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The Presidential Green Chemistry Challenge Awards Program

Summary of 2000 Award Entries and Recipients

GREEN CHEMISTRY CHALLENGE

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The Presidential Green Chemistry Challenge Awards Program

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Summary of 2000 Award Entries and Recipients

The Pollution Prevention Act of 1990 established a national policy to prevent or reduce pollution at its source whenever feasible. Green chemistry, the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations, all through voluntary partnership programs.

The Presidential Green Chemistry Challenge promotes pollution prevention and industrial ecology through an EPA (U.S. Environmental Protection Agency) Design for the Environment partnership with the chemistry community. Through high level recognition and support, the Presidential Green Chemistry Challenge promotes innovative developments in and uses of green chemistry for pollution prevention. The technologies recognized and supported by the Presidential Green Chemistry Challenge directly reduce risks to human health and the environment by reducing the hazards associated with the design, manufacture, and use of chemicals.

Entries received for the 2000 Presidential Green Chemistry Challenge Awards were judged by an independent panel of technical experts convened by the American Chemical Society. The criteria for judging included health and environmental benefits, scientific innovation, and industrial applicability. Five projects that best met the scope of the program and the criteria for judging were selected for 2000 awards and were nationally recognized on June 26, 2000.

This document provides summaries of the entries received for the 2000 Presidential Green Chemistry Challenge Awards. The approaches described in these summaries illustrate how numerous individuals, groups, and organizations from academia, small businesses, industry, and government are demonstrating a commitment to designing, developing, and implementing green chemical methodologies that are less hazardous to human health and the environment. The approaches described in these summaries also illustrate the technical and economic feasibility of implementing green chemical methodologies and are recognized for their beneficial scientific, economic, and environmental impacts.

Note: The summaries provided in this document were obtained from the entries received for the 2000 Presidential Green Chemistry Challenge Awards. They were edited for space, stylistic consistency, and clarity, but they were not written or officially endorsed by EPA. In many cases, these summaries represent only a fraction of the information provided in the entries received and, as such, are intended to highlight the nominated projects, not describe them fully. These summaries were not used in the judging process; judging was conducted on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.

Academic Award

Enzymes in Large-Scale Organic Synthesis

Professor Chi-Huey Wong
The Scripps Research Institute

Organic synthesis has been one of the most successful of scientific disciplines and has contributed significantly to the development of the pharmaceutical and chemical industries. New synthetic reagents, catalysts, and processes have made possible the synthesis of molecules with varying degrees of complexity. The types of problems at which non-biological organic synthesis has excelled, ranging from stoichiometric reactions to catalysis with acids, bases, and metals, will continue to be very important. New synthetic and catalytic methods are, however, necessary to deal with the new classes of compounds that are becoming the key targets of molecular research and development.

Compounds with polyfunctional groups, such as carbohydrates and related structures, pose particular challenges to non-biological synthetic methods, but are natural targets for biological methods. In addition, biological methods are necessary to deal with increasing constraints imposed by environmental concerns. Transition metals, heavy elements, and toxic organic solvents are often used in non-biological processes. When these materials are used with great care and efficiency, they may still be environmentally acceptable, but their handling and disposal pose problems. The ability to use recombinant and engineered enzymes to carry out environmentally acceptable synthetic transformations that are otherwise impossible or impractical offers one of the best opportunities now available to chemistry and the pharmaceutical industry.

Professor Chi-Huey Wong at the Scripps Research Institute has pioneered work on the development of effective enzymes and the design of novel substrates and processes for large-scale organic synthesis. The methods and strategies that Professor Wong has developed have made possible synthetic transformations that are otherwise impossible or impractical, especially in areas vitally important in biology and medicine, and have pointed the way toward new green methodologies for use in large-scale chemistry. A recent study by the Institute for Scientific Information ranked Professor Wong in the top 15 of the most-cited chemists in the world for the period 1994 to 1996. According to this study, he is also the most-cited chemist worldwide working in the area of enzymes.

Some of the strategies and methods developed by Professor Wong are breakthrough achievements that laid the framework for much of the current use of enzymes as catalysts in large-scale organic synthesis. The techniques and reagents developed in this body of pioneering work are used widely today for research and development. The scope of contributions ranges from relatively simple enzymatic processes (e.g. chiral resolutions and stereoselective syntheses) to complex, multi-step enzymatic reactions (e.g. oligosaccharide synthesis). For example, the irreversible enzymatic transesterification reaction using enol esters in environmentally acceptable organic solvents invented by Wong represents the most widely used method for enantioselective transformation of alcohols in pharmaceutical development. The multi-enzyme system based on genetically engineered glycosyltransferases coupled with in situ regeneration of sugar nucleotides developed by Professor Wong has revolutionized the field of carbohydrate chemistry and enabled the large-scale synthesis of complex oligosaccharides for clinical evaluation. All of these new enzymatic reactions are carried out in environmentally acceptable solvents, under mild reaction conditions, at ambient temperature, and with minimum protection of functional groups. The work of Professor Wong represents a new field of green chemistry suitable for large-scale synthesis that is impossible or impractical to achieve by non-enzymatic means.

Small Business Award

RevTech, Inc.

Envirogluv™: A Technology for Decorating Glass and Ceramicware with Radiation Curable Environmentally Compliant Inks

Billions of products are sold in glass containers in the United States every year. Most, if not all, of these glass containers are labeled in some fashion. Typically, decorative indicia are applied to glass using paper labels, decals, or a process known as applied ceramic labeling (ACL). ACL involves first printing the glass with an ink composition that contains various heavy metals such as lead, cadmium, and chromium, then bonding the ink to the glass by baking in an oven known as a lehr at temperatures of 1,000 °F or more for several hours.

All of these processes have disadvantages. Paper labels are inexpensive but can be easily removed if the container is exposed to water or abrasion. In addition, paper labels do not provide the aesthetics desired by decorators who want rich, expensive-looking containers. Decals are expensive and difficult to apply at the high line speeds that are required in the decoration of most commercial containers. More importantly, decals are made from materials that are not biodegradable, which causes serious problems in the recycling of glass containers that are decorated by this method. The use and disposal of the heavy metals required in ACL presents serious environmental concerns. Moreover, the high-temperature lehr ovens required in ACL decorating utilize substantial amounts of energy and raise safety issues with respect to workers and plant facilities that use this equipment. The inks used in ACL decorating also tend to contain high levels of volatile organic compounds (VOCs) that can lead to undesirable emissions.

Clearly there has been a need in the glass decorating industry for a decorated glass container that is aesthetically pleasing and durable and can be obtained in a cost-effective, environmentally friendly, and energy-efficient manner. Envirogluv™ technology fills that need. Envirogluv™ is a glass decorating technology that directly silk-screens radiation-curable inks onto glass, then cures the ink almost instantly by exposure to ultraviolet light. The result is a crisp, clean label that is environmentally sound, with a unit cost that is about half of that achieved with traditional labeling.

Envirogluv™ technology offers many human health and environmental benefits. The ink compositions used in the Envirogluv™ process do not contain any heavy metals and contain little to no VOCs. All pigments used are biodegradable. The Envirogluv™ inks are cured directly on the glass by exposure to UV radiation, eliminating the high-temperature baking in a lehr oven associated with the ACL process. This provides additional safety and environmental benefits, such as reduced energy consumption and reduced chance of worker injury. In addition, there is less raw materials use and the process does not generate any waste ink. Furthermore, Envirogluv™ decorated glass containers eliminate the need for extra packaging and are completely recyclable. Applications suitable for the Envirogluv™ process include tableware, cosmetics containers, and plate glass.

Alternative Synthetic Pathways Award

An Efficient Process for the Production of Cytovene®, A Potent Antiviral Agent

Roche Colorado Corporation

The design, development, and implementation of environmentally friendly processes for the large-scale production of pharmaceutical products is one of the most technically challenging aspects of business operations in the pharmaceutical industry. Roche Colorado Corporation (RCC), in establishing management and operational systems for the continuous improvement of environmental quality in its business activities, has, in essence, adopted the Presidential Green Chemistry Challenge Program's basic principles of green chemistry: the development of environmentally friendly processes for the manufacture of pharmaceutical products. In particular, RCC has successfully applied these principles to the manufacture of Cytovene®, a potent antiviral agent used in the treatment of cytomegalovirus (CMV) retinitis infections in immunocompromised patients, including patients with AIDS, and also used for the prevention of CMV disease in transplant recipients at risk for CMV.

In the early 1990s, Roche Colorado Corporation developed the first commercially viable process for the production of Cytovene®. By 1993, chemists at RCC's Boulder Technology Center designed a new and expedient process for the production of Cytovene®, which at the time had an estimated commercial demand of approximately 50 metric tons per year. Leveraging the basic principles of green chemistry and molecular conservation into the design process, significant improvements were demonstrated in the second-generation Guanine Triester (GTE) Process. Compared to the first-generation commercial manufacturing process, the GTE Process reduced the number of chemical reagents and intermediates from 22 to 11, eliminated the (only) two hazardous solid waste streams, eliminated 11 different chemicals from the hazardous liquid waste streams, and, efficiently recycled and reused 4 of the 5 ingredients not incorporated into the final product. Inherent within the process improvements demonstrated was the complete elimination of the need for operating and monitoring 3 different potentially hazardous chemical reactions. Overall, the GTE Process provided an expedient method for the production of Cytovene®, demonstrating a procedure that provided an overall yield increase of more than 25% and a 100% increase in production throughput.

In summary, the new GTE Process for the commercial production of Cytovene® clearly demonstrates the successful implementation of the general principles of green chemistry: the development of environmentally friendly syntheses, including the development of alternative syntheses utilizing nonhazardous and nontoxic feedstocks, reagents, and solvents; elimination of waste at the source (liquid waste: 1.12 million kg/year and solid waste: 25,300 kg/year); and, elimination of the production of toxic wastes and byproducts. The process establishes new and innovative technology for a general and efficient method for the preparation of Cytovene® and other potent antiviral agents and is registered with the FDA as the current manufacturing process for the world's supply of Cytovene®.

Alternative Solvents/Reaction Conditions Award

Bayer Corporation and Bayer AG

Two-Component Waterborne Polyurethane Coatings

Two-component (2K) waterborne polyurethane coatings are an outstanding example of the use of alternative reaction conditions for green chemistry. This technology is achieved by replacing most or all of the volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) used in conventional 2K solventborne polyurethane coatings with water as the carrier, without significant reduction in performance of the resulting coatings. This may seem an obvious substitution, but due to the particular chemistry of the reactive components of polyurethane, it is not that straightforward.

Two-component solventborne polyurethane coatings have long been considered in many application areas to be the benchmark for high-performance coatings systems. The attributes that make these systems so attractive are fast cure under ambient or bake conditions, high-gloss and mirror-like finishes, hardness or flexibility as desired, chemical and solvent resistance, and excellent weathering. The traditional carrier, however, has been organic solvent that, upon cure, is freed to the atmosphere as VOC and HAP material. Use of high-solids systems and aqueous polyurethane dispersions ameliorate this problem, but do not go far enough.

An obvious solution to the deficiencies of 2K solventborne polyurethanes and aqueous polyurethane dispersions is a reactive 2K polyurethane system with water as the carrier. In order to bring 2K waterborne polyurethane coatings to the U.S. market, new waterborne and water-reducible resins had to be developed. To overcome some application difficulties, new mixing/spraying equipment was also developed. For the technology to be commercially viable, an undesired reaction of a polyisocyanate crosslinker with water had to be addressed, as well as problems with the chemical and film appearance resulting from this side reaction. The work done on the 2K waterborne polyurethanes over the past several years has resulted in a technology that will provide several health and environmental benefits. VOCs will be reduced by 50-90% and HAPs by 50-99%. The amount of chemical byproducts evolved from films in interior applications will also be reduced, and rugged interior coatings with no solvent smell will now be available.

Today, 2K waterborne polyurethane is being applied on industrial lines where good properties and fast cure rates are required for such varied products as metal containers and shelving, sporting equipment, metal- and fiberglass-reinforced utility poles, agricultural equipment, and paper products. In flooring coatings applications where the market driving force is elimination of solvent odor, 2K waterborne polyurethane floor coatings provide a quick dry, high abrasion resistance, and lack of solvent smell ($\leq$0.1 lb/gal organic solvent). In wood applications, 2K waterborne polyurethane coatings meet the high-performance wood finishes requirements for kitchen cabinet, office, and laboratory furniture manufacturers while releasing minimal organic solvents in the workplace or to the atmosphere. In the United States, the greatest market acceptance of 2K waterborne polyurethane is in the area of special-effect coatings in automotive applications. These coatings provide the soft, luxurious look and feel of leather to hard plastic interior automobile surfaces, such as instrument panels and air bag covers. Finally, in military applications, 2K waterborne polyurethane coatings are being selected because they meet the demanding military performance criteria that include flat coatings with camouflage requirements, corrosion protection, chemical and chemical agent protection, flexibility, and exterior durability, along with VOC reductions of approximately 50%.

Designing Safer Chemicals Award

Sentricon Termite Colony Elimination System, A New Paradigm for Termite Control*

Dow AgroSciences

The annual cost of termite treatments to the U.S. consumer is about $1.5 billion, and each year as many as 1.5 million homeowners will experience a termite problem and seek a control option. From the 1940s until 1995, the nearly universal treatment approach for subterranean termite control involved the placement of large volumes of insecticide dilutions into the soil surrounding a structure to create a chemical barrier through which termites could not penetrate. Problems with this approach include difficulty in establishing an uninterrupted barrier in the vast array of soil and structural conditions, use of large volumes of insecticide dilution, potential hazards associated with accidental misapplications, spills and off-target applications, and worker exposure. These inherent problems associated with the use of chemical barrier approaches for subterranean termite control created a need for a better method. The search for a baiting alternative was the focus of a research program established by Dr. Nan-Yao Su of the University of Florida who, in the 1980s, had identified the characteristics needed for a successful termite bait toxicant.

The unique properties of hexaflumuron made it an excellent choice for use in controlling subterranean termite colonies. The Sentricon* Termite Colony Elimination System, developed by Dow AgroSciences in collaboration with Dr. Su, was launched commercially in 1995 after receiving EPA registration as a reduced risk pesticide. Sentricon* represents truly novel technology, employing an Integrated Pest Management approach using monitoring and targeted delivery of a highly specific bait. Because it eliminates termite colonies threatening structures using a targeted approach, Sentricon* delivers unmatched technical performance, environmental compatibility, and reduced human risk. The properties of hexaflumuron as a termite control agent are attractive from an environmental and human risk perspective, but more importantly, the potential for adverse affects is dramatically reduced because it is present only in very small quantities in stations with termite activity. The comparisons to barrier methods show significant reduction in the use of hazardous materials and substantial reduction in potential impacts on human health and the environment.

The discovery of hexaflumuron's activity with its unique fit and applicability for use as a termite bait was a key milestone for the structural pest control industry and Dow AgroSciences. The development and commercial launch of Sentricon* changed the paradigm for protecting structures from damage caused by subterranean termites. The development of novel research methodologies, new delivery systems, and the establishment of an approach that integrates monitoring and baiting typify the innovation that has been a hallmark of the project. More than 300,000 structures across the United States are now being safeguarded through application of this revolutionary technology, and adoption is growing rapidly.

* Trademark of Dow AgroSciences LLC

2000 Presidential Green Chemistry Challenge—Entries From Academia

Affordable Composites from Renewable Sources (ACRES)

Professor Richard P. Wool, Center for Composite Materials, University of Delaware

In the past two years, the ACRES group has examined several hundred chemical pathways to convert soy oil to high-performance plastics, adhesives, and composites and has developed affordable soy resins that are compatible with high-volume composite manufacturing processes. New soy-based plastics and adhesive materials are being evaluated and tested by end-users and converters for high-volume applications in agricultural equipment (tractors and farming machines) and in the automotive (car and truck parts), civil (bridges and highway components), marine (pipes and offshore equipment), rail infrastructure (carriages, box cars, and grain hoppers), and construction (formaldehyde-free particle board, ceilings, engineered lumber) industries. Recent advances in genetic engineering, natural fiber development, and composite science offer significant opportunities for new, improved materials from renewable resources with enhanced support for global sustainability.

Benign Syntheses in Nearcritical Water

Professor Charles A. Eckert, School of Chemical Engineering, and Professor Charles L. Liotta, School of Chemistry and Biochemistry, Georgia Institute of Technology

"Nearcritical water" (NCW) is water at elevated temperatures, typically at 250-300 °C, but still well below the critical point. It is, of course, environmentally benign and far safer for human health than typical organic solvents, but it also offers exceptional performance characteristics. It offers wide-ranging advantages, ranging from human health to pollution prevention and waste minimization. As water is heated to near its critical region, the fluid becomes similar to acetone in density and dielectric constant and, as such, dissolves both salts and organic chemicals, offering the possibility to run aqueous/organic reactions homogeneously. Also, as the temperature is increased, the dissociation constant for water, K_W, goes up by several orders of magnitude, so that the water itself is both a natural base and acid and can act to catalyze reactions. Since no base or acid catalysts need to be added, this avoids subsequent neutralization and salt disposal.

Professors Eckert and Liotta at Georgia Tech have formulated an outstanding research partnership. By a synergistic combination of chemistry and engineering, they explore interdisciplinary areas of science and technology. The Eckert-Liotta Research Group has carried out extensive studies over the past four years to demonstrate the novel chemistry available in NCW and to show the wide span of synthetic applications and the economic and environmental benefits of using this solvent, heretofore almost neglected. Working with industrial partners, they have demonstrated the value of NCW processes. This team has exploited the properties of nearcritical water to demonstrate its potential for benign and novel synthetic processes. Examples include Friedel-Crafts alkylations and acylations, aldol condensations, Dieckmann condensations, Knoevenagel condensations, and ester and ether hydrolyses.

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

Catalysts for the Copolymerization of Carbon Dioxide and Cyclic Ethers

Generating monomers and polymers from CO_2 is a task that green plants accomplish daily on a global scale, yet is one that remains difficult for polymer scientists. Nature has developed an efficient system for extracting an abundant raw material (CO_2) from dilute solution and generating a variety of monomers and polymers from it. Professor Beckman's group has created a series of sterically hindered aluminum catalysts (SHACs) that efficiently copolymerize carbon dioxide and cyclic ethers to form ether-carbonate copolymers. Unlike previously reported catalysts for CO_2/oxirane copolymerization, SHACs allow complete conversion at 10-50 °C in only hours, permit incorporation of a variety of cyclic ethers (including ethylene and propylene oxides), generate copolymers with narrow molecular weight distribution, and permit generation of products where the percentage carbonate can range from zero to a completely alternating copolymer. The Beckman group has employed simple alcohols as chain transfer agents during copolymerization; the molecular weight of the copolymer dropped as predicted, yet the polymerization proceeded to 100% yield in the same time as that without the transfer agent. Effective chain transfer in a living polymerization is crucial, in that if one is to use the catalyst to generate low molecular weight polymers, it is important that one catalyst fragment generate more than one polymer chain, minimizing the amount of catalyst required. Further, dry-box procedures are not needed to employ SHACs for copolymerization. This is significant from a practical perspective, as commercial oxiranes are usually contaminated with up to 0.1% water, and exhaustive drying is not feasible.

These catalysts allow the use of a renewable resource, CO_2, in the generation of aliphatic polycarbonates, replacing phosgene. Further, the copolymers themselves contribute to green chemistry through their uses. The Beckman group observed that these ether-carbonate copolymers are more "CO_2-philic" than fluorinated polymers and, hence, can be used as low-cost CO_2-philes in processes employing CO_2 as a solvent and as additives in all CO_2-blown foam. Finally, ether-carbonate copolymers will hydrolyze enzymatically and, hence, can be used in degradable polymers and soaps.

Professor Chao-Jun Li, Department of Chemistry, Tulane University

Chemical and Material Syntheses by Using Metal-Mediated and Catalyzed Reactions in Water

To synchronize the advancement of science and technology with the advancement of green chemistry, rather than sacrificing one or the other, is the key feature of the research carried out by Tulane. A range of technologies has been developed that uses water as solvent for chemical, pharmaceutical, and material syntheses. The technologies developed not only offer many benefits for human health and the environment, but also the use of water as solvent plays an essential role in the success of this research. The use of large quantities of organic solvents for industrial scale operations eventually leads to environmental problems. In fact, volatile organic compounds are the principle pollutants of all organic compounds. On the other hand, water is nontoxic, nonexplosive, nonflammable, as well as being the basis and bearer of life in nature.

Numerous biochemical reactions affecting the living system have inevitably occurred in aqueous medium. On the other hand, most organic reactions and syntheses have been carried out in organic solvents. At Tulane, Professor Chao-Jun Li has developed various synthetic methodologies by using water as solvent. By using these methodologies, he has synthesized biologically important natural products, novel electronic and optical materials, and nano-car-

bon materials. In most cases, the studies have the dual advantages of being aqueous and being "atom economical". The use of water as the reaction solvent makes these reactions environmentally friendly and is essential to the success of this research.

ChemInformatics: Faster, Better, Cheaper, Greener Chemical Analyses

Professor Albert Robbat, Jr., Chemistry Department, Tufts University

A total of 10 million environmental samples were analyzed last year by 900 independent testing labs, manufacturing companies, and government and university-owned laboratories. Although no estimates exist for samples analyzed in support of drug discovery programs, growth in the biomedical and life science markets is expected to dramatically increase the number of samples analyzed by liquid chromatography/mass spectrometry (LC/MS). Analyses made in support of state and federal regulatory programs and for research, development, manufacturing, and quality control in these two markets alone use more than two million gallons of solvent annually. The spent waste solvent must be discarded as hazardous material at a cost of $51 million.

The primary objective of the proposed technology is to dramatically reduce solvent consumption at the source, namely, during the sample preparation process and in the analysis itself. The data analysis software, called Ion Fingerprint Detection™ (IFD), makes ultrafast GC/MS and LC/MS possible. The patented peak deconvolution algorithms identify and quantify target compounds in the presence of other target compounds and highly contaminated matrices without extensive sample cleanup. IFD should eliminate approximately 90% of the solvent needed to prepare and analyze samples by GC/MS and as much as 50% for LC/MS.

The proposed technology, Ion Fingerprint Detection™ (IFD) software, should reduce solvent consumption in the two fields dealt with by approximately two million gallons annually and save $50 million in hazardous waste disposal costs. If forensic, petrochemical, drugs of abuse, quality control, and other routine types of analyses are included, solvent consumption and cost savings may be ten times the estimated numbers. Toward this end, Professor Robbat has shown that IFD, when combined with large volume gas chromatography (GC) inlets, provides quantitative analysis of EPA pollutants in minutes. The data produced have been verified by state and federal regulators and used to determine contaminant risk to ground water and to delineate the extent of contamination at twenty-five Superfund sites. The proposed technology increases measurement precision, accuracy, and sensitivity, and reduces the per-sample analysis costs.

Environmentally Benign Lithography for Semiconductor Manufacturing

Professor Karen K. Gleason, Department of Chemical Engineering, Massachusetts Institute of Technology, and Professor Christopher K. Ober, Materials Science and Engineering, Cornell University

Current lithographic processes employed by the microelectronics industry have significant environmental, safety, and health (ESH) impacts. For example, many microelectronics foundries (fabs) require thousands of gallons of water and solvents for chip production, yet are often located in arid climates. Both the application and development steps of the sacrificial resist layer generate large volumes of waste solutions. In the nominated work, solventless (dry) application of resist is accomplished by chemical vapor deposition (CVD), an alternative method to spin-coating films from solution. In an equally important part of this process, supercritical fluids (SCF), particularly SCF CO_2, are used as an alternative to conventional solvents as the resist development medium. If the functionality of the resist and low dielectric constant thin films are combined, the dielectric layer (an important component in many

microelectronic devices) may be directly patterned. This would dramatically simplify microelectronics fabrication by eliminating steps associated with application, patterning, and stripping of the sacrificial resist layer.

Both 157-nm light and e-beam irradiation were investigated as a means to afford differential solubility of the exposed region to supercritical CO_2. Both of these irradiation techniques have sufficient resolution to achieve the nanoscale patterning desired for future generations of integrated circuits. The micron-scale images were fully developed using SCF CO_2. This result represents the first time that fluorocarbon CVD films have been directly patterned on the micron scale. This is a proof of concept that low dielectric constant films can be directly patterned without the use of resist or conventional solvents, affording the opportunity to greatly reduce processing complexity and waste relative to conventional lithography.

Dr. Nancy W. Y. Ho, Laboratory of Renewable Resources Engineering, Purdue University

Genetic Engineering of Saccharomyces Yeasts for Effective Production of Ethanol and Other Green Chemicals from Renewable Biomass

Ethanol is an effective, environmentally friendly, non-fossil transportation biofuel that produces far less pollutants than gasoline. Furthermore, ethanol can be produced from plentiful, domestically available, renewable cellulosic biomass. This reduces our nation's dependency on imported oil, protects our energy security, and reduces our trade deficit. Furthermore, cellulosic biomass is renewable, available at low cost, and extant in great abundance all over the world, especially in the United States. Cellulosic biomass is, therefore, an attractive feedstock for the production of ethanol-fuel and numerous other industrial products by fermentation. Although ethanol has been produced by the fermentation of glucose-based feedstocks with *Saccharomyces* yeasts since the pre-industrial age, the conversion of cellulosic biomass to ethanol presented a major challenge. This is because cellulosic biomass contains two major sugars (glucose and xylose), and the *Saccharomyces* yeasts cannot ferment xylose to ethanol.

Dr. Ho has developed genetically engineered *Saccharomyces* yeasts that not only ferment xylose but can also effectively coferment glucose and xylose to ethanol. The genetically engineered yeasts produce at least 30% more ethanol from cellulosic biomass than the non-engineered parent yeasts. Dr. Ho's group has also recently found that their stable, metabolically engineered yeasts can repeatedly coferment glucose and xylose (using pure sugars or sugars from cellulosic biomass hydrolysates) to ethanol with high efficiencies for numerous cycles requiring very little nutrients. The technology outlined can easily be expanded to make yeast for the production of other important industrial products, such as lactic acid and citric acid, using glucose and xylose derived from cellulosic biomass as the feedstock.

Professor James M. Tanko, Department of Chemistry, Virginia Polytechnic Institute and State University

Green Chemistry through the Use of Supercritical Fluids and Free Radicals

Professor Tanko explored the use of supercritical carbon dioxide (SC-CO_2) as a replacement for many of the toxic and/or environmentally-threatening solvents used in chemical synthesis. This research demonstrated that SC-CO_2 is a viable, environmentally benign alternative to a variety of health or environmentally hazardous solvents and that there are also numerous advantages from a chemical perspective associated with the use of SC-CO_2 . The

research led to the development of a new, environmentally friendly chemical process for hydrocarbon functionalization and C-C bond formation.

SC-CO_2 is especially attractive because its critical parameters (temperature and pressure) are moderate, thereby permitting access to the supercritical state without a disproportionate expenditure of energy. The newly developed hydrocarbon functionalization accomplishes (in a single, high-yield step) a transformation which would normally require multiple steps and the use of toxic reagents or strong acids and bases. This reaction should scale up readily for large-scale (or industrial) applications.

In Vivo Synthesis of Lepidopteran Pheromone Precursors in Saccharomyces cereviseae: An Economical Process for the Production of Effective, Nontoxic, Environmentally Safe Insect Control Products

Dr. Douglas C. Knipple, Department of Entomology, Cornell University

Since the advent of DDT more than 50 years ago, broad spectrum neurotoxic insecticides have provided the principle means for the control of economically important insects in agriculture and public health programs. Whereas the use of synthetic insecticides initially resulted in spectacular increases in crop yields and the suppression of some important human and animal disease vectors, the development of insecticide resistance in insect pest populations and the environmental damage caused by insecticides were quickly recognized as serious drawbacks to their use. Today, the environmental and human health effects associated with the manufacture and use of insecticides for pest control are widely recognized, including their acute toxicity to nontarget organisms (including human applicators), their persistence in the biosphere, and major point-source pollution associated with their manufacture. Despite these effects, the scale of release of active ingredients in insecticide formulations into the global environment is enormous; in the United States alone it is more than 400 million kg/year.

Pheromones have been used on a worldwide basis for the control of insect pests for more than 15 years. Unlike conventional broad-spectrum insecticides, pheromones are nontoxic and highly specific for the species they are intended to control. Unfortunately, their effectiveness and selectivity depend upon high chemical and stereospecific purity, making them expensive to synthesize. The latter factor has limited their commercial success versus conventional insecticides. The major market for pheromone-based disruption products is in the United States and amounts to less than $50 million/year. In contrast, the worldwide insecticide market is greater than $6 billion/year. The goal of the work of Dr. Knipple at Cornell University is to develop a cheaper process for pheromone synthesis. Toward this goal, he has proposed to use genetic and molecular technology to clone and functionally express in vivo genes encoding desaturase enzymes present in the pheromone glands of adult female moths, which catalyze the formation of key unsaturated pheromone intermediates. Accomplishment of the technical objectives of this work will contribute materially and methodologically to development of an alternative biosynthetic process for commercial pheromone production. Achievement of the latter goal will significantly improve the economic competitiveness of existing pheromone products and could provide the basis for the expansion of this promising insect control technology into other markets.

Professor Joan F. Brennecke, Department of Chemical Engineering, University of Notre Dame, and Professor Eric J. Beckman, Department of Chemical and Petroleum Engineering, University of Pittsburgh

Ionic Liquid/CO_2 Biphasic Systems: New Media for Green Processing

Room-temperature ionic liquids are considered to be environmentally benign reaction media because they are low-viscosity liquids with no measurable vapor pressure. However, the lack of sustainable techniques for the removal of products from the room-temperature ionic liquids has limited their application. Professors Brennecke and Beckman have shown that environmentally benign carbon dioxide, which has been used extensively, both commercially and in research for the extraction of heavy organic solutes, can be used to extract nonvolatile organic compounds from room temperature ionic liquids (Blanchard et al., *Nature*, 1999, *399*, 28). They found that extraction of a material into carbon dioxide represents an attractive means for recovery of products from ionic liquids because (a) CO_2 dissolves in the ionic liquid to facilitate extraction, and (b) the ionic liquid does not dissolve appreciably in the CO_2, so the product can be recovered in pure form.

The research groups of Professors Brennecke and Beckman have shown that ionic liquids (using 1-butyl-3-methylimidazolium hexafluorophosphate as a prototype) and CO_2 exhibit extremely unusual, and very attractive, phase behavior. The solubility of CO_2 in ionic liquids is substantial, reaching mole fractions as high as 0.6 at just 8 MPa. Yet the two phases do not become completely miscible, so CO_2 can be used to extract compounds from the ionic liquids. Most importantly, the composition of the CO_2-rich phase is essentially pure CO_2; that is, there is no measurable cross-contamination of the CO_2 by the ionic liquid. Moreover, nonvolatile organic solutes (using naphthalene as a prototype) may be quantitatively extracted from the ionic liquid with CO_2, demonstrating the tremendous potential of ionic liquid/CO_2 biphasic systems as environmentally benign solvents for combined reaction and separation schemes.

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

Microwave-Induced Organic Reaction Enhancement (MORE) Chemistry for Eco-Friendly Syntheses

Microwave-assisted organic synthesis is an emerging technology of great potential. Dr. Ajay K. Bose at the Stevens Institute of Technology has contributed to this field through the development of nontraditional methods for using domestic microwave ovens for conducting a wide variety of organic reactions that are fast, safe, and friendly to the environment. Dr. Bose's group has shown that for a wide variety of reactions, microwave irradiation of reaction mixtures in open glass vessels can lead to faster reaction rates, fewer byproducts, and higher steric control. Because microwaves interact directly with molecules with dipoles, there is little need for a liquid medium to convey heat from the glass walls as in conventional heating. The key features of Microwave-Induced Organic Reaction Enhancement (MORE) chemistry techniques are the use of limited amounts of high-boiling solvents (or no solvents) — enough to form the reaction into a slurry at room temperature — and efficient control of microwave energy input to reach the desired reaction temperature without allowing the reaction mixture to come close to its boiling point. Such reactions can be completed on several-hundred-grams scale in a few minutes. Larger-scale synthesis should be possible by using commercial microwave equipment used by the food industry.

The elimination or reduction of the use of organic solvents, and the purer products formed, lead to reduced chemical waste (e.g., organic solvents for reactions and recrystallization and chromatographic material for purification). To demonstrate 'atom economy' (more product for all the chemicals used) and the versatility of MORE chemistry techniques, Dr. Bose's group has conducted multistep syntheses (including one-pot reactions for two or more

steps) of advanced intermediates for lactam antibiotics, amino sugars, alkaloids, and other biologically active compounds such as Taxol. They have also found that an efficient and eco-friendly nitration method can be accomplished by irradiating with microwaves, have observed mild acceleration of chemoenzymatic reactions under low-intensity microwave irradiation, and have devised a very eco-friendly oligopeptide synthesis that needs no conventional peptide bond forming agents. In brief, MORE chemistry techniques can offer very significant reductions in pollution at the source for small-scale as well as large-scale synthesis, and thus make the development and production of life-saving drugs more eco-friendly.

On-Line Detection of Subsurface Pollutants by Thermal Extraction Cone Penetrometry-Thermal Desorption Gas Chromatography/Mass Spectrometry

Professor Albert Robbat, Jr., Chemistry Department, Tufts University

The ability to rapidly assess or monitor the disposition of environmental contaminants at purported or existing hazardous waste sites is an essential component of the nation's environmental restoration program. Last year, 900 independent environmental testing labs analyzed five million samples in support of regulatory programs. Soil samples have to be collected from surface to ground water and then shipped off-site for analysis with waiting periods exceeding months. Soil samples, which represent approximately half the total number, are extracted with solvent then further separated using additional solvent to produce chemical-specific fractions. Each fraction is then analyzed by an appropriate method. The proposed technology is aimed at reducing or eliminating solvent usage during the sample collection and sample analysis process by collecting and detecting organic pollutants at depth without bringing the actual soil sample to the surface.

A thermal extraction cone penetrometry probe coupled to an ultrafast gas chromatography/mass spectrometer (TECP-TDGC/MS) has been developed to collect and analyze subsurface organic contaminants in situ. The TECP is capable of heating the soil to 300 °C, which is sufficient to collect volatile and semivolatile organics bound to soil, in the presence of soil-water content as high as 30%. Rather than using solvents to extract organics from soil, the TECP uses heat, then traps the hot vapor in a Peltier-cooled thermal desorption GC sample inlet for on-line analysis. In addition, the proposed technology reduces solvent usage when decontaminating sample collection probes and utensils used to homogenize samples. No other technology exists that is capable of thermally extracting organics as diverse as PCBs, explosives, or PAHs under these conditions. When combined with the ION Fingerprint Detection™ software, ultrafast TDGC/MS is capable of analyzing complex environmental samples in less than 5 minutes.

Overcoming the Recalcitrance of Cellulosic Biomass and Envisioning the Role of Biomass in a Sustainable World

Dr. Lee R. Lynd, Thayer School of Engineering, Dartmouth College

This project addresses technical and visionary issues associated with utilizing plant biomass, the only foreseeable sustainable source of organic fuels, chemicals, and materials. The project involves multiple topics related to consolidated processing, a widely applicable potential breakthrough in cellulose processing entailing production of cellulose enzymes, hydrolysis of biomass components, and fermentation of resulting soluble carbohydrates in a single process step. Additional project elements aimed at overcoming the recalcitrance of cellulose biomass encompass aspects of applied enzymology and microbiology, kinetics and reactor design for enzymatic hydrolysis of cellulose, pretreatment of biomass using compressed hot water, and conversion of paper sludge. Process design and analysis work support the con-

tention that advanced biomass-based processes have the potential to be cost-competitive with petroleum-based processes even at low oil prices. Accomplishments involving resource and policy analysis include analysis that identifies and explores the potential of biomass-based processes to have near-zero net CO_2 emissions, prioritizes among uses for the large but ultimately limited biomass resource, and seeks to reconcile the vast range of estimates for the magnitude of potential biomass availability for industrial uses.

Professor Craig L. Hill, Department of Chemistry, Emory University, and Dr. Ira A. Weinstock, U. S. Department of Agriculture Forest Service, Forest Products Laboratory

Pollution-Free Conversion of Trees to Paper Using Air in Place of Sulfur and Chlorine

A completely new approach to the delignification of wood or wood pulp — composites of cellulose and lignin — for paper manufacture has been developed. This chemistry achieves a goal no other technology developed thus far does, but one that is operable in nature — the selective delignification of wood or wood pulp using only the readily available and nontoxic agents air and water. Wood is comprised principally of two biopolymers: cellulose, which imparts strength to trees and paper, and lignin, which imparts color, texture, and mechanical properties to wood. The goal in the manufacture of high-quality paper is to remove the lignin with as little damage to the cellulose fibers as possible (high-quality paper is composed of lignin-free cellulose fibers).

Nature carries out this chemically and technically challenging multistep process by using a complex ensemble of selective metalloenzymes (glyoxal oxidase, ligninase, and Mn peroxidase). The pulp and paper industry, since its inception many decades ago, has yet to achieve what nature has. Chlorine compounds, not O_2, have been the dominant oxidants. While decades of optimization have led to highly selective delignification (minimally damaged cellulose), these man-made technologies produce waste streams that contain environmentally deleterious phenolic compounds as well as non-biodegradable chloroaromatics. In consequence, societal and legislative pressure in all developed countries is compelling pulp manufacturers to phase out chlorine. The most attractive alternative oxidants, hydrogen peroxide (H_2O_2) or ozone (O_3), are encumbered by inherent limitations. Hydrogen peroxide is simply not effective. Ozone processes, while potentially effective, fall far short of the selectivity required for general commercial use or of the selectivity seen in nature.

The new catalytic biomimetic approach uses versatile, nontoxic, and inexpensive inorganic clusters known as polyoxometalates (POM) in two steps. The first step involves selective reaction of lignocellulose (wood or pulp) with the oxidized POM leaving high quality cellulose fibers. As the POM is reversibly reduced, the lignin is oxidized and solubilized. In the second step, O_2 is added and the same POM catalyzes the complete conversion (mineralization) of the dissolved lignin fragments to CO_2 and H_2O. The two steps sum to the selective removal of lignin from wood, using only air and water, an ideal process that only nature has achieved to date. This biomimetic and catalytic technology eliminates the environmental problems associated with conventional chlorine-based processes while overcoming the limitations inherent in other chlorine-free pulp bleaching strategies. It is green in at least six ways, including the complete elimination of waste streams (a "closed process" is achieved). The high selectivity entails less consumption of the natural renewable resource, wood. It is energy-efficient and, as current analyses indicate, cost-effective.

Pollution Prevention through Simultaneous Reduction of Emissions and Commercial Utilization of Energy Related Waste Streams

Dr. M. Mercedes Maroto-Valer, The Energy Institute, The Pennsylvania State University

The U.S. electric power industry relies heavily on the use of coal as its main energy source, where coal-fired units generate annually over 55% of the total electricity produced in the United States. However, the U.S. power utility industry faces environmental challenges due to emissions of pollutants such as NO_X and the associated increase in byproduct waste streams. The installation of low-NO_X burners has efficiently decreased NO_X emission levels by lowering the temperature of combustion, but this results in reduced combustion efficiency and an increase in the concentration of uncombusted coal in the fly ash. This increased concentration of unburned carbon restricts the use of fly ash in the cement industry; consequently, the carbon-rich ash is placed in holding ponds or landfilled.

Dr. Maroto-Valer has addressed this problem by combining the installation of low-NO_X burners in coal combustion furnaces with strategies that manage the associated increase of byproduct streams, mainly fly ash and unburned carbon. Two novel, cost-effective routes for the commercial utilization of unburned carbon present in fly ash have been established. In the first route, steam activation of the unburned carbon generates activated carbons suitable for water purification applications. In the second route, the unburned carbon serves as a superior replacement for petroleum coke in the manufacture of carbon artifacts used in applications ranging from brushes for electrical machines to anodes for aluminum smelting. This program offers a sustainable source of energy for the next century by simultaneously reducing emissions and byproduct waste streams.

Production of Hydrogen Peroxide Directly from Hydrogen and Oxygen in CO_2

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

Hydrogen peroxide is an environmentally benign oxidant that has replaced chlorinated reagents in paper processing, is used in drinking water treatment, and is increasingly suggested as a green oxidant in chemical processing. 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. Despite its "green" characteristics, H_2O_2 is not produced in a particularly green manner. The current method for production, the sequential hydrogenation and oxidation of an alkyl anthraquinone, has been in use for over 50 years, produces significant volumes of waste, and consumes sizeable quantities of energy during the purification and concentration of the product. Because H_2O_2 is produced in organic solvent, then recovered by stripping into water, the solvent contaminates the aqueous product, creating a situation that requires downstream remediation before the product can be sold. The rates of both the hydrogenation and oxidation steps of the synthesis are limited by transport between the gas and liquid phases, and by the low solubility of hydrogen and oxygen in liquids. Multiple phases present in the reactors also prevent strict control over anthraquinone residence time, leading to generation of a byproduct waste stream. There has been great interest over the past three decades 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.

Professor Beckman has synthesized a series of highly CO_2-soluble palladium catalysts and has subsequently generated H_2O_2 from O_2 and H_2 in a biphasic mixture of CO_2 and water. The use of CO_2 as a solvent permits the use of reasonable concentrations of H_2 and O_2 without danger of explosion, and homogeneous catalysis eliminates diffusional limitations to the

reaction. The H_2O_2 produced is rapidly stripped into water, minimizing the degradation of the product by the catalyst commonly observed in heterogeneous systems. This process configuration eliminates waste streams owing to anthraquinone degradation and the use of organic solvent and also eliminates the need for distillation, reducing energy requirements substantially. In summary, production of H_2O_2 directly from H_2 and O_2 in CO_2 reduces waste, eliminates the use of the organic solvent, and eliminates three energy-intensive units: the oxidation reactors, the stripping column, and the distillation train. This process will produce a cleaner product, while using less energy, at a significantly lower cost than the anthraquinone route.

Dr. Thomas Mitzel, Department of Chemistry, Trinity College

Stereoselective Synthesis of Epoxy Alkynes: Use of α–Chlorosulfides to Control Syn/Anti Selectivity in Indium Promoted C-C Bond Formation in an Aqueous Medium

In response to increasing demands for the chemical industry to implement more environmentally friendly practices, chemists have begun to probe the development of organic transformations in an aqueous medium. The use of water as a solvent in these transformations is attractive for a number of reasons: 1) water is the cheapest solvent on earth, making it economically favorable; 2) synthetic efficiency may be increased by eliminating the need for traditional protecting groups; 3) reaction conditions are simplified, because an inert atmosphere and anhydrous solvents are not needed; and 4) pollution caused by use and disposal of traditional organic solvents is eliminated. Indium metal has proven effective in promoting C-C bond formation in aqueous media, forming chelates that allow good stereocontrol in the formation of coupling products.

Professor Mitzel has employed indium in water to selectively synthesize epoxy alkynes from α-chlorosulfides. Because epoxyalkyne functional groups are prevalent in a variety of natural products, stereoselective syntheses of these molecules have potential industrial applications. Utilizing indium metal allows this reaction to be carried out in water, a benign solvent that is more readily recycled than traditional organic solvents, thereby decreasing organic emissions while increasing safety.

Professor Harold S. Freeman, Department of Textile Engineering Chemistry and Science, North Carolina State University

Synthetic Dyes Based on Toxicological Considerations

This nomination pertains to the design of nontoxic alternatives to currently used metal-complexed dyes containing metals designated as priority pollutants. Specifically, iron-complexed dyes were synthesized as substitutes for metal-complexed dyes currently used in situations requiring colorants possessing very high photostability and resistance to removal under wet conditions. The dyes investigated were iron (Fe) complexes of ligands and provided the foundation for a pollution prevention approach to environmental problems associated with the manufacture and use of organic dyes based on chromium (Cr) and cobalt (Co). As a starting point for this study, the Freeman group synthesized and evaluated Fe-complexed analogs of commercial azo and formazan dyes containing Cr and Co. Fe (II) sulfate was employed as the metallizing agent because it has exhibited low aquatic toxicity in studies.

This investigation led to the discovery of nontoxic alternatives to high-volume chromium-based commercial black dyes, without compromising the desirable photostability of the latter. In addition, red and blue 1:2 Fe-complexed dyes (1 iron atom per 2 dye molecules) were discovered, an achievement heretofore unreported and presumed unachievable. An

explanation for the dull colors that have traditionally characterized Fe-complexed dyes was also developed, providing a basis for further achievements in this area.

Tandem Enzymatic-Electrochemical Methods for Green Manufacturing: Efficient Synthesis of Pharmaceuticals from Halogenated Aromatic Waste

Professor Thomas Hudlicky, Department of Chemistry, University of Florida

The prevention of pollution at its source is addressed by the replacement of currently used methods of oxidation and reduction (i.e., all based on metal reagents) with enzymatic and electrochemical techniques (i.e., all performed in water, alcohols, or other environmentally accepted solvents). The combination of enzymatic transformations with electrochemistry, along with efficient designs, yields unprecedented brevity in the attainment of important pharmaceuticals from metabolites of the arene cis-diol type. 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 added economic benefits of strategic conversion that would not be available through outright incineration of such compounds. It must be emphasized that the enzymatic conversion of the toxic aromatic materials takes place in the very first step of the synthetic pathway and that all subsequent intermediates are harmless. The residual mass from enzymatic or electrochemical processes is judged 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 the illustration of the technology. Given that the length of a synthesis plays a direct role in the attendant accumulated waste mass for the process, it follows that short and efficient syntheses lead to lesser accumulation of waste and thus reduce pollution at the source.

The Use of Soluble Polymers to Recover Catalysts and to Control Catalytic Reactions

Professor David E. Bergbreiter, Department of Chemistry, Texas A&M University

New strategies for the use and recovery of homogeneous catalysts and for carrying out chemical processes are of increasing interest because of problems associated with the use of organic solvents and the costs associated with purification and the removal and disposal of byproducts. This nomination recognizes the work by Bergbreiter's group at Texas A&M, which uses polymeric ligands and new separation strategies to facilitate homogeneous catalysis. This technology uses the well-known properties of polymers to recover and separate catalysts and ligands for reuse. By employing relatively simple polymer chemistry, a wide variety of known homogeneous catalysts can be attached to such polymers without significant alteration of their reactivity or selectivity. Separation and recovery strategies that use solid/liquid separation of precipitate polymers or liquid/liquid separations of polymer solutions/product solutions have both been demonstrated. The utility of simple linear polymers in the formation of aqueous and fluorous phase soluble catalysts has also been demonstrated by this work. Finally, this technology has also demonstrated a unique approach to regulate and control reactions using soluble polymer-bound "smart" ligands that precipitate on heating.

2000 Presidential Green Chemistry Challenge—Entries From Small Business

Biodegradable Thermoplastic Material (Mater-Bi™)

BIOCORP, Inc.

Mater-Bi™ is a completely biodegradable and compostable resin that has the physical and mechanical properties of conventional plastics. Mater-Bi™ is designed to be used in the manufacture of a wide range of disposable products such as trash bags, shopping bags, food serviceware, and packagings. Mater-Bi™ is a product technology that offers enormous advantages for dealing with the problems of solid waste disposal. Disposal of conventional plastic products, which constitute the largest share of disposable products, has a significant negative impact on the environment. Typically, disposal products are landfilled and rapidly diminish landfill capacity. Being compostable, disposable products made of Mater-Bi™ are fully recyclable.

Biodegradable food serviceware, for example, presents a significant opportunity for reducing the volume of the solid waste stream. In 1994, nearly 39 billion pieces of disposable cutlery (knives, forks, and spoons) were used in the United States. More than 113 billion disposable cups and nearly 29 billion disposable plates were used. Biodegradable products are being developed for medical products, textiles, and other new and significant applications. Such products can be transformed into much needed composts and soil amendments for agricultural and horticultural use. Mater-Bi™ resin used for films and sheets is made of starch and a polymer, polycaprolactone. Biodegradation time is between 20 and 45 days in composting conditions. Mater-Bi™ resin used for dimensionally stable injection molded items is made from completely natural products, including cotton seeds and cornstarch. Biodegradation time is between 75 and 120 days in normal composting conditions.

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. 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 the product shows greater corrosion resistance than the cadmium compounds generally used. This formula change, MULTIPLATE N-2000, received two U.S. Patents.

Mechanical Coatings, a Madison Chemical customer, was able to reduce their usage of cadmium by 100 pounds per week using the MULTIPLATE N-2000 process. In addition to that reduction, Mechanical Coatings also eliminated one complete waste stream, and a second waste stream containing mainly zinc is now recyclable. Mechanical Coatings also completely eliminated its hazardous waste, saving at least $12,000 per year in disposal costs. MULTIPLATE N-2000 has also made compliance with local, state and federal environmental laws much easier.

CerOx Corporation

The CerOx Process: A Non-Thermal Alternative for Hazardous Waste Destruction

The release and subsequent presence of persistent, bioaccumulative, and toxic (PBT) materials in the environment have recently come to the forefront of the public consciousness. The adverse health effects of PBTs, such as dioxins, have been well documented and have led to the placement of very strict limits on the releases of these materials to the environment by industrial processes, particularly from waste disposal by incineration. The chemistry and physics of the thermal processes, particularly with incineration, are such that the production of dioxin-type materials is obligatory given the process conditions. Materials pass through the high temperature zone without being completely combusted and continue to "burn" at lower temperatures. It is here that the dioxin-type materials are synthesized.

The CerOx Process is a cerium-catalyzed chemical process for the destruction of organic hazardous materials under mild reaction conditions, atmospheric pressure, and temperatures less than 100 °C. The CerOx Technology is an alternative to incineration that does not produce the products of incomplete combustion that have plagued high temperature destruction methods. The process uses the high oxidizing power of Ce(IV) in a closed liquid solution to destroy the organic compounds. Upon reaction, the Ce(IV) is reduced to a nonreactive Ce(III) that, in turn, is recycled to the active Ce(IV) oxidation state via an electrochemical oxidation. The cerium ion is a true (electro)catalyst and is not consumed in the reaction.

Virtually all organic materials can be processed and destroyed by the CerOx Process, including PCBs, dioxins, pesticides, chlorocarbon wastes, and chemical weapons agents. The organic materials are converted to carbon dioxide and water; the other reaction products are chlorine from chlorocarbons, sulfate from organosulfur compounds, phosphate from organophosphates, and nitric acid from amines. Comparison of the process conditions and economics of the CerOx Process to standard incineration indicates that this new nonthermal technology is economically competitive with existing technologies and, in many cases, is more economical than the incinerator alternative.

ClearMate, Inc.

ClearMate

Process chemicals used in the electroplating industry are subject to a number of harmful contaminants that ultimately decrease the usable capacity of a process solution. Once a bath is no longer usable it must be waste-treated, usually in the form of an expensive batch dump. In particular, the clear chromate bath is most susceptible to harmful contaminants and its life can vary in length from one week to one month based on heavy to moderate use, respectively. The major contaminant of the clear chromate solution is iron, which is introduced to the system when raw metal parts are submerged during processing or dropped and left at the bottom of a chromate tank.

Clearmate developed a process for recovering a spent clear chromate solution and then developed an additive that prevented premature iron contamination in the first place. The ClearMate chemical additive is an innovative, yet simple, chemical combination that drastically extends the longevity and quality of the clear chromate conversion solution for the metal finishing industry. It can extend the lifetime of conventional clear chromate solutions by a factor of 12. The additive protects raw metals from the acidic nature of the chromate solution. On initial contact with raw metal substrates, iron begins to dissolve into solution as an ion. The additive contains highly charged cationic polyelectrolytes that surround and impede any attack on the substrate by the acidic chromate solution. Extending the bath life by a factor of 12 has the potential to reduce the 70 million gallons of clear chromate waste produced annually in the United States to 6 million gallons.

Crystal Simple Green®

Sunshine Makers, Inc.

Hydrocarbon and petroleum solvents are the current "workhorses" for industrial cleaning and degreasing. Current practice is to utilize solvent recovery systems to minimize solvent waste streams from such cleaning/degreasing operations. This process has four negative aspects with regard to human health and the environment: (a) solvent recovery requires consumption of energy; (b) air emission of solvent fugitives cannot be eliminated; (c) recovery of solvent from the solvent and dirt/grease mixture concentrates the dirt/grease into a potentially toxic sludge; and (d) spent solvent must eventually be handled as hazardous waste.

Crystal Simple Green®, through its unique formulation and mode of action, allows users to clean and degrease without using the hydrocarbon and petroleum-based solvents or solvent systems that are the backbone of current technology in this area. Crystal Simple Green® is approximately 85% water. Thus, use of Crystal Simple Green® in place of solvents in cleaning/degreasing reduces the demand for these solvents in this application. The total organics content of Crystal Simple Green® is only about 12%, thereby reducing the need for organic feedstocks and conserving valuable petrochemical resources.

The product utilizes proprietary technology to effectively clean/degrease substrates that are heavily loaded with industrial oils, greases and hydrogenated animal fats. Crystal Simple Green® contains only biodegradable, water-soluble ingredients, reduces air emissions due to its low VOC content, and eliminates the formation of concentrated cleaning/degreasing waste sludges and spent hazardous solvent waste. Crystal Simple Green® offers a safer and less toxic alternative to solvent cleaners/degreasers currently used in industry.

Development of a Practical Model and Process to Systematically Reduce the Environmental Impact of Chemicals Utilized by the Textile and Related Industries

Burlington Chemical Company, Inc.

It was discovered in the early 1980s that discharges from textile dyeing and finishing operations were adversely impacting publicly owned waste treatment facilities. The results of early toxicity reduction evaluations pinpointed toxic and poorly degraded textile chemicals and surfactants as culprits. It was decided that elimination of toxic agents prior to formulation was an important long-term objective to provide for a sustainable textile industry in the United States. To achieve products "Designed for the Environment", a means to inexpensively screen chemicals and raw materials and communicate results internally and externally to consumers and regulators was needed.

Burlington Chemical discovered that the results from three OECD tests (OECD 301D, 202, and 209) could be related in an expert computer system (AQUATOX®) to design textile chemicals with greatly reduced environmental impacts. This discovery led to the development of a waste/toxicity reduction program, Burco® Care, based on this information. Burco® Care has resulted in the production of low-impact wet processing chemicals. It spawned a system of comparing textile chemicals for environmental impact that can be utilized in purchasing decisions by textile manufacturers and has been found suitable by U.S. textile market leaders. Burco® Care is a giant leap away from simple regulatory compliance to the creation of a systems-based thinking approach to building value by reduction of risk and improvement of the environment. It is estimated that millions of dollars of waste treatment costs are saved annually by customers who are improving the chemistry of their processes utilizing this tool.

U.S. Polychemical Corporation

Dispersit™: A Waterbased Oil Dispersant for Oil Spills in Salt and Fresh Water

Oil spills are a well-documented environmental and economic catastrophe. They present a long-term threat to populations of marine life, birds, aquatic mammals, and plants. The economic loss due to spills can be similarly devastating. Clean up costs can be enormous, and the long-term costs of a major spill in a populated or resort area could be incalculable. Petroleum-based dispersants have proven more effective than booms and skimmers in cleaning up oil spills, but they pose health hazards and do not work in low salinity.

Dispersit™ is an effective and non-toxic oil spill dispersant that is a unique blend of water, surfactants, and a coupling cosolvent. The product combines oil-soluble and water-soluble surfactants with a cosolvent for coupling a mixture of the oil-soluble surfactant and oil spill with the water-soluble surfactant. Water is included in the combination to help advance the interaction between the surfactants and cosolvent and to reduce the viscosity of the dispersant to allow it to be pumped under pressure. Dispersit™ is more effective than petroleum-based dispersants, less toxic to marine life, safer to apply, and works well in fresh, brackish, and salt water.

H and H Associates, Inc.

DUAL-ICE®: A Non-Toxic, Non-Caustic Instant Cold Compress

Instant cold compresses have been employed by both industry and the general public for decades. Instant cold compresses employed for trauma or heat stress are mainly a combination of water and ammonium nitrate encased in a thin polyplastic bag. Ammonium nitrate is classified as a hazardous substance by the EPA and is recognized as potentially explosive and detrimental to the environment. In addition, the generically low-stress packaging applied by most commercial manufacturers of items employing this chemical places the consumer at unnecessary risk. In response to a need by the U.S. Marine Corps, which was prohibited from deploying current instant cold compresses for numerous factors, H and H Associates developed DUAL-ICE®, an environmentally safe alternative to ammonium nitrate cold packs.

Following proof-of-principal testing, H and H engineers deduced that a combination of ammonium chloride, urea, and water would act to provide the necessary endothermic reaction. The product is fully non-toxic, non-caustic, non-hazardous, and heavily packaged for rough handling. DUAL-ICE® demonstrates a high cooling potential, maintains a shelf life of at least one year, and is air- and ground-shippable. Furthermore, the postendothermic reaction chemical byproduct is such that, after the initial use as an instant cold compress, DUAL-ICE® is fully reusable as a refreezable cold pack that remains flexible and conforms to an injured appendage or area.

Environmental Technology and Education Center

High Energy Efficiency, Environmentally Friendly Refrigerants

For several decades chlorofluorocarbons (CFCs) were the most widely used refrigerant fluids because of their nonflammability, low toxicity, low cost, and reasonably high performance. Because CFCs have been implicated in stratospheric ozone depletion, their production worldwide was stopped at the end of 1995 under the provisions of the Montreal Protocol as amended in Copenhagen in 1992. The phaseout of CFCs and HCFCs and increasing concern about greenhouse gases create the urgent need for nontoxic, nonflammable, environmentally safe refrigerants with high capacity and energy efficiency.

Dr. Jonathan Nimitz and his co-inventor, Lance Lankford, have discovered and patented a family of improved refrigerants based on blends containing trifluoromethyl iodide (CF_3I). CF_3I has attractive physical properties, zero ozone depletion potential (ODP), low global warming potential (GWP), relatively low toxicity, and is a combustion inhibitor. CF_3I can be combined with high-capacity, energy-efficient, environmentally friendly, but flammable refrigerant compounds to obtain excellent refrigerant blends that remain nonflammable. The result is an energy-efficient, environmentally friendly, safe refrigerant.

The inventors and Dole Food Company have formed a new company, Ikon, Inc., to support testing and commercialization of the refrigerants. The first formulation developed, Ikon® A, has extremely low GWP and can be used in R-12 or R-134a systems. Ikon® A has been demonstrated for over 3 years in Dole Food Company refrigerated transports, with excellent results. Ikon® A was also tested in a new R-134a domestic refrigerator, with results of 19% higher energy efficiency and 15% greater volumetric cooling capacity versus R-134a. Ikon® B was developed as a less expensive version of Ikon® A; it has been tested and demonstrated in refrigerated transport units, a 5-ton water chiller (sponsored by NASA Kennedy Space Center), and a new R-134a domestic refrigerator (sponsored by EPA).

A 20% market penetration of Ikon® B by 2010 will result in a decrease in carbon dioxide emissions of approximately 4 million tons per year. There would also be annual reductions of approximately 12 thousand tons particulate, 16 thousand tons nitrogen oxides, and 24 thousand tons sulfur oxides. The installation cost for Ikon refrigerants will be repaid within 3 years in most applications. At 20% market penetration by 2010, $0.08 per kWhr and 15% lower energy use, estimated energy cost savings by 2010 are $400 million per year. The human health and environmental benefits of the Ikon refrigerants will be significant. Their use will result in improvements in human health, improvements in air and water quality, and reductions in skin cancer and ecological and crop damage from UV radiation.

The MICARE Liquid CO_2 Dry Cleaning Process

Micell Technologies

The commercial dry cleaning industry faces a tremendous burden of environmental liability due to reliance on chlorinated and organic solvents. Over 72 million pounds of perchloroethylene was sold to the industry in 1998. This material ultimately ends up in the environment or in consumer clothes, impacting the health of communities and consumers. No one has previously been able to integrate an environmentally friendly technology with an effective cleaning process that alleviates this burden to our personal and environmental health.

The application of CO_2 to the dry cleaning industry has been suggested since 1977. However, commercial realization of this goal has been hindered by two main factors: the unavailability of an appropriate process and high-pressure equipment and the inability of unmodified CO_2 to provide effective cleaning. Micell has overcome equipment barriers by designing a dry cleaning process and manufacturing equipment that use liquid CO_2 just below ambient temperature (~18-22 °C) and vapor pressure (~50 bar). As for the second factor, Micell has translated the fundamental discoveries of CO_2 surfactants to create detergent packages appropriate for use in liquid CO_2 at saturated vapor pressure. The end result is a system that cleans clothes effectively, substantially reduces garment damage due to linting from heat, substantially reduces dye and finish loss from aggressive organic solvents, and is friendly to the environment. The successful combination of these elements has led to the launch of the first national chain of dry cleaning stores to offer liquid CO_2 garment care to the consumer.

TechMatch, Inc.

N-Methylmorpholine-N-oxide (NMMO): A Novel, Nontoxic Solvent for Cellulose for Source Reduction in the Production of Textile Fibers

For decades, scientists had been searching for an environmentally friendly means of forming a cellulosic fiber. The standard procedure for producing cellulosic fibers had been the viscose process, invented in 1894. There were no neutral organic solvents for dissolving cellulose until 1965 when Dee Lynn Johnson, working in the laboratories of Eastman Kodak, discovered that N-methylmorpholine-N-oxide (NMMO) is a solvent for cellulose. In addition, he demonstrated that the cellulose solution can be filtered and the cellulose filaments regenerated by precipitation into water. Furthermore, the NMMO could be recovered by evaporating the water and reused. This new solvent has now been commercialized by Huntsman Petrochemical Corporation, and several fiber manufacturers have developed commercial processes for producing the fibers. Fibers made by use of NMMO are called lyocell fibers, meaning cellulose spun from solution. The previous viscose process produces rayon fibers, but it requires a chemical reaction between carbon disulfide and cellulose in the presence of a strong base to produce a xanthate complex. Carbon disulfide is highly flammable and toxic to humans as well as being a greenhouse gas. Further, to produce fibers, the xanthate must be regenerated by extrusion into an acid coagulating bath where it decomposes and produces polluting byproducts that are discharged into water.

KM Limited, Inc.

The PIX Module Software: Combining Life Cycle Assessment with Activity-Based Costing to Reduce Global Environmental Impact and Sustain Industrial Profitability

The LCAPIX module is the first commercially available software package that simultaneously allows the user to perform both Activity Based Costing and Life Cycle Assessment (LCA). By using an industrial engineering approach employing drivers and driver values, the model and relational database provide a unique combination of two strategies that complement and enhance the implementation of an Environmental Management Strategy (EMS). This approach has strong appeal to those involved in any manufacturing sector — the point source for more than 50% of "undesirable effluents" affecting our global climate.

The conventional approach to LCA studies has been the application of "simple" mass and energy balances to manufacturing facilities. This approach is useful in providing guides for cost reduction and large-scale beneficial changes, but it requires difficult definitions of system boundaries, time-consuming data collection, and limits final inventory calculations. In contrast, the LCAPIX module provides a stand-alone software application that can analyze processes on a product basis, determine environmental load centers, and allow for development of a comprehensive database. The software package is a multifunctional tool in that it provides for inexpensive, rapid, and simple, strategic or environmental LCA comparisons of any product, process, or service.

Polymers and Plastics from Lignin Biomass

Center for Forest Products Research, Inc.

The most easily available as well as renewable supply of carbon is biomass: the trees, shrubs, and foliage around us. Meeting society's needs from trees requires that new chemistry and technology be invented to convert plant mass into industrial supplies, consumer goods, and the drugs we use. Cellulose, the major component of wood plants, is already well-used to make paper and chemicals. Lignin, the other one-fifth to one-third of the plant, is often landfilled or burned as a byproduct at the rate of 20 million tons per year. This means that, on average, one quarter of every tree harvested is wasted. Through 15 years of research, the Center for Forest Products has developed methods to convert lignin and wood into the polymers, plastics, and engineering materials that society will need in the future.

The methods involve reacting lignin with a polymer building block in the presence of a salt and peroxide bleaching agent to generate a new graft copolymer. This simple and fairly general reaction allows a byproduct of the paper industry to be converted into water treatment chemicals for purifying water, dewatering agents for compacting sewage sludge, chemicals for insulation and furniture foams, biodegradable and consumer plastics, binders for wood-plastic composites, and reinforcing fillers for tire rubber. In addition, this modified lignin can replace up to 37 million tons of monomers such as acrylamide, styrene, vinyl chloride, and acrylomidomethylpropane, all of which are flammable, toxic, explosive, or carcinogenic. By developing a chemical method to alter lignin, future generations can obtain the supplies and materials they need while harvesting fewer trees, wasting less of each tree, and depending less on toxic and carcinogenic compounds.

Primer for Antifouling Paint

BAT Technologies, Inc.

This technology and material is a primer to be used in conjunction with the bottom paint (antifouling paint) that is found on the bottoms of all ocean-going boats. Every year, thousands of ocean-going boats receive a coating of antifouling paint that typically must be removed and reapplied annually. Current technology mandates that the paint be sanded off. The resultant powder is dangerous, as it can be blown into the water and inhaled by the people sanding the bottom of the boat. Copper oxide is commonly used as an antifoulant, but it is toxic to all forms of life, including humans. Every year, 1.5 million pounds of copper oxide paint dust are dumped into the ocean in the United States alone because of boat bottom sanding.

A method and material have been developed that allow antifouling paint to be removed quickly, in large sheets, without sanding. The primer uses a sophisticated wax/water emulsion. Once the water from the emulsion has evaporated, the antifouling paint is applied. The boat is used, as usual. When the boat is to be hauled and the antifouling paint is to be reapplied, the old antifouling paint is removed with hot water at a temperature just above the melting point of the wax. The spent antifouling paint is easily collected in drums and either recycled or properly disposed of in a hazardous waste disposal site.

CHEMECOL, LLC

PVC Alternative Technology

CHEMECOL's technology can promote and expand the elimination of chlorine and phthalates, two components of polyvinyl chloride (PVC) products, which are among the synthetic chemicals that environmental activists and medical researchers claim are health risks. Several organizations are seeking to phase out the use of PVC. The European Commission, citing health risks to small children, formally decided to ban phthalates from PVC toys, and concerns about the hazards of PVC are growing in the United States.

CHEMECOL's patented technology allows the incorporation of a liquid monomer with a metallocene polymer to form an interpenetrating network polymer system offering processing similar to PVC with the unique property characteristics of a metallocene polyolefin. The technology can be processed on conventional PVC manufacturing equipment, which will save manufacturers added capital expenditure. In addition to improved quality, new product features, and ease of processing, there are also environmental improvements with the new technology. Specifically, the liquid monomer acts and behaves like a plasticizer without being a plasticizer, preventing migration of phthalates that may be unsafe for biological systems.

An additional benefit of the technology is that no dioxins are produced during incineration, which is a common problem associated with PVC and is a particular concern for the medical industry. Even more advantageous from an environmental and cost consideration aspect is the ability to recycle products made as a result of using the technology. These commodity products may also be customized to contain enhanced product features such as increased flame retardancy, an important factor in products used for construction. As such, CHEMECOL's technology provides the capability for development of environmentally friendly products, with enhanced product features as compared to PVC, at a system cost that is competitive with PVC.

Nextec Applications, Inc.

Solventless Process for Improving Fabric Performance Properties

In the areas of apparel and protective gear there has always been an ongoing thrust to achieve improved fabric performance properties. Properties of interest range from the quantifiable, like water resistance/repellency, fire resistance, and adhesion performance, to the subjective, such as comfort. One of the main ways of achieving improved properties is through surface modification. Difficulties encountered with surface modification have included durability as well as economically feasible and environmentally friendly processing. In textile technology, surface modifications are applied via immersion, coating, or lamination. Immersions, coatings, and laminates can be applied as 100% solids, solvent dissolved solids, or aqueous emulsions.

The Nextec process delivers performance benefits to manufacturers of rubber-treated fabrics through a process that utilizes no solvents, has no volatile organic compounds (VOCs), utilizes essentially nontoxic starting materials, and yields inert residuals that have passed biocompatability testing. The unique patented technology that is practiced by Nextec Applications, Inc. replaces processes in which rubbers are dissolved in toxic aromatic or chlorocarbon solvents and are coated or spread on fabrics. Nextec's process allows precise placement of thin polymeric films around fibers and crossover points and allows filling in or leaving open interstitial spaces within fabrics. The choice of polymer, substrate, and placement of polymer allows for improvement of properties such as breathable barrier performance, controlled porosity, resistance to fluids, and adhesion/release behavior. This technology has found applications in such industries as aerospace, automotive, apparel, and medical.

Solvox Special 5501, an Antiagglomerate and Stickies Neutralizer for the Paper Industry

Solvox Manufacturing Company

The scope of papermaking over the last twenty years has changed dramatically, in large part because of the use of secondary fibers as a source of furnish. Economics have made secondary fiber a mainstay for a variety of paper producers because it is an inexpensive source of fiber and is readily available. Furthermore, legislation has mandated the use of secondary fibers whenever possible to conserve valuable natural resources. With these forces in play, there have been numerous challenges that have presented themselves not only to the paper industry but also to its chemical suppliers. One of these challenges, "sticky" control, has provided Solvox Manufacturing Company with an opportunity to position itself as the problem-solver to customers world wide.

"Stickies" refer to any insoluble resin that has tacky properties and adversely affects papermaking. Commonly used items such as Post-it® notes, address labels, and envelopes contribute to the problem of sticky control. Pressure sensitive adhesives alone cost the paper recycling industry an estimated $700 million per year. Recently, Solvox has formulated a special chemical additive, Solvox Special 5501, that enables the paper industry to make quality paper with recycled furnish equal in quality to that made with virgin fiber. This additive is an antiagglomerate that can be considered a stickies neutralizer. Solvox Special 5501 coats the sticky to make it dimensionally stable, thereby allowing it to be removed by mechanical means, while preventing reagglomeration of the stickies. When compared with additives currently in use, Solvox Special 5501 reduces VOC emissions, eliminates costly downtime, and produces a higher quality end paper product.

This additive is important to the paper industry and the environment for several reasons. First, this one additive does the job of three or more chemicals. But more importantly, this chemical has a very low VOC level (approximately 0.50% by weight) compared to the chemicals that it replaces (some over 50% by weight). Additionally, it eliminates costly downtime, thereby decreasing the total cost of making paper. Finally, it is now possible to make an end paper product of high recycled content that is equal in quality to that of virgin fiber. This will lower the amount of waste paper entering our landfills. Ultimately, this will reduce the use of trees and preserve this planet for generations to come.

Sugars from Lignocellulosic Materials for the Production of Bio-Based Fuels and Chemicals

Arkenol Holdings, L.L.C.

The disadvantages of relying on fossil fuels are well known. Environmental problems linked to fossil fuel usage include acid rain, global warming, and air and water pollution. Production and use of carbohydrate-based chemicals can overcome many of these environmental issues. Yet, widespread production and use of biobased chemicals have not occurred. The return to the carbohydrate economy is stymied in an environment of artificially low petroleum prices, an uneven playing field tilted toward the use of fossil fuels, and a lack of technology to competitively produce products from biomass.

Arkenol, Inc. has developed an environmentally sound and cost competitive technology for the carbohydrate industry. While completely analogous to the petrochemical industry, Arkenol's technology uses innocuous and renewable feedstocks. The Arkenol process utilizes concentrated sulfuric acid to break down the cellulosic structure in lignocellulosic feedstocks and then, with water, to complete the new formation of individual C6 and C5 sugars for further processing into chemicals and fuels. The lignin is processed for soil amendment or solid fuel. Silica, uniquely present in rice straw, can be recovered and converted to high value pre-

cipitated silicas and zeolites. Trace amounts of sulfuric acid in the sugar solution are converted into gypsum for soil amendment or ammonium sulfate for fertilizer. The sugars can be converted into alcohols and carbon dioxide, acids, ethers, solvents, or surfactants either by direct chemical conversion, fermentation, or a combination of both. With over 200 different chemicals and an even greater number of downstream chemical product combinations that can be derived from biomass, the market opportunities are considerable.

Arkenol is pursuing several opportunities worldwide to convert feedstocks such as rice straw, sugar cane bagasse, and municipal solid waste into ethanol and other chemicals. An advanced project in Sacramento County, California, will use Arkenol's technology to divert approximately 132,000 tons per year of rice straw from open-field burning to produce up to 12 million gallons per year of ethanol and coproducts. While eliminating burning on some 60,000 acres of rice fields, the Sacramento project will provide a much needed disposal alternative for rice growers faced with the legislative mandate to phase out open-field burning. In addition, by diverting the rice straw from open-field burning, the Sacramento project creates significant improvements in the region's air quality. Avoidance of open-burning of about 140,000 tons per year of rice straw results in annual net emissions reductions of 280 tons of NO_X, 173 tons of PM_{10}, 130 tons of VOCs, 138 tons of SO_2, and 4,988 tons of CO.

The successful implementation of Arkenol's technology will lead to decentralized and competitive economic production of fuel ethanol and other biobased chemicals (ethanol is produced from the Arkenol process at a cost of $0.66 per gallon, compared to $1.29 per gallon from the industry standard process). Arkenol's ability to use a wide variety of feedstocks will enable placement of production facilities (or "biorefineries") near the market for the products. Large scale conversion of waste materials into fuels and chemicals is a novel solution to waste management, pollution prevention, and economic development.

Anderson Chemical Company

Total Impact Program (TIP®): An Environmentally Preferable Program for Laundry

Anderson Chemical Company's Total Impact Program® employs chemistry with a more positive environmental profile for human health and the environment than that used in conventional laundry systems. Historically, institutional markets (hospitality, hospitals, nursing homes, and others) have maintained a program of high alkaline breaker in conjunction with an alkaline wash bath, sodium hypochlorite bleaching, acid souring to reverse the alkaline breaker, and softening with poorly biodegradable softeners. Temperatures have been kept high (150 °F to 160 °F) for performance, and high volumes of water for dilution and additional neutralization baths have claimed large volumes of energy for heating these water baths.

The Total Impact Program (TIP®) targets three main impact areas: user safety and health, environmental impact for pollution prevention via source reduction, and efficiency through resource consumption reduction by decreasing processed pound costs. It was the intent of the TIP® to reduce the toxicity of the washroom chemicals to achieve benefits in the areas of human safety and health and subsequent effluent improvement as well. TIP® chemistry is designed so that the NFPA rating is never higher than 1-0-0 for Health, Flammability, and Reactivity. Alkaline breakers, acid sours, sodium hypochlorite, and alkylphenol ethoxylates are not used in TIP®. This provides the facility and personnel using the TIP® a large degree of safety.

The TIP® incorporates a neutral pH detergent enhanced with enzymes and surfactants, oxygen bleach, and biodegradable softeners. Decreased water use and temperatures provide energy and water savings. Shorter machine running times are a function of fewer baths needed for alkalinity building and souring down steps. Water savings of 33% and energy savings of 27% are typical for the TIP® when compared to conventional programs. Effluent savings run at 33% as well. Fabric savings and linen replacement costs typically are in the range of 17-20% for the institutional markets worked with to date. As such, the change from conventional laundry programs to the environmentally preferable TIP® provides a real environmental management solution.

Waste Oil Source Reduction through Extended Oil Service Life

AMSOIL, Inc.

According to National Petroleum Refiners Association estimates, 1.1 billion gallons of oil were used in passenger vehicles and 916 million gallons were used in diesel engine vehicles in the United States in 1996. Much of the motor oil changed by passenger vehicle owners is improperly introduced into the environment. The management of used oil is a major environmental issue because of its hazardous nature. Used oil contains toxins such as lead, benzene, cadmium, chromium, and other heavy metals. These contaminants can cause illness in plants and animals and can contaminate drinking water. Waste oil has been granted special regulatory status, exempting its management from conventional hazardous waste rules in an attempt to encourage its beneficial use as a source of energy. Overall, this has had some success in the management of used oil in the business sector. Used oil generated by households, however, is currently disposed of improperly at an alarming rate nationally—220 million gallons per year as estimated by the U.S. Department of Energy.

In 1972, AMSOIL, Inc. introduced the first 100% synthetic motor oil to meet American Petroleum Institute service requirements, passing performance testing for gasoline-fueled consumer passenger vehicles. AMSOIL, Inc. has since developed synthetic oil formulas that extend oil service life up to 11 times that of conventional petroleum lubricants in consumer and commercial automobile and truck service and that work much longer when used with an oil analysis program. AMSOIL, Inc. also manufactures extended life, premium-grade lubrication and related products for commercial and industrial applications, including hydraulics, compressors, gears, and diesel-engine power plants. The scope of AMSOIL lubricating products' ability to provide uncompromising engine and machine wear protection, while reducing the volume of waste oil generation at the source, benefits the consumer, the commercial goods and services provider, and the upstream industrial entity. Synthetic oil basestocks are comprised of well-defined particular molecule types that can be designed for specific performance characteristics. One distinct advantage over crude petroleum is that they can be tailored to fit the requirements of the application. The uniform molecular structure of synthetic oil base-stocks reduces the lubricant volatility (aromatic boil off) in extreme heat, which in turn reduces oil consumption. With long drain synthetics, the average American can use 75% less oil, reducing the volume and the potential for accidental environmental contamination.

Zero-Waste Dry Plating of Cadmium

Electroplated cadmium is widely used in the defense and aerospace industries for the corrosion protection of steel. Cadmium, however, is a known toxic material. In addition, the electroplating process generates large quantities of toxic sludge and effluents. A typical, medium-sized electroplating shop, for example, discharges well over 100,000 gallons of effluents daily and disposes of 15 to 20 tons of hazardous sludge per week.

As an alternative to this conventional process, IonEdge Corporation has developed and commercialized a novel "zero-waste" dry plating technology. The dry plating does not use liquid chemicals and recycles solid materials in situ, resulting in elimination of waste. In this dry plating technique, a vapor-bath concept has been used in vacuum as opposed to the liquid bath of electroplating. This vapor bath allows for multidirectional and economical plating of cadmium only in the intended parts, resulting in a green technology. In addition, the amount of water used, filtered, and deionized on the line is reduced by at least one order of magnitude, and the energy consumption in the dry plating process is only 35% of that in electroplating. Estimated water treatment and disposal cost savings on the dry plating line are greater than $1,000 per day, and the capital costs in setting up the line are substantially lower. At IonEdge Corporation's facility in Fort Collins, Colorado, a complete dry plating line has been set up for production. The plating line consists of only four processes and a quality inspection as opposed to more than a dozen baths and related operations in electroplating. This plating line has been certified by a major aerospace parts supplier, and two dry plating machines are in service for plating cadmium on aerospace components.

2000 Presidential Green Chemistry Challenge—Entries from Industry and Government

ADVAFLEX™ Organic Stabilizer

Morton International, Inc.

ADVAFLEX™ Organic Stabilizers (ADVAFLEX) are novel organic polyvinyl chloride (PVC) heat stabilizers primarily geared toward flexible PVC applications. While PVC is a versatile polymer with many useful properties, it cannot be processed without the addition of heat stabilizers. Conventional flexible PVC stabilizer technology relies on complex mixtures consisting of as many as 10 components, with primary active ingredients that include lead, cadmium, and barium compounds with metal contents in the range of 8 to 10%. Most of the components originate from nonrenewable resources, and many are health and environmental hazards.

ADVAFLEX™ is an entirely new concept in PVC stabilizer technology that offers numerous advantages over conventional stabilizers. First and foremost, these are two-component systems containing new organosulfur chemistry and low levels of metal activators, such as zinc. The performance advantages include excellent thermal performance, competitive costs, good secondary performance attributes, compatibility with coadditives chemistries, and simplicity of PVC formation. The environmental and health benefits include: very low metal content (as low as 0.4%); low odor and volatility; and the absence of barium, cadmium, lead, phosphorous, alkylphenol, and other aromatic chemicals that are used in conventional technology.

ADVAFLEX™ has undergone a thorough toxicity screening that demonstrates that the product is essentially nontoxic and not mutagenic, carcinogenic, or environmentally hazardous. The metal activators in ADVAFLEX™ formulations are generally required at catalytic levels, and the preferred metal, zinc, is a required element of the human diet. ADVAFLEX™ technology is a commercially attractive alternative that improves on all aspects of the conventional technology, especially with respect to human and environmental safety.

Ashless Friction Modifier/Antioxidant for Lubricants

Ciba Specialty Chemicals Corporation

Cars consume roughly half the oil used in the United States and account for about one quarter of the greenhouse gases generated. There are at least two important benefits to improving passenger car fuel economy: conserving natural petroleum resources and improving the environment through reduced volatile emissions. While automobile manufacturers work on improving vehicle fuel economy through upgrading engine efficiency and utilizing lighter weight materials in automobile construction, products that can improve the performance of cars already on the road could have a more immediate impact. Development of engine oils that improve engine efficiency are in this category.

Engine oil is a mixture of petroleum base stock and additives that protect the metal surfaces, expand the useful temperature range of the lubricant, and extend the useful life of the oil. Additives in a typical engine oil include detergents to keep the metal surfaces deposit-free; dispersants to keep the insoluble particles suspended in the oil; viscosity modifiers, which stabilize lubricant thickness at various temperatures; antiwear agents, which reduce metal-to-metal contact; metal deactivators, which reduce friction between metal parts in motion; and antioxidants, which reduce oxidation and breakdown, preserving the lubricant's properties over its lifetime.

Developing a combination friction modifier/antioxidant reduces the number of additives that a lubricant requires. More importantly, it has the capability to extend the durability of the friction modifier, leading to improved lubricants. This in turn can positively influence gas mileage and reduce environmental emissions. Irgalube F10 is a unique ashless, multifunctional, combination friction modifier and antioxidant. Chemically it is a high molecular weight phenolic antioxidant with hydroxyl functionalities providing friction modifying properties. It has been designed to replace glycerol monooleate, a friction modifier that tends to promote oxidation at higher temperatures, and molybdenum dithiocarbamates (MoDTC), which are metal-containing and can form undesirable, metal-containing inorganic particulates upon combustion.

Irgalube F10 is made via the reaction of coconut oil, glycerol, and a phenolic antioxidant and, as such, is the only commercially available, metal-free, multifunctional friction modifier/antioxidant in the world. Irgalube F10 passed the ASTM fuel economy test procedure, registering a fuel economy improvement of 1 to 1.5% over the standard test oil. A fuel-efficiency improvement of 1% could have an annual impact of reducing carbon monoxide by 1.2 billion pounds, NOx emissions by 240 million pounds, and particulate matter emissions by 17 million pounds (based on National Air Quality and Emissions Trends Reports, 1996).

DuPont Crop Protection

Biocatalytic Production of 5-Cyanovaleramide

The first step in the manufacture of DuPont's new herbicide azafenidin (Milestone®), the base component of a total weed control program, is the catalytic hydration of adiponitrile to 5-cyanovaleramide (5-CVAM). Using a traditional catalyst, manganese dioxide, the process suffers from several problems: (1) the manganese dioxide recovered from a single hydration reaction is inactive and not reusable, (2) it would be difficult and expensive to recover and reactivate the catalyst, (3) significant amounts of adipamide are produced, and (4) a difficult solvent extraction using toluene is required for the separation of 5-cyanovaleramide from unreacted adiponitrile. In addition, rapid catalyst deactivation when using manganese dioxide requires the use of large amounts of this catalyst, resulting in the production of 1.25 kg catalyst waste/kg 5-CVAM.

As an alternative to traditional chemical catalysis, a biocatalytic process was developed for the highly regioselective hydration of adiponitrile. 5-Cyanovaleramide is produced in aqueous solution under mild conditions, with 96% selectivity at 97% conversion, and at concentrations comparable to standard chemical processes (19 wt%). The biocatalyst, *Pseudomonas chlororaphis* B23 cells immobilized in alginate beads, is a naturally-occurring, Biosafety Level 1 bacterium containing a nitrile hydratase enzyme. This biocatalytic process reduces catalyst waste production by 99.5% and no longer requires the use of toluene for product purification. To date, 77 metric tons of 5-cyanovaleramide have been manufactured by this method, eliminating the production of 97 metric tons of metal oxide catalyst waste. At full commercialization, it is predicted that several hundred metric tons/year of catalyst waste will be avoided.

The novel, biocatalytic hydration of an aliphatic dinitrile to the corresponding monoamide with high regioselectivity at high conversion and at concentrations equivalent to standard chemical processes is an environmentally friendly route that is generally applicable to a large and broad-based segment of the chemical industry. In addition, this biocatalytic process is easy to perform in standard chemical equipment at standard production rates and it is readily transferred to other facilities because of the simple reaction conditions and common equipment required. In the present case, the biocatalytic process is the low-cost option

for 5-CVAM production; DuPont expects to realize a cost savings of more than $2,000,000/year at full commercialization, relative to the cost of using an alternate chemical process.

BioPreparation™ of Cotton Textiles: A Cost Effective, Environmentally Compatible Preparation Process

Novo Nordisk BioChem of North America, Inc.

In textiles, one of the most potentially damaging activities to the environment originates from traditional processes used to prepare cotton fiber, yarn, and fabric. Fabric preparation consists of a series of various treatments and rinsing steps critical to obtaining good results in subsequent textile finishing processes. These water-intensive wet processing steps generate large volumes of wastes. Scouring, for example, is a cleaning process that removes impurities from cotton substrates during textile processing. Conventional scouring processes use large quantities of sodium hydroxide, high temperatures, and acid neutralization steps to remove impurities, thereby generating large amounts of salts, acids, and alkali. In view of the 40 billion pounds of cotton fiber that are prepared annually on an international level, it becomes clear that the preparation process contributes environmentally harsh chemicals to the effluent, with the major offender being sodium hydroxide and its salts.

BioPreparation™ is an enzymatic process for treating cotton textiles that meets the performance characteristics of alkaline scour systems while reducing chemical and effluent load. This pectate lyase process degrades pectin to release the entangled waxes and other components from the surface. Successful full-size industrial mill trials in preparing yarn and knitted textiles confirmed the processing advantages of the technology. These advantages, relative to chemical preparative routes, include ease of operation (no modification of existing equipment) and selective degradation of components that enhance properties with minimal weight loss (maintaining the quality/integrity of the cotton fiber). In addition, a substantial reduction in biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids was documented during these trials. The trials with knit, for example, gave 20% and 50% reduction in BOD and COD, respectively, when a two-step alkaline treatment was replaced with a one-step enzymatic preparation and dyeing process.

Furthermore, the BioPreparation™ technology also significantly reduces water, time, and energy consumption. Shortened water rinses, for example, give 33 to 50% water savings. Considering a recent statistical survey that determined that 162 knitting mills used 89 million m^3/year of water in processing goods from scouring to finishing, the BioPreparation™ approach would save from 27 to 45 million m^3/year of water. These BOD, COD, and water reductions would allow a mill to save 30% in waste and water costs. In conclusion, this biocompatible process provides an economical and environmentally friendly alternative to alkaline scour systems, or any combinations thereof, currently used in the textile industry today.

The Chemical Kinetics Simulator Program

IBM Research Division

Computer simulators offer a powerful means of minimizing waste generated through physical experimentation during process development and optimization, a waste stream not usually addressed in green chemistry programs. The potential impact of simulations will not be realized, however, unless they are widely accessible in an organization. The Chemical Kinetics Simulator (CKS) Program, developed at the IBM Almaden Research Center to meet this need, is a general purpose, easy-to-use package that allows outcomes of reactions to be predicted for a large variety of gas, solution, and solid phase systems in static and flowing

reactors. Its basic computational method is well-founded in theory and has been significantly enhanced through new algorithms that have been awarded U.S. patents. CKS has been in use at IBM for three years for process research and development. Since May 1996, the package has been available globally for a no-cost license through the World Wide Web and is used in many other industries for process research and development because of its exceptional ease-of-use and functionality. It also has been frequently licensed by environmental researchers in universities, corporate and government laboratories, and environmental regulatory agencies to develop models and evaluate hazards.

Argonne National Laboratory

Clean-Diesel Breakthrough: Simultaneous Decrease in Emissions of Both Particulates and Oxides of Nitrogen during Combustion

One of today's most challenging environmental problems is air pollution by oxides of nitrogen (NO_X) and particulates, created largely by diesel engines, particularly in urban areas. NO_X and particulate emissions from diesel engines are a major source of urban air pollution. Particulate matter contains organic compounds that may potentially cause cancer or mutations. Nitrogen oxides contribute to the formation of acid rain, ground-level ozone, and smog. Although the availability of oxygen enrichment in diesel engines has long been known to reduce particulate levels, it has not been a feasible technology because it increased NO_X levels. By using only a modest increase in the oxygen levels in engine intake air and by optimizing fuel conditions, Argonne National Laboratory (ANL) has broken through the technical barriers to create an oxygen enrichment technology that simultaneously reduces both particulates and NO_X.

The breakthrough came when ANL tested a new combination of three changes to engine operating conditions: 1) increased oxygen content in the engine air supply; 2) retarded timing of fuel injections; and 3) increased fuel flow. ANL tests were the first to adjust all three parameters. Previous strategies had changed only one or two of these conditions. This breakthrough technology is made practical by the development of a compact advanced polymer membrane that is a passive design and can be retrofitted to existing engines. The mass-production cost is expected to be modest ($75 to $160), compared with particulate traps ($200 plus 2 cents per gallon to operate) and NO_X treatment catalytic converters ($300 plus periodic maintenance).

This is the first oxygen enrichment technology to simultaneously reduce both NO_X (by 15%) and particulates (by 60%). It is an all-in-one, in-cylinder treatment that solves the emissions problems at the source, does not drain engine power (in fact, increases gross power by 18%), and improves fuel efficiency (2 to 10% improvement in brake-specific fuel consumption across the entire load range in a locomotive notch schedule). This breakthrough technology will be important to diesel-engine manufacturers, who are faced with helping their customers meet tougher regulatory standards beginning in model year 2002.

Air Products and Chemicals, Inc.

DEOXO-FLUOR™ Reagent

The importance of organofluorine compounds in the pharmaceutical and agricultural industries has stimulated the discovery and development of simple, safe, and efficient methods for introducing fluorine in organic molecules. Deoxofluorination, the conversion of carbon-oxygen to carbon-fluorine bonds, is one such method for the selective introduction of fluorine in organic molecules. This transformation has traditionally been accomplished with dialkylaminosulfur trifluorides, such as DAST [(diethylamino)sulfur trifluoride,

NEt_2SF_3], but only for laboratory-scale reactions. Due to the well-known catastrophic decomposition (explosion or detonation) of DAST on heating to greater than 90 °C, it is not used for large scale industrial applications.

Air Products and Chemicals, Inc. embarked on a scientific and technological program to provide deoxofluorination reagents and processes that would be safe for large scale industrial use. This led to the discovery and development of the DEOXO-FLUOR™ reagent, [bis(2-methoxyethyl)aminosulfur trifluoride]. Various thermal analysis data from DSC, ARC, Radex, and Setaram calorimetry clearly show the superior thermal stability of the DEOXO-FLUOR™ reagent over DAST. This greater thermal "robustness" of the reagent over DAST is satisfactorily rationalized on the basis of ab initio quantum mechanics calculations that show an interaction between one of the ether oxygens and sulfur, resulting in a shielding of the SF_3 group by the ether side chain, thus making the reagent less prone to decomposition by bimolecular disproportionation reactions, as putatively occurs with DAST. The DEOXO-FLUOR™ reagent is effective for the conversions of alcohols to alkyl fluorides, of aldehydes and ketones to the corresponding gem-difluorides, and of carboxylic acids to their trifluoromethyl derivatives with, in some cases, superior performance compared to DAST.

BetzDearborn

Designing an Environmentally Friendly Copper Corrosion Inhibitor for Cooling Water Systems

Copper alloys are widely used in industrial cooling systems because of their good heat transfer qualities. However, unless they are protected by an inhibitor, copper alloys will corrode in cooling systems. This corrosion produces extremely toxic copper compounds that are then released into the environment. Azole materials are the best available copper corrosion inhibitors and, in general, they protect copper very well. Tolyltriazole (TTA) is by far the most frequently used azole and is considered to be the industry standard. However, azole materials have a serious drawback in that they are not compatible with oxidizing halogens, such as chlorine and bromine. Oxidizing halogens are the most common materials used to control microbiological (MB) growth in cooling water systems. TTA reacts with chlorine, producing a chlorinated species that is not protective to copper. When corrosion protection is lost, TTA feed rates are usually increased in an attempt to overcome the reaction with chlorine and maintain a high enough residual to protect the copper surface. Very high TTA dosages are frequently applied to improve performance, often with limited success.

BetzDearborn has developed a new Halogen-Resistant Azole (HRA) that does not react with chlorine and protects copper when chlorine is present. The substitution of this new material for TTA provides substantial environmental benefits. These were demonstrated in a field test at a nuclear power plant that was utilizing chlorine for MB control. HRA was compared to TTA with respect to copper corrosion rates and discharge toxicities. Upon examination of the discharge, it was clear that copper-containing compounds, formed as a result of copper corrosion, were the most significant causes of toxicity to aquatic species.

The use of HRA resulted in a five-fold decrease in the amount of copper released to the environment, compared to TTA. Since HRA does not react with oxidizing biocides, considerably less chlorine or bromine is required for prevention of MB activity. A reduction in chlorine usage of 10 to 20% was observed at the above nuclear power plant, and reductions of 35 to 40% have been observed at other industrial sites. Lower chlorine usage means lower amounts of chlorine- or bromine-containing compounds ultimately being released in discharge waters. In addition, substantially lower concentrations of HRA are required for copper alloy protection compared to TTA. At the nuclear power plant trial, the five-fold reduction in the copper discharged was obtained with 2.0 ppm HRA compared to 3.0 ppm TTA.

Furthermore, a mass balance showed that only 9% of the TTA was recovered (compared to 90% of the HRA). The TTA loss was due to the reaction with chlorine and the formation of a chlorinated azole. Thus, the use of HRA resulted in a net reduction in the amounts and types of azole and halogenated azole compounds that were released into the environment. Finally, direct measurement of LC50 acute toxicities for fathead minnows, done on site in the plant effluent at the nuclear facility, showed a reduction in toxicity when TTA was replaced by HRA.

Nalco Chemical Company

Designing an Environmentally Sensible Chlorine Alternative

Industrial water treatment is necessary for energy conservation and to ensure a sustainable global supply of fresh water. Far more chlorine is used to control microbial fouling in industrial water treatment as compared to any other chemical. An environmentally sensible chlorine alternative is needed because the gas is hazardous, the liquid is not stable, chlorine is too volatile, free residuals do not efficiently control fouling biofilms, combined residuals are not very effective, reactivity with scale and corrosion inhibitors is counter-productive, and disinfection byproducts are toxic. Chloramines are not effective antimicrobials and are especially toxic to aquatic wildlife.

STABREX was purposefully designed to imitate the stabilized bromine antimicrobials produced naturally in the mammalian immune system. STABREX is the first biomimetic industrial biocide. It is chemically analogous to the antimicrobial product of the oxidative respiratory burst in eosinophils, a type of mammalian white blood cell. These cells consume oxygen in a cellular process recently proven to produce stabilized bromine antimicrobials. In eosinophils, HOBr is produced by the enzymatically-catalyzed oxidation of bromide with H_2O_2 . The HOBr then immediately reacts with 2-aminoethanesulfonic acid (taurine). The product of this natural stabilization reaction is a potent antimicrobial, N-bromo-aminoethanesulfonic acid; it is the design model for STABREX.

The design and performance benefits of STABREX Microorganism Control Chemical have been proven in two hundred billion gallons of successfully treated industrial water since commercial introduction in May 1997. This water, mostly in cooling systems, would have otherwise been treated with thirty million pounds of chlorine or its equivalent. Compared to chlorine, the new product is more than 10-fold less toxic, generates 50% fewer disinfection byproducts, is much more effective in controlling microbial biofilms, is many orders of magnitude less volatile, is much simpler to handle and feed, is 50% less reactive with other water treatment chemicals, and degrades an order of magnitude less in storage or transport. STABREX is manufactured in six locations on five continents. Seventy percent of production is used in the United States; 30% is applied internationally throughout Asia, Europe, Africa, Latin America, and Australia.

The Lubrizol Corporation

Durable AMPS® Antimist Polymers for Aqueous Metalworking Fluids

The generation and accumulation of metalworking fluid (MWF) mists in the plant environment during metalworking production gives rise to worker health and safety concerns. It is estimated that about 1.2 million workers are potentially exposed to MWFs annually. In response to increasing worker health concerns from MWF mists, the United Auto Workers Union has petitioned the Occupational Safety and Health Administration to lower the permissible exposure limit (PEL) of oil mists in the workplace from the current PEL of 5 to 0.5

mg/m^3. The current mist control methods being used for exposure control have drawbacks. For instance, engineering mist controls based on machine enclosures and mist collection are exorbitantly expensive to install and maintain. A second type of chemical mist control method, based on high molecular weight polymers as antimist (AM) additives for aqueous MWFs, has found limited acceptability because AM polymers lose their performance due to shear degradation, requiring frequent additions to maintain performance.

The development of durable AMPS® polymers at Lubrizol solves this problem. These polymers suppress mist formation at the source by stabilizing MWF against breaking up into small droplets that get suspended in the plant environment as mist. The reduction in mist minimizes worker exposure to MWF chemicals and other pollutants present in the mist, creating a safer worker environment. Because they are shear stable, the AMPS® polymers provide long-lasting mist reduction. The application and performance of the AMPS® polymers were evaluated during field trials at small machine shops and large Ford manufacturing plants. In a small machine shop field test, a one-time addition of 1,000 ppm AMPS® polymer resulted in a stable 60% mist reduction. During large-scale plant trials at Ford Motor Company, a one-time addition of 1,000 ppm AMPS® polymer resulted in stable 40 to 60% mist reduction over two months in the plant environment. The worker response to reduced mist levels during these trials was extremely positive. It was felt that after the polymer addition, there was a distinct improvement in plant air quality, general improvement in working conditions, and less slippery floors from oil mist deposits.

AMPS® polymers provide a low-cost method of suppressing mist generation and controlling exposure because they provide long-lasting mist suppression at low (ppm) concentrations. These polymers are less labor-intensive to implement in the field because they disperse easily in the MWF and do not require frequent addition. They are manufactured as aqueous solutions and do not contain any volatile organic compounds. Extensive sensory, inhalation, and dermal toxicity tests have shown that AMPS® polymers exhibit a profile of minimal toxicity under conditions of use. Waste water treatment evaluations have shown that they do not affect the waste treatability of aqueous MWFs.

Electronic and Photonic Polymers from Biocatalysts

U.S. Army Soldier and Biological Chemical Command (SBCCOM)

As technologies continue to become more sophisticated in this fast-paced information age, the need for new and advanced electronic and photonic materials becomes a critical requirement for future leaps in performance, size, and speed. Simultaneously, however, with this drive for new advanced materials is the growing concern over the negative impact that these new technologies will have on the environment. Conventional conducting polymers are synthesized, for example, from reactions that involve strong chemical oxidants and the use of toxic solvents for solubilization and processing. Earlier studies had shown that enzymes were an exciting, environmentally friendly alternative to the synthesis of many of these polymers. However, the mechanisms involved in these reactions only led to highly branched and often insoluble polymers that had very poor electrical conductivities and optical activity.

While investigating new ways to overcome these limitations with the enzymatic approach, it was found that simple addition of a charged molecular species (polyelectrolyte or surfactant) to the reaction medium provides a type of biocompatible nanoreactor that not only optimizes enzymatic function and monomer coupling, but also provides water solubility of the final complex. The final polymers have enhanced electrical and optical properties and are processable, and the entire process is environmentally compatible.

A number of templated polyanilines and polyphenols have been produced and characterized using this process. Enzymatic polymerization of anilinic and/or phenolic monomers is

carried out in the presence of ionic templates to yield high-molecular-weight and water-soluble complexes of the polymer and the template used. This approach is particularly attractive because it is completely benign and 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 because toxic catalysts or solvents are no longer required for the synthesis or processing of these polymers into useable forms.

The technological applications for these enzymatically synthesized polymers are significant and diverse. Polyaniline is already well known as a promising material for electrochromic displays, electromagnetic interference (EMI) shielding, corrosion protection, electrostatic dissipation, and sensing. There is also great potential for these materials in photonic devices and batteries. Polyphenols are currently being investigated in polymeric batteries that could be coupled to photovoltaic devices containing conducting polymers and light absorbing dyes to create environmentally friendly energy harvesting and storage devices. It was recently found that the mild and benign conditions of this biocatalytic approach even allow for the use of DNA as a template to form a conducting DNA/polyaniline complex. This material could have enormous opportunities in medical diagnostic devices, probes, and bioconductors. This technology offers both potential economic and environmental benefits to industry and society due to the commercial potential of the products made and the environmentally benign methods used to produce them.

Radtech International, North America

Eliminating Air Pollution (VOC and HAP) at the Source through the Use of Ultraviolet and Electron Beam Polymerization

Air pollution remains a major environmental concern in the United States. Ground-level ozone, a major pollutant formed by the reaction of nitrogen oxides with volatile organic compounds (VOC), affects more people than all other pollutants combined. Most of the VOC emissions in the United States result from the practice of using volatile solvents in the manufacture and use of coatings, inks, adhesives, and similar products where polymers are dissolved or dispersed in solvents. After application, the products are exposed to heat in curing or drying ovens to drive off the solvents. Attempts to reduce the VOC generated by source reduction approaches have resulted in high solids and water-based materials. These advances reduced VOC emissions for a while, but as the economy has soared and production increased, VOC emissions again climbed to undesirable levels.

The only way to achieve permanent control of VOCs without impeding economic growth is to remove all VOC generators (solvents) at the source. Use of powder coatings is one approach that has been successful for metallic products that can withstand the high cure temperatures required. For heat-sensitive substrates, such as paper, plastic, and wood, the answer has been found in technology depending on the use of low-level radiation energy (i.e., ultraviolet light (UV) or electron beams (EB)) to polymerize coatings, inks, adhesives, etc. without heat.

Radtech International has developed a UV/EB procedure that eliminates solvents completely. The UV/EB technology uses low-molecular-weight oligomers dissolved in monomers of similar activity. These liquid resins can be used as clear finishes or formulated with pigments and other conventional additives. When applied and cured with UV or EB, the liquid materials are converted 100% to solids with virtually no emissions. As a consequence of this environmental achievement, combined with other advantages such as high speed curing, greater efficiency, no end-of-pipe requirement, space savings in oven elimination, excellent

performance properties, etc., the use of UV and EB has been increasing rapidly over the past five years.

This technology is currently in use in a wide variety of industries and is growing at a 10 to 12% annual rate. The Coors Company, which makes over four billion beer cans a year, switched their production entirely to UV curing. They reduced their emissions in the manufacture of each billion cans from 28.9 tons/year for a water-based enamel to 1.677 tons/year for a UV-cured acrylic (free radical) enamel and thence to 0.224 ton/year for a UV-cured epoxy (cationic) enamel. In short, they reduced their emissions by 94% using the acrylate and over 99% using the epoxy, without the use of add-on pollutant collection and destroying equipment. Other industries using UV/EB technology include (with 1999 estimated usage) fiber optics (2,400 tons), wood products (12,500 tons), plastic products (5,200 tons), graphic arts (36,000 tons), electronics (4,000 tons), and adhesives (1,500 tons).

Environmentally Benign Antibacterial Agents

U.S. Department of Agriculture, Agricultural Research Service, Southern Regional Research Center

Many effective antibacterial agents for consumer and health care applications on textiles and fibrous substrates are no longer available on the market or are restricted due to their deleterious environmental effects in streams and watersheds. Chlorinated phenols and chlorinated bisphenols are coming under scrutiny because their structure is similar to that of polychlorinated biphenyls (PCBs), and they could potentially lead to the formation of the very toxic substance dioxin. Tributyltin and related trialkyl tin oxides are also being restricted or closely monitored because of their adverse effects of polluting water sources. Thus, there is a need for new, environmentally benign antibacterial agents to replace ones such as those described above. Moreover, it would be useful if the new agents had chemistries compatible with bleaching processes in the fiber and paper industries that increasingly utilize the environmentally acceptable agent hydrogen peroxide in place of environmentally deleterious bleaching agents, such as hypochlorite and other chlorinating agents.

Such agents have been synthesized and patented. These new environmentally benign antibacterial agents, containing only magnesium and peroxide, are affixed as aqueous dispersions to textiles to impart antibacterial activity to natural, synthetic, and blended fibers by conventional pad-cure processes (10 to 17% active ingredients cured at 2 to 4 minutes at 120 to 150 °C.). Modified textiles contain bound peroxide (0.1 to 1.7% by weight) that is active against bacteria with contents as low as 0.10% active oxygen. These agents have been shown to have excellent resistance to representative gram-positive and gram-negative bacteria.

Fixation of aqueous dispersions of these agents to a wide variety of fiber types and fabric constructions has been demonstrated, as well as the long-term durability of these agents to laundering to retain antibacterial activity. These agents have also been applied to a variety of cotton and wood-pulp cellulosic nonwovens. Thus, these agents have the additional benefit of being more suitable for renewable fibers, such as cotton and cellulosic fibers derived from wood pulp, than the nonrenewable synthetic fibers (such as polyester and polypropylene). Moreover, because cellulosic fibers are bleached with hydrogen peroxide, these agents have compatible chemistry with prior purification processes. The agents themselves may also be used in other applications (e.g., skin disorders, toothpastes, virus inactivation) yet to be evaluated.

U.S. Department of Agriculture, National Center for Agricultural Utilization Research

Environmentally Benign Synthesis of Monoglyceride Mixtures Coupled with Enrichment by Supercritical Fluid Fractionation

Supercritical fluid extraction (SFE), supercritical fluid fractionation (SFF), and, more recently, synthesis under supercritical conditions have attracted considerable attention as possible alternatives to existing processes that employ organic solvents or catalysts requiring postreaction disposal. These methods utilizing carbon dioxide (CO_2) have received the preponderance of attention due to CO_2's compatibility with the environment (i.e., toxicity, flammability). To date, however, no one has demonstrated how CO_2 can be utilized in a series of processes embodying synthesis, extraction, and/or fractionation, thereby creating an entire process or plant that practices green chemistry from start to finish.

Studies conducted at the National Center for Agricultural Utilization Research have produced two alternative syntheses for producing monoglyceride-containing mixtures (via gylcerolysis) that employ CO_2, either as a catalyst or transport medium coupled with a lipase biocatalyst, to produce mixtures of varying monoglyceride content. Further, the same carbon dioxide medium can then be used in a sequential fashion to effect an enrichment of the synthesized glyceride mixtures to yield products having a monoglyceride content in excess of 90 weight percent that have high value as emulsifiers, lubrication aids, and food additives. Using carbon dioxide under pressure, metal-based catalysts can be eliminated from the traditional batch stirred-reactor glycerolysis to yield a product that is lighter in color, less odoriferous, and has a monoglyceride content between 35 to 45 weight percent, depending on the botanical oil source.

Alternatively, the National Center for Agricultural Utilization Research has demonstrated and patented a synthesis that uses CO_2 in the supercritical state to dissolve vegetable-based oils prior to transport over a supported enzyme catalyst to yield designer glyceride mixtures having a variable monoglyceride content between 50 to 90 weight percent. Finally, by coupling one of the two CO_2-based synthesis processes with a thermal gradient fractionation column, it is possible to utilize a totally environmentally benign process for production and enrichment of high value oleochemicals from natural resources.

U.S. Department of Agriculture, National Center for Agricultural Utilization Research

Environmentally Benign Two-Step Synthesis of Fatty Alcohol Mixtures Using Supercritical Carbon Dioxide (SC-CO_2) and SC-CO_2/Hydrogen Mixtures

Fatty alcohols and their derivatives are important in many industrial processes where they are used as raw materials for surfactants and lubricants. The annual production of fatty alcohols is over one million metric tons. Commercially, fatty alcohols are produced by one of three processes: the Ziegler process, the Oxo process, or by a high pressure hydrogenation of fatty acids or esters. The last process is the only one that uses renewable, natural fats/oils, whereas the first two processes utilize petrochemical feedstocks. This last method involves the transesterification of the candidate oil/fat substrate with alkaline earth catalysts in a batch reactor followed by hydrogenation of the resultant fatty acid methyl esters, also in a batch autoclave with copper chromite catalysts. This synthetic route suffers from the use of environmentally objectionable catalysts that must be filtered from the products; long reaction times due to inefficient contact between hydrogen, the catalyst surface, and the methyl esters; and slow production cycles due to the need to empty batch reactors and recharge them.

In an improved process, the above reactions have been implemented in environmentally friendly supercritical carbon dioxide (SC-CO_2), using an enzyme catalyst in the transesterification step followed by hydrogenation with a chromium-free catalyst. Further, the reactions are run under supercritical conditions sequentially in two connected flow reactors, thereby speeding up the turnaround time attendant with a continuous process. The hydrogenation step can be achieved in 4 to 9 seconds due to the superior mass transport properties exhibited by H_2 in SC-CO_2. Methanol produced as a byproduct in this reaction can be recycled back to the first reaction (tranesterification) for use as a reactant. Using soybean oil as a substrate, yields greater than 96% can be achieved using the candidate lipase for as many as 20 production runs.

The resultant products, methylated fatty acids, are readily soluble in SC-CO_2 and can be transported to the second reactor, where 10 to 25 mole % hydrogen is added to the pressurized CO_2 stream. The high pressure/temperature hydrogenation to produce the saturated alcohol mixtures employs a commercially available, chromium-free catalyst, T-4489. A consequence of using renewable soybean oil as the initial starting substrate is the production of a saturated fatty alcohol mixture that consists of 90% steryl alcohol. The described process is the first example of conducting a sequential two-step synthesis entirely in SC-CO_2, resulting in a totally green synthesis with environmentally safe catalysts.

Filter Leak Test Using Ozone-Benign Substances

U.S. Army Soldier and Biological Chemical Command, Edgewood Chemical Biological Center

Air purification filters operate by adsorbing impurities from flowing contaminated streams onto high-surface-area microporous materials, such as activated carbon. For such a filter to operate properly, it must be packaged so that leak channels are eliminated. Testing to ensure proper adsorbent material filling of manufactured fibers is routine and has traditionally been performed using substances such as chlorotrifluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12). It is now well known that small chlorocarbons, chlorinated fluorocarbons (CFCs), and certain bromine-containing, fire-extinguishing materials (halons) are detrimental to the environment because of their extreme environmental stability in the lower atmosphere and their ability to release chlorine and bromine atoms upon vacuum ultraviolet irradiation in the stratosphere. Chlorine and bromine atoms produced in the stratosphere destroy ozone catalytically, thereby compromising the UV-protection that the stratospheric ozone provides.

With the advent of the Montreal Protocol eliminating production of ozone-depleting substances, the search for substitute materials for common items including air-conditioning and fire extinguisher fluids has to be intensive. Work at the U.S. Army Edgewood Research, Development, and Engineering Center was directed at finding filter leak test materials that were not destructive to earth's stratospheric ozone layer and were capable of rapidly identifying filter assembly problems. Materials investigated included several hydrogenated fluorocarbons (HFCs) of differing volatility. HFCs do not contain chlorine or bromine, which have been implicated as potent stratospheric ozone destroyers. Two HFCs were identified as substitute filter leak test vapors: 1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC-4310mee) for in-service filters and 1,1,1,2-tetrafluoroethane (HFC-134a) for new filters. These materials have been adopted by the U.S. Army to test the integrity of filters used to provide respiratory protection against chemical warfare agents.

3M

Hydrofluoroethers (HFEs) — The Right Balance of Properties

Research on hydrofluoroethers (HFEs) started in 1994, and the first commercial compound came to the marketplace in 1996. The design of the hydrofluoroethers provides a balance of properties that make them excellent substitutes for ozone-depleting compounds.

3M formed a technical team in the early 1990s to find a substitute for ozone-depleting substances (ODSs, i.e., CFCs and HCFCs). In addition to addressing the issue of ozone depletion, the team also set criteria for candidate molecules on the basis of flammability, toxicity, photochemical reactivity (potential for smog formation), and global warming potential. The 3M team investigated the performance, health, and environmental attributes of more than 100 compounds before the invention of HFEs. HFEs did not require the team to compromise on any of its desired qualities for an ODS replacement. HFEs do not deplete the ozone layer, do not contribute to photochemical smog, are very low in toxicity, are nonflammable, and have very low global warming potentials.

The first commercial product for the HFE program was HFE-7100. HFE-7100 ($C_4F_9OCH_3$) was brought to the market in 1996 and was followed by HFE-7200 ($C_4F_9OCH_2CH_3$) in 1997. Both of these compounds are approved for use under EPA's Significant New Alternatives Policy Program (SNAP) for solvent cleaning, aerosol, and heat transfer applications. EPA also declared these materials as VOC exempt on August 25, 1997. The acute and subchronic toxicity of HFE-7100 has been thoroughly investigated. An evaluation of these data by the American Industrial Hygiene Association Workplace Environment Exposure Limit Committee yielded an exposure guideline of 750 ppm. The exceptional low toxicity of HFEs make them unique in a marketplace that has traditionally had to compromise on the toxicity of available alternatives.

Mallinckrodt Baker, Inc.

Hydrogen Sulfide Elimination

Mallinckrodt Baker has developed a method that eliminates hydrogen sulfide from the substances not precipitated by H_2S test. The existing method uses hazardous hydrogen sulfide, takes about 5 hours to perform, and is precise only for combined alkali results. The new method is safer (does not use hazardous reagents), takes only 30 minutes to perform, and is accurate for individual element determinations.

Evergreen Nylon Recycling LLC

Innovative Green Chemistry for Sustainable Manufacture of Caprolactam

Honeywell and DSM chemicals have both manufactured caprolactam and nylon 6 for decades. Demand for nylon has continued to grow at a steady pace, and both companies have continually improved their productivity to meet the increasing demand. In the mid-1990s, Honeywell and DSM reached a point where demand outstripped their ability to supply from their traditional plants. Expansion of capacity was necessary. The most financially attractive and environmentally beneficial alternative was the Evergreen technology.

The Evergreen technology is a unique, proprietary green chemistry process for the depolymerization of nylon 6 and purification of the resulting caprolactam. It uses an alternative and sustainable feedstock in the form of nylon 6 waste carpet and eliminates the use and generation of toxic materials as compared to traditional caprolactam manufacturing. The waste carpet is converted into first-quality caprolactam that is then used, without limitation, in crit-

ical and aesthetic applications including carpet fibers, engineering plastics, and films. The coproduct is used for its raw material and fuel value in the manufacture of cement.

Evergreen is the world's first large-scale, sustainable nylon recycling process. It eliminates the annual use of 700,000 barrels of crude oil, 83 million pounds of benzene, 120 million pounds of cumene, and 86 million pounds of phenol as the source feedstock for caprolactam. Additionally, numerous direct environmental benefits are gained. Over 200 million pounds of waste carpet (nearly 20% of nylon 6 waste carpet in the United States) are diverted from landfills each year. All 200 million pounds of carpet (including backing materials) are recycled into valuable end products; hence, the Evergreen process produces no solid waste. There is zero use, generation, or emission of toxic materials in the Evergreen process. Air emissions are significantly reduced (by 89%) compared to traditional caprolactam manufacturing, and the feedstock for the process is indefinitely renewable because nylon 6 can be recycled by Evergreen over and over again without ever degrading product quality.

Manufacturing Qualification of an All Dry Via Deveil Plasma Process

Motorola Corporation and ULVAC Technologies, Inc.

The semiconductor industry is known for its heavy use of toxic and hazardous compounds. The industry has taken a very responsible position in protecting workers from these hazards; however, protective equipment, alarm systems, and special materials handling equipment are all expensive items. If the use of these hazardous materials can be substantially eliminated, then the costs associated with worker protection will also be reduced.

The process of plasma dry etching through silicon oxide layers creates submicron-sized vias for interlevel metal contacts on silicon wafers patterned with photoresist. The process also leaves the wafer surface contaminated with polymer residues, which must be removed. These residues are called "veils" because of their appearance in the scanning electron microscope. Conventionally, residue removal has been accomplished using special solvents and acids, and although these materials are very costly, hazardous, and an environmental disposal burden, the use of sulfuric acid/hydrogen peroxide mixtures for wafer cleaning and resist removal has gone on for more than 30 years.

Collaborators at ULVAC Technologies, Inc. have developed a replacement technology that uses dry plasma chemical processes for treating the polymeric residues, which renders them 100% soluble in deionized water, along with the associated processing equipment for using this capability in manufacturing. Together, Motorola Corporation and ULVAC Technologies, Inc. have performed a comprehensive program evaluating the equipment and processes in the manufacturing environment and have developed appropriate methods for employing the technology in the production environment to render it useful and available to the entire worldwide industry. Process repeatability and reliability, integrity of devices manufactured in terms of electrical performance, yields, and operating lifetimes have been demonstrated to meet or exceed the levels of the conventional acid-solvent technology. Adoption of this technology by the semiconductor industry is anticipated to have a significant impact on reducing the environmental burden associated with this industry, as well as offering major manufacturing cost savings.

ECOGAS Corporation

McCommas Bluff Landfill Gas Processing Facility

The McCommas Bluff Landfill Gas Processing Facility utilizes landfill gas, a renewable feedstock, to produce energy. Landfill gas, containing primarily methane, carbon dioxide, and volatile organic compounds, is produced by the anaerobic decomposition of solid waste material located in municipal landfills. The facility is located in Dallas, Texas, adjacent to the McCommas Bluff Sanitary Landfill. Landfill gas is collected from interconnected wells located within the landfill itself. The gas is processed to remove liquids, volatile organic compounds, and carbon dioxide. The McCommas Bluff facility employs a technology called Vacuum Pressure Swing Adsorption, or VPSA, to produce pipeline-quality gas that contains greater than 97% methane. VPSA operates on the premise that certain gases are more readily adsorbed at certain pressures than others. This application works especially well for the separation of carbon dioxide from methane. Carbon dioxide is adsorbed on molecular sieve material within a pressure vessel, while methane passes through the vessel unaffected. Desorption of carbon dioxide then occurs by applying a vacuum to the vessel, effectively grabbing the carbon dioxide from the molecular sieve. Not only does the facility use a renewable feedstock in a unique process, but it also reduces greenhouse gas and volatile organic compound emissions, provides odor control, and prevents methane migration from the landfill.

Mobil Oil Corporation

Membrane Separation in Solvent Lube Dewaxing

Mobil Oil Corporation and W. R. Grace have developed a pioneering technology that significantly reduces the impact of solvent refining of lubricants on the environment. The membrane-based process provides greater lubricant selectivity and reduces waste generation, while simultaneously decreasing emissions of volatile organic compounds and greenhouse gases.

The use of membranes to facilitate the solvent dewaxing of lubricants represents the first significant, environmentally focused improvement in this technology in over 40 years. In conventional lube dewaxing, a lube oil/solvent mixture is generated as part of the process. The solvent is removed from this mixture by distillation to isolate the lube oil product. The solvents are then cooled and refrigerated to the desired process temperature before being recycled to the process. The improved process uses a proprietary polymeric membrane material developed by W. R. Grace to separate up to 50% of the dewaxing solvents from the lube oil/solvent mixture. Consequently, the spirally wound membranes significantly reduce energy consumption by minimizing the need for energy-intensive distillation, cooling, and refrigeration.

As a result, a single commercial facility could reduce fuel oil consumption by 36,000 bbl/yr. This equates to a reduction in greenhouse gas emissions of about 20,000 tons/yr for each plant in which the technology is installed. The same plant would reduce cooling water use by nearly 4 million gal/day, or about 15 billion gal/yr. The use of membranes allows more solvent to be recirculated in the dewaxing operation, which in turn leads to higher lubricant yields and a reduction in the amount of undesirable byproducts generated in the process. The higher process yields reduce by about 5% the volume of crude oil required to produce a given volume of lube oil. For a world-scale plant, this equates to a savings of about 2 million barrels of crude oil per year. Finally, the loss of dewaxing solvents, which are volatile organic materials, into the environment could be decreased by 50 to 200 tons/yr per plant depending on the age and mechanical condition of the dewaxing equipment. This results from a reflection in the number of pieces of equipment required to refine a given volume of lube oil.

This technology was first implemented commercially at Mobil's Beaumont, Texas, refinery. It can easily be retrofitted into existing plants or incorporated into new plant designs and is currently available for license.

Minimizing Environmental Emissions by Using Different Solvents in Manufacturing Processes

Eastman Kodak Company

Solvent selection is an important aspect of chemical process development. Two well-known effects of solvents are their influence on the desired reaction kinetics and their potential to minimize the effects of hazardous undesired reactions through dilution and heat absorption as solvent is vaporized.

Recent testing of energetic chemicals has demonstrated that the chemistry and kinetics of their undesired decomposition reactions are also significantly altered by solvents. Eastman Kodak has successfully applied this knowledge to the process safety element of process development by systematically evaluating potential solvents for their effectiveness in minimizing the potential environmental impacts of accidental process upsets. For example, the batch size of an existing process had been very restricted because of the potential severity of a thermal runaway. Research on chemistry/solvent-specific decomposition data was utilized to select candidate replacement solvents that would minimize environmental hazards. A cooperative effort by safety engineers and development chemists ensued, resulting in a final process that entirely eliminated the possibility of loss of containment due to a thermal runaway. The end result of this work is that a new tool is available to help chemists and chemical engineers develop inherently safer chemical processes.

Historically, changing a process to mitigate a potential hazard has been accomplished through drastic changes in process conditions, process chemistry, or through equipment modifications, all of which require significant capital and resources. It is demonstrated by example that the application of recent investigations into the effects of solvents on the decomposition kinetics of energetic chemicals can be leveraged to substantially decrease the potential environmental impact of thermal runaways in production-scale equipment. The technology described has the potential for broad application in chemical manufacturing processes that make or use thermally unstable materials.

A New Environmentally Friendly Corrosion Inhibitor

Albright & Wilson Americas, Inc.

Corrosion is estimated to cost the United States well over $300 billion per year. The industrial water treatment market for corrosion inhibitors is 50 million pounds per year, growing at 5 to 7% annually, with more than 500,000 individual use sites in this industry category. Exposure to corrosion inhibitors is thus a major concern. Conventional corrosion inhibitors used in industrial cooling systems are either hazardous to the environment or have other drawbacks, such as instability in the presence of oxidizing biocides, limiting their applicability.

A new, all-organic corrosion inhibitor, Bricorr® 288, a phosphonocarboxylate mixture, has been discovered and patented. Bricorr® 288 is a highly effective corrosion inhibitor with wide applicability to industrial cooling systems. Bricorr® 288 is an aqueous solution, does not contain VOCs (Volatile Organic Compounds), is halogen free (bromine, chlorine, etc.), is heavy metal free (zinc, chromate, etc.), and does not contribute to dioxin or AOX (Absorbable Organic Halide) formation. Bricorr® 288 has an environmental profile permitting, in many instances, discharge of treated water directly into rivers without any adverse effects. In many cases, the recommended treatment level is at least an order of magnitude below that which would be toxic to fish. Bricorr® 288 is extremely water-soluble and, therefore, will not bioaccumulate. Bricorr® 288 has excellent handling characteristics due to its low mammalian toxicity, helping to improve safety. Additionally, the manufacturing process for Bricorr® 288 is environmentally benign in that it is solvent-free and does not result in discharges to water or air, nor does it produce any byproducts requiring disposal.

Ciba Specialty Chemicals Corporation

New Organic Corrosion Inhibitors Help Replace Toxic Heavy Metals and Reduce Solvent Emissions

The coatings industry in the United States has had to focus its efforts to develop products that are compliant with an ever-expanding set of Federal, state, and local regulations, all designed to reduce or eliminate materials that pose a threat to either human health and safety or more broadly, environmental safety. The Irgacor family of organic corrosion inhibitors was designed and developed specifically to replace the standard anticorrosive pigments that are based on heavy metals such as lead, chromium, zinc, strontium, and barium. These heavy metals are classified as being harmful to humans and/or the environment. In addition to the toxicity generally associated with them, heavy metal-based anticorrosive pigments are not particularly effective in low volatile organic content (VOC) waterborne coatings due to incompatibility.

Irgacor organic corrosion inhibitors are free of heavy metals. They offer effective replacements for heavy-metal-based products and can produce commercially viable waterborne and high solids solvent-based coatings. Replacement of all conventional corrosion inhibitors by these organic corrosion inhibitors could result in a potential overall annual source reduction of heavy-metal-based inhibitors of approximately 11.0 million pounds (4.2 million pounds chromate, 3.9 million pounds zinc/nonchromate, and 3.0 million pounds barium borates and silicates). Irgacor corrosion inhibitors are typically used at levels (based on total solids) of 1.5% to 4% compared to 10% to 20% or more for anticorrosive pigments. The volume of Irgacor necessary to replace the 11.0 million pounds, therefore, will be only 2.0 million pounds. In addition, if Irgacor can further stimulate the replacement of solvent-based systems with waterborne coatings in the maintenance, auto finish, and marine markets by 20%, the annual volume of VOCs being emitted to the atmosphere would be reduced by 6.7 million pounds (from 8.0 million pounds to 1.3 million pounds). Irgacor organic corrosion inhibitors provide both long-term anticorrosive properties as well as excellent protection against flash rust. This provides the coatings industry with effective materials to further the development of waterborne coatings as replacements for solvent-based, higher VOC products.

CDTech

A New Process for Producing Dimethyl Carbonate

Over the past several decades, the chemical industry has been interested in finding economic alternatives to phosgene as a chemical intermediate to introduce carbonate functionality into molecules (e.g., in the production of polycarbonates and polyurethanes). These products have multibillion pounds per year markets. The goal was to eliminate the use of a very hazardous material and the need to dispose of chloride-containing waste streams. It has long been known that dimethyl carbonate (DMC) could be used for this purpose, but it was not until relatively recently that a technology was available to produce DMC at a cost that could justify its use in new polycarbonate plants. This technology is based on the reaction of methanol, carbon monoxide, and oxygen in the presence of a copper chloride catalyst. The cost of production, however, is still too high to encourage the replacement of phosgene in existing polycarbonate plants.

A practical process for DMC production was never developed because available catalysts were not sufficiently active, byproduct formation was too high, and product recovery was complicated and expensive. These problems were solved by employing a novel catalyst system and innovative reaction and separation technologies. The patented catalyst system is a homogeneous complex of dibutyltin dimethoxide in triglyme (triethylene glycol dimethyl ether). Triglyme has low volatility under the reaction conditions and is a nonhazardous low

volatility solvent that is readily contained in the reaction zone. A further discovery was that DMC selectivity is enhanced by rapidly removing the DMC from the reaction zone. Near-stoichiometric yield of DMC was demonstrated using methanol as the stripping vapor in laboratory-scale experiments. The new process efficiently produces DMC and ammonia from methanol and urea while affording significant environmental and economic advantages. The potential for accidental release of phosgene is eliminated along with the salt waste stream. Furthermore, integrating the DMC plant with a urea plant allows efficient recycling of the ammonia to urea production, with a net effect of producing DMC from methanol and CO_2.

Oxidizer Scrubber Project

Dynacs Engineering Company, Inc. and Kennedy Space Center

NASA, in conjunction with its previous Engineering Support Contract contractor, INET, and the current contractor, Dynacs Engineering Co., Inc., has developed an innovative process that converts hypergolic oxidizer waste to a fertilizer used by Kennedy Space Center (KSC). The Toxic Vapor Detection (TVD) Laboratory of the KSC has demonstrated that the efficiency of the oxidizer scrubbers can be increased, a hazardous waste stream can be avoided, the operating cost of the process can be lowered, and fertilizer purchases can be reduced.

Hypergolic propellants are used in spacecrafts such as the Space Shuttle, Titan IV, Delta II, and other vehicles and payloads launched at KSC and Cape Canaveral Air Station (CCAS). Fueling and deservicing spacecrafts constitute the bulk of operations in which environmental emissions of NOx occur. Monoethylhydrazine, nitrogen tetroxide, and hydrazine are the main propellants of concern. The scrubber liquor waste generated by the oxidizer scrubbers (approximately 311,000 pounds per year) is the second largest waste stream at KSC. The waste disposal for this oxidizer scrubber liquor is approximately $0.227 per pound, or $70,600 per year.

With the new process change, the scrubber liquor waste stream at KSC and CCAS will be converted to a high-grade fertilizer, which will be applied to citrus groves. The process reacts nitrogen tetroxide with 1% hydrogen peroxide and potassium hydroxide to produce potassium nitrate, which is a main ingredient in commercial fertilizers. This process avoids the generation of hazardous wastes, which occurs when sodium hydroxide is used as the scrubber liquor. In addition, the new scrubber liquor is more efficient in catching nitrogen tetroxide than when sodium hydroxide is used. For example, when the new and existing scrubber liquors were compared under the same test conditions, the efficiencies were improved from 72.6 to 98.7% for the old scrubber liquor to 98.3 to 99.99% for the new scrubber liquor. Therefore, the emissions from the scrubber were 10 to 200 times lower for the new scrubber liquor than the emissions from the sodium hydroxide scrubber liquor. This new chemical change has eliminated the second largest hazardous waste stream at KSC and developed a new scrubber liquor, which is approved for application as fertilizer to the lawns and citrus groves at KSC. The cost savings with this new system amount to approximately $80,000 per year.

Oxygenation of Hydrocarbons by Photocatalysis: A Green Alternative

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory

The chemical industry is a significant component of the domestic economy, generating well over $250 billion in sales and a trade surplus exceeding $15 billion in each of the last five years. The industry is also a major source of industrial waste and is the dominant source of hazardous waste in the United States. The costs of handling, treating, and disposing of wastes generated annually in the United States have reached 2.2% of gross domestic product

and continue to rise. The chemical manufacturing industry generates more than 1.5 billion tons of hazardous waste and 9 billion tons of nonhazardous waste annually. Organic chemicals constitute the largest source of the toxic releases. Many of these releases can be minimized by improving the conventional housekeeping methods and pollution prevention techniques. However, cleaner production methods can be achieved by adopting green synthetic methods.

In recent years, there has been considerable work aimed at utilizing semiconductor photocatalysts for a variety of applications. High-value oxygenated organic compounds have been successfully synthesized from linear and cyclic hydrocarbons by a low-temperature photocatalytic oxidation using the semiconducting material titanium dioxide (TiO_2). Various hydrocarbons were partially oxidized in both aqueous and gaseous phase reactors using ultraviolet light and titanium dioxide under mild conditions. The conversions and selectivities obtained for the partial oxidation of hydrocarbons have been comparable to those achieved with the conventional method. For example, vapor phase photocatalytic oxidation of toluene with air, using a continuous reactor at 160 °C and 27 mW/cm^2 irradiation, resulted in a 12% conversion per pass to benzaldehyde and benzoic acid, with 95% selectivity to benzaldehyde. The gas phase photocatalytic reactors eliminated the separation step involved with liquid solvents and catalyst slurry mixtures and minimized the adsorption of products to the catalyst.

Initial life-cycle analysis studies have shown that this technology has the potential to reduce water contaminants and eliminate the use of toxic metal catalysts and solvents. Light-induced catalysis expands the possibilities of using molecular oxygen in partial oxidation reactions that are now being conducted with far more expensive polluting oxidants. This technology also promises the potential of visible light-induced chemistry for commercially important syntheses. Furthermore, the high selectivity and mild conditions achieved with photochemical routes will be especially attractive for the manufacturing of fine chemicals.

U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory

Paris II Solvent Design Software

There is a need to replace solvents currently used in industry whose continued use presents health difficulties, such as worker health concerns, and environmental impacts, such as toxicity. The replacement of these objectionable solvents, however, is a difficult task. In part, this is because solvent parameters and different compositions for mixtures need to be considered. The list of solvent parameters, such as density, viscosity, and surface tension, can be quite large. Trying to accomplish this replacement by hand is an interminable task. It is also desirable and more economical to replace the solvent but not the process or the equipment where the solvent is used. At the U.S. EPA's National Risk Management Research Laboratory, an effort has been underway to address this problem by developing a computer program that will allow users to design more benign replacement solvents and solvent mixtures.

A new Program for Assisting the Replacement of Industrial Solvents entitled PARIS II for the Windows® operating system has been developed. The program is capable of solvent design. The solvent design capability allows the user to match or to enhance desirable solvent properties while simultaneously suppressing undesirable ones, such as toxicity. This is achieved by designing mixtures of pure solvents and manipulating the composition. The composition is manipulated by a solvent search algorithm aided by a library of routines with the latest fluid property prediction techniques. The program contains a database of 1600 pure solvents with solvent properties. The solvent properties adequately characterize both the static and the dynamic behavior of pure solvents and solvent mixtures. The solvent properties include comprehensive measures of toxicity and the means to estimate volatile organic emissions, among other features. PARIS II is able to design replacement solvents that meet the

technical requirements of any solvent now in use while having better environmental performance (lower VOC's, less toxicity, lower environmental impacts), irrespective of the intended application of the solvent. PARIS II has demonstrated the design of technically effective replacement solvents for many environmental requirements.

Pollution-Free Conversion of Trees to Paper Using Air in Place of Sulfur and Chlorine

U.S. Department of Agriculture Forest Service

NOTE: This project is a partnership between the U.S. Department of Agriculture and Professor Craig Hill of Emory University. This entry was submitted by each party of the project and, therefore, was judged in both the academic and industry categories. The project summary appears in the academic entries section on page 16.

Process to Produce Biodegradable Polylactic Acid Polymers

Cargill Dow Polymers LLC

Polylactic acid (PLA), a highly versatile biodegradable polyester derived from 100% renewable resources, offers great promise as a replacement for petrochemical-based plastics in a wide range of commodity applications. While the environmental benefits of PLA, dubbed the "sleeping giant" of biodegradable polymers, have long been appreciated, its commercial viability has been limited by high production costs, often leading to resin prices greater than $2/lb. Until now PLA has enjoyed little success in replacing petroleum-based plastics in commodity applications.

Cargill Dow Polymers LLC (CDP) has developed a novel, solvent-free process for the production of lactide and polylactic acid. This environmentally friendly process is the first to allow the economical manufacture of a biodegradable and renewable-resource-based polymer that can effectively compete with petrochemical-based, commodity plastics on a cost/performance basis. The patented, multi-step process starts with L-lactic acid, a fermentation product derived from 100% renewable resources. Aqueous lactic acid undergoes a condensation polymerization to produce low-molecular-weight PLA pre-polymer. Next, the pre-polymer is depolymerized by an intramolecular cyclization reaction into a mixture of L- and meso-lactide diastereomers. The lactide isomers are then isolated with high purity using vacuum distillation. Finally, PLA high polymer is continuously produced via a ring-opening polymerization of neat lactide using very low levels of tin catalyst. Two major advantages of this new synthetic process are that 1) the use of costly and environmentally unfriendly solvents is completely eliminated, and 2) all side streams can be recycled internally within the process.

Millions of pounds of PLA have been produced by this process in the CDP semiworks using lactic acid derived from both corn and sugar beets. Increasing market demand has prompted Cargill Dow Polymers LLC to plan the construction of a 250 MM lb/yr facility in 2001. The combination of versatile production capability and low-cost economics uniquely positions EcoPLA™ resins to be competitive with petrochemical-based plastics in a wide variety of applications—demonstrating that green chemistry can indeed make good business sense.

PPG Industries, Inc.

Replacement of Asbestos in the Diaphragm Cell Process for Manufacture of Chlorine and Caustic Soda

Approximately 75% of the chlorine and caustic soda (NaOH) produced in the United States (54 million lbs/day of chlorine and 58 million lbs/day of caustic soda) is made by the electrolysis of salt brine in diaphragm electrolysis cells. In these cells, salt dissolved in water is supplied as anolyte to an electrolysis cell consisting of an anode, a cathode, and a "diaphragm." Historically, asbestos is the material used as the diaphragm to maintain the critical separation of both the gas phase and liquid phase products.

PPG has developed the Tephram® nonasbestos diaphragm for use in diaphragm electrolysis cells for the production of chlorine and caustic soda. The Tephram diaphragm uses nonhazardous Teflon® fluoropolymer microfiber materials to replace asbestos. The Tephram diaphragm technology offers advantages in decreasing the complexity in handling raw materials (both asbestos itself and the corrosive chemicals used in asbestos diaphragm deposition) as well as in the disposal of asbestos materials at the end of their useful lives. Tephram diaphragms not only are easier to handle safely and are more environmentally friendly than asbestos diaphragms, but they also last much longer than asbestos diaphragms. At PPG's Lake Charles, Louisiana, chlor-alkali complex, an advantage in energy efficiency has also been demonstrated. These advantages of greater durability and efficiency combine to reduce cell renewal labor and consumption of both materials and energy.

Laboratory development at PPG's Chemicals Technical Center, and, over the last three years, full-scale demonstrations at PPG's Lake Charles, Louisiana, chemical complex, have demonstrated performance that has led to the decision to replace asbestos diaphragms in Lake Charles's largest chlorine production facility, Plant C, with the Tephram nonasbestos diaphragm.

Eka Chemicals, Inc.

SVP-Pure™ ClO_2 Process Technology

In the water and water-treatment industries, the need to reduce trihalomethane (THM) and haloacetic acid (HAA) formation, control taste and odor, remove soluble iron and manganese, and effectively eliminate bacteria and viruses has substantially increased the demand for chlorine dioxide. While several methods exist to generate ClO_2, previous technologies have been limited by low efficiencies, concern over unreacted chlorite, excess chlorine/hypochlorite, and cost. Eka's SVP-Pure™ ClO_2 process technology eliminates these concerns with its state-of-the-art aqueous sodium chlorate/acidic hydrogen peroxide process.

SVP-Pure™ is the first sodium chlorate based ClO_2 process to receive EPA registration for use as a disinfectant in drinking water and waste water. The two-chemical feed system adopts Eka Chemicals' patented hydrogen peroxide chemistry and applies a proprietary blend of sodium chlorate and hydrogen peroxide called Purate™. In comparison to competitive technologies, SVP-Pure™ chemistry requires no gaseous or liquid chlorine feed and no chloride ion addition. This process eliminates byproduct chlorine, thereby reducing the potential for the formation of THM, HAA, and chloroform disinfection byproducts. Eka Chemicals' proprietary reaction vessel design optimizes mixing of feed chemicals, yielding high conversion rates. Some technologies frequently overfeed the chlorine and chlorite precursor chemicals to meet the 95% efficiency standard that results in the pass-through of feedstock chemicals to the receiving water. In contrast, SVP-Pure™ incorporates a microprocessor-based electronic controller to regulate reactor feed, calculate efficiency, and control output. Fail-safe emergency shut-down logic programmed into the controller minimizes operator feedback requirements providing the safest, most user-friendly system.

Water-Based Synthesis and Purification of Mannich Base Modified Polyphenols

Henkel Surface Technologies

Polyphenol copolymers are common in industrial and consumer products. 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 (eliminating 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; biological and chemical oxygen demand and residual formaldehyde reductions; and the elimination of worker exposure to organic volatiles during manufacture.

The amount of organic solvent eliminated to date is greater than 500,000 lbs. This has been a great help to customers who need to meet ever-decreasing limits on the amount of volatile organic compounds emitted from their manufacturing plants. These products have been highly effective at reducing widespread heavy metal use in the past. The continued application of these new synthesis technologies today helps insure the continued development and wise use of these important polymers well into the future.

Yttrium as a Lead Substitute in Cationic Electrodeposition Coatings

PPG Industries, Inc.

In 1976, PPG Industries introduced the first Cationic Electrodeposition Primer to the automotive industry. During the succeeding years, this coating technology became widely used in the industry so that today, essentially all automobiles are given a primer coat using the chemistry and processing methods developed by PPG. The major benefits of this technology to the automotive industry are corrosion resistance, high transfer efficiency (low waste), reliable automated application, and very low volatile organic emissions. Unfortunately, the high corrosion resistance property of electrocoat has always been dependent on the presence of small amounts of lead salts or lead pigment in the product. For over 20 years, PPG and other paint companies have sought a substitute for lead in this application.

The electrocoat process itself complicates the problem of replacing lead in electrocoat primers. Most common corrosion-inhibitive materials interfere with the deposition process, are environmentally undesirable, or are not active when applied by electrodeposition. Also, a wide variety of metal substrates are used in the automotive industry. Inhibitors that work well over one substrate may not perform effectively over another. Furthermore, the performance of a given inhibitor is dependent on the quality of cleaning and pretreatment of the metal in question. Metal pretreatments have traditionally relied on nickel and chromium for corrosion performance and, like lead, these metals have also come under regulation and are often

removed or used sparingly in modern automotive applications. Thus, obtaining corrosion resistance over multiple substrates and treatments without lead is more difficult today than ever before.

During recent years, efforts at PPG to find new organic and inorganic corrosion inhibitors have identified yttrium as a potentially superior anticorrosive in the electrocoat primer application. This is based on several criteria. The pollution prevention assessment of yttrium performed in cooperation with the U.S. EPA shows yttrium to be of a low level of concern to aquatic organisms. In addition, yttrium is twice as effective as lead on a weight basis to produce the required corrosion performance. Thus, the levels of yttrium in commercial coatings will contain less than one-half the yttrium by weight relative to lead in comparably performing lead-containing products. Also, when the dust hazard of yttrium (as indicated by TLV) is compared to that of lead, it is roughly 100 times safer than lead at typical levels of use of each element. Last, it has been found that as yttrium is deposited in an electrocoat film, it deposits as the hydroxide. The hydroxide is converted to yttrium oxide during baking of the electrocoat. The oxide is extraordinarily nontoxic by ingestion as indicated from the LD50 of greater than 10 g/kg in rats.

Several commercial applications of this technology are in place, and qualification of yttrium containing formulations with Automotive OEM manufacturers is under way. As PPG customers implement yttrium over the next several years, approximately one million pounds of lead (as lead metal) will be removed from the electrocoat applications of PPG automotive customers. In addition, implementation of yttrium should result in the elimination of 25,000 pounds of chromium and 50,000 pounds of nickel (annually) for PPG pretreatment customers.

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