaction time, energy requirements, and the production of greenhouse gasses such as CO_2.

The key aspect of metabolism responsible for these inefficiencies in many fermentation processes which could produce industrially useful materials from renewable resources resides in the catabolic pathways. Metabolix has developed microbial systems in which catabolic pathways have been altered, with enhanced productivity, for the production of PHAs. This technology will open the door to the sustainable production of new high performing chemicals and plastics (including medical applications) from agricultural raw materials.

An Economically Advantaged, Green Process,
for the Fabrication of Printed Circuit Boards
Micro Interconnect Technology

An environmentally cleaner and a more economical process 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 dispersion 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 new method for the 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 implemented wherever possible, aqueous, non-toxic chemicals in contrast with conventional board manufacture.

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

High CO Tolerant Polymer Electrolyte Membrane Fuel Cell Technology
Plug Power Inc.

Polymer electrolyte membrane (PEM) fuel cells are a paradigm shift technology in power generation because they use an electrochemical process to convert hydrogen and oxygen into electricity without combustion and combustion associated pollution. A fuel cell operating on natural gas produces less than 1 ounce of air pollutants as compared to 25 lbs. of pollution produced by conventional combustion generation. Existing PEM fuel cells, however, are very sensitive to carbon monoxide (CO) poisoning and membrane hydration. Trace amounts of CO in the fuel can reduce fuel cell performance, and a reduction in the hydration of today's membranes can shorten the membrane life. With such a high sensitivity to CO and hydration, current PEM fuel cells are expensive to maintain, and have limited lifetime and reliability.

Under the NIST Advanced Technology Program, Plug Power, Inc. has demonstrated a high CO tolerant fuel cell technology using a novel polymer electrolyte membrane. This new membrane does not require external humidification and because it operates at high temperature (160C), this new version of a PEM fuel cell can operate with over 1% (10,000 ppm) of CO without performance degradation. The significant increase in CO tolerance and the elimination of membrane hydration have substantially improved fuel cell operational performance and greatly simplified the overall system; thereby reducing system related cost and increasing system life. A reliable and low cost PEM fuel cell system with commercial viability is now being developed based on this new technology.

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

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

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

RYNEX® Dry Cleaning Solution
Rynex Holdings, Ltd.

Rynex Holdings, Ltd. developed, demonstrated, and implemented an environmentally safe and effective dry cleaning method that is economical to use. RYNEX® is composed of an azeotropic mixture of Dipropylene glycol t-butyl ether (DPTB) and water. This product is the result of extensive research in the field of modern organic chemistry and dry cleaning technology. RYNEX® dry cleaning solution has low volatility and is non-flammable, non-carcinogenic and non-persistent in the environment. It has the ability to separate and float on water. RYNEX® cleans water-soluble and fatty acid stains using the same molecule providing, effective detergency and compatibility with existing dry cleaning technology. It has superior cleaning abilities and does not cause shrinkage to fabrics and is non-bleeding with respect to all types of dyes. The RYNEX® base molecule in combination with small amounts of water has the advantage of behaving like a single substance. This unique technological breakthrough brings forth new properties that allow for the effective removal of water and oil soluble stains without shrinkage of wool fibers that occurs with wet cleaning methods. Other enhancements include greater optical brightness in the garments and the clothes are softer to the hand. The product is now commercially available throughout the world.

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.

Development of a Safer and More Effective Biodegradable Antimicrobial Cleaning Product
Treyco Supply

Currently most antimicrobial cleaners are harmful to inhale or for skin contact as they use chlorine, phenol, alcohol or Quaternary amine based ingredients. TPP1is a special blend of enzymes, bacteria, and surfactants which work together at a high pH. It is very effective at killing harmful bacteria and fungi. It is operator safe and can maintain surfaces free of antimicrobials for extended lengths of time. Funding is needed at this point to carry out further Environmental Protection Agency required testing in order to register the product for use. The TPP1 product already is known to kill certain microorganisms as noted. This product may also have applications in defending against a biological weapon attack. Its use in this area would be an added benefit.

Entries from Industry and Government

ACRAMITE™—A New Selective and Safe Miticide
Crompton Corporation

ACRAMITE is a new selective acaricide from a unique class of chemistry with a novel mode of action, which was discovered by Crompton Corporation. 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 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. Because of this safety, ACRAMITE will replace many less effective, more hazardous acaricides and contribute to lowering the total amount of pesticides used in the US. It contains no halogens or heavy metals.

The entire above mentioned array of 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. ACRAMITE has been granted reduced risk status at EPA and is registered for use on ornamentals, apples, pears, stonefruit, grapes, strawberries, hops, and cotton.

Airflex® EF811 Vinyl Acetate Ethylene (VAE) Emulsion Polymer—A Binder for Environmentally Friendly, High Performance, Cost Effective Architectural Coatings
Air Products Polymers, L.P.

Through product development of “a safer chemical,” Air Products Polymers, L.P. has solved a regulatory compliance problem for paint manufacturers. The architectural coatings industry is being challenged to implement strict environmental regulations regarding the use of volatile organic compounds (VOCs). This will require paint manufacturers to significantly reduce the level of solvents added to “water-based paints,” the evaporation of which creates objectionable odor as paint dries. Paint performance is significantly compromised as solvent levels are reduced. Many of the polymers that are currently utilized in paints require solvent addition to form a film, which will adequately protect the painted surface. Air Products Polymers has developed a new Vinyl-Acetate-Ethylene copolymer, Airflex EF811 emulsion, which solves this formulation challenge. Airflex EF811 emulsion can be formulated at very low solvent levels and is a replacement for vinyl acrylics, the workhorse polymer for architectural coatings, which typically require significant added solvent. Beyond environmental benefits, Airflex EF811 emulsion provides superior performance, and is cost-effective, priced similarly to vinyl acrylics. The size of the coatings market and vinyl acrylic segments is large. Broad replacement of vinyl acrylics with Airflex EF811 emulsion will result in significant reduction in solvent use, improving indoor and outdoor air quality.

Conversion of the Herbicide, Metolachlor, to S-Metolachlor in the U.S. Marketplace
Syngenta Crop Protection, Inc.

Metolachlor, a racemic mixture of two diastereoisomers, was used in the US for over 20 years on > 30 crops at about 65MM lbs./yr. Syngenta discovered increased herbicidal activity of the optically active S-isomer pair in the 1980s (US 5,002,606). A practical synthesis route could not be found until the mid-1990s, when Syngenta discovered a chiral diphosphine catalyst route for enantioselective hydrogenation of an imine intermediate for S-metolachlor synthesis (US patents 5,463,097; 5,563,309 and RE37344E). Syngenta developed an optimized process, designed, and constructed a high volume manufacturing plant capable of supporting commercialization. All metolachlor products have been replaced, at equal grower cost, with 35% reduced-rate S-metolachlor products. Charles Benbrook (see citation) estimated that in the conversion years, S-metolachlor reduced total US corn herbicide use by 12-14MM lbs./yr. With complete conversion, an 18-22MM lbs. annual reduction has been achieved. S-metolachlor is used by >135,000 US farmers annually. It reduces environmental and human exposure risks throughout its life cycle—including manufacture, distribution, application, and container disposal. It meets EPA's goals to reduce pesticide use and to substitute reduced risk pesticides for higher risk pesticides. Publications document commercialization of the chiral catalyst system for sterospecific production of high volume chiral products.

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

Green Chemistry objectives were emphasized in the Discovery and Development of the commercial route to sildenafil citrate, the active ingredient in the important medicine Viagra™. The commercial synthesis generates only 9 Kg of organic waste per kilogram sildenafil, several fold less than is typical for a pharmaceutical product. The key breakthrough in achieving this exceptional result was the discovery of a new, convergent, synthetic route, which was designed with a clean cyclisation reaction as the final step hence eliminating purification operations. Subsequent careful chemical development and diligent solvent recovery optimized the environmental performance.

Achievements include a nine-fold yield increase from the pyrazole (1) to sildenafil citrate. The amount of organic and aqueous waste is reduced 15 and 5 fold eliminating 4000 tonnes and 3900 tonnes of organic and aqueous waste respectively. A tin chloride (toxic heavy metal) reduction was replaced by an environmentally benign catalytic hydrogenation reaction. Hydrogen peroxide (a worker safety issue) was eliminated. Three chemical steps were combined, using a single solvent that was recovered. In eight chemical steps there is no reaction that requires a work-up involving extraction, again leading to low organic waste. The technological achievements were implemented at the outset of commercial manufacture.

Enviromask—A Zero VOC Method to Aircraft Metal Forming
AC Products, a subsidiary of Quaker Chemical

Chemical milling is a process of forming metal. The primary metal used is aluminum. Milling is a fundamental step in the production of airplanes and other items that are composed of metal parts with precise specifications of weight and dimension. The most important material in the process is called maskant. Maskant is the coating applied to the metal part. It stops hot caustic or acid from contacting and dissolving the metal. After the milling process, it is hand-peeled to make a finished part.

Today’s available maskants are chiefly rubber type polymers dispersed in solvents such as xylene, toluene, and perchloroethylene. In order to be a viable product for milling, a maskant must completely stop all acid or caustic from passing through it, and be able to be peeled easily after the process is complete.

Our project entry, Enviromask, consists of 100% solids, solvent-free-polyurea technology. Similar technology exists today and is used in different industries, but we are not aware of any application where the thickness of film and consistency of performance properties such as peel strength and instant chemical resistance are so critical. Controlling such properties of a polyurea material makes our project a true chemical and mechanical breakthrough.

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

The U.S. Army Corps of Engineers Engineer Research and Development Center (U.S. Army ERDC) led a research team composed of Federal Government, academic, and private industry researchers to develop a greener approach to water treatment for boilers and cooling towers. The project objectives included the formulation and field evaluation of two green chemical formulations. U.S. Army ERDC teamed with the Garratt-Callahan Chemical Company; Trevino Mechanical, a small business mechanical sub-contactor; SurTech Corporation and the Illinois State Water Survey for verification of field data. The water treatment formulae were applied and their performance monitored at three military installations.

Enzymes as an Alternative to Toxic Materials for Treatment of Slime Deposits in the Paper Industry
Buckman Laboratories International, Inc.

The accumulation of biofilm is a serious operational problem in papermaking systems, and can cause fouling in many other industrial systems as well. In such systems where large amounts of water are used, microorganisms attach to surfaces and form a “biofilm,” composed of carbohydrates and protein. This can foul machinery, 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, which involve significant risks in handling and transportation.

This nominated technology utilizes stabilized enzymes to clean surfaces, removing the deposit, in many cases eliminating the use of 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 active ingredients are specific protease enzymes.

We will show how this innovation provides products that are significantly less toxic to our environment than the chemicals it can replace. In addition, this new technology is much safer to handle, to manufacture, transport, and use than the conventional chemistries.

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

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

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

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

Kemiko and Sta-Crete Low VOC Architectural Coatings
Epmar Corporation, a subsidiary of Quaker Chemical Corporation

All of Epmar’s Kemiko and Sta-Crete low VOC architectural coating products referred to in this paper are water-based and significantly reduce the emission of ozone-producing VOCs. These products promote the EPA’s goal of reducing negative health effects from commonly used products, especially in cases such as architectural coatings to which humans will have long-term exposure.

In order to maintain the low VOC emission characteristics of the Kemiko and Sta-Crete product lines, Epmar and their raw material suppliers maintain strict manufacturing and quality specifications of the raw materials and finished product.

Epmar’s formulating technology minimizes the use of VOC-emitting materials. These unique products utilize commercially available raw materials and are commercially competitive in terms of performance, handling and pricing.

Pure Performance ™
“Zero” VOC Latex Coating
PPG Architectural Finishes, Inc.

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

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, reduce toxicity, degrade rapidly and innocuously, reduce accident risk, and be made from renewable sources. A chlorine alternative is needed for microbial control. 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: It is much less toxic and generates 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. It is made from completely renewable resources. Its use has been shown to reduce adsorbable organic halide generation in real industrial water systems by more than 60%. These technical attributes result in valuable benefits: Less environmental toxicity, less chemical waste, and lower accident potential. One hundred fifty million pounds of chlorine or its equivalent have been replaced with 38 million fewer pounds of STABREX in 5,000 water systems. Five hundred billion gallons of industrial water have been successfully treated. This innovation is original and unique: It is the first biomimetic industrial antimicrobial, having been designed to imitate compounds naturally produced in mammalian immune systems.

Xerographic Dry Ink Resin Manufacturing Hazard & Emission Reduction Using Design for the Environment Xerox Corporation

The process and material change described entails replacement of a hazardous, pollution generating solid free radical initiator, benzoyl peroxide, with a less hazardous liquid initiator, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, that generates far less pollution, to produce a low melt temperature cross-linked polyester resin for use in xerographic dry-ink formulations. Specifically, Xerox developed a proprietary process for cross-linking an unsaturated polyester resin by mixing a peroxide initiator with the polymer and then passing the polymer through a high shear melt mixer. The process is termed “reactive extrusion” because the reaction occurs during the melt mix step. Desiccation of the benzoyl peroxide occurred in vessels and the nuisance dust collection system. Impact testing showed that the residual left in the equipment was shock sensitive, with potential for explosive decomposition. Benzoyl peroxide was also inefficient in the cross-linking of the polyester and large quantities of benzoic acid were generated as the major decomposition product, necessitating manual steam cleaning of the sublimed benzoic acid from piping and generating aqueous hazardous waste. The alternate liquid initiator eliminated the risk of explosion and generated only neat tertiary butyl alcohol as a by-product.