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The Presidential Green Chemistry Challenge Awards Program

Summary of 1997 Award Entries and Recipients

GREEN CHEMISTRY CHALLENGE

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President Clinton announced the Green Chemistry Challenge on March 16, 1995, as one of his Reinventing Environmental Regulations Initiatives. According to President Clinton, the Green Chemistry Challenge was established to "promote pollution prevention and industrial ecology through a new U.S. Environmental Protection Agency (EPA) Design for the Environment partnership with the chemical industry." More specifically, the program was established to recognize and support fundamental and innovative chemical methodologies that are useful to industry and that accomplish pollution prevention through source reduction.

EPA Administrator Carol Browner announced the Green Chemistry Challenge Awards Program on October 30, 1995. She described the program as an opportunity for individuals, groups, and organizations "to compete for Presidential awards in recognition of fundamental breakthroughs in cleaner, cheaper, smarter chemistry." The Green Chemistry Challenge Awards Program provides national recognition for technologies that incorporate green chemistry principles into chemical design, manufacture, and use.

Entries received for the 1997 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 1997 awards and nationally recognized on June 24, 1997.

This document provides summaries of the entries received for the 1997 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 1997 Presidential Green Chemistry Challenge Awards. They were edited for space, stylistic consistency, and clarity, but they were not written by nor are 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.

Alternative Synthetic Pathways Award

BHC Company

BHC Company Ibuprofen Process

BHC Company developed a new synthetic process to manufacture ibuprofen, a well-known, nonsteroidal, anti-inflammatory painkiller marketed under brand names such as Advil™ and Motrin™. Commercialized since 1992 in BHC's 3,500 metric-ton-per-year facility in Bishop, Texas, the new process was cited as an industry model of environmental excellence in chemical processing technology. For its innovation, BHC was the recipient of the Kirkpatrick Achievement Award for "outstanding advances in chemical engineering technology" in 1993.

The new technology involves only three catalytic steps, with approximately 80 percent atom utilization (virtually 99 percent including the recovered byproduct acetic acid) and replaces technology with 6 stoichiometric steps and less than 40 percent atom utilization. The use of anhydrous hydrogen fluoride as both a catalyst and solvent offers important advantages in reaction selectivity and waste reduction. As such, this chemistry is a model of source reduction, the method of waste minimization that tops EPA's waste management hierarchy. Virtually all starting materials are either converted to product or reclaimed byproduct, or are completely recovered and recycled in the process. The generation of waste is practically eliminated.

The BHC ibuprofen process is an innovative, efficient technology that revolutionized bulk pharmaceutical manufacturing. The process provides an elegant solution to a prevalent problem encountered in bulk pharmaceutical synthesis (i.e., how to avoid the large quantities of solvents and wastes associated with the traditional stoichiometric use of auxiliary chemicals when effecting chemical conversions). Large volumes of aqueous wastes (salts) normally associated with such manufacturing are virtually eliminated. The anhydrous hydrogen fluoride catalyst/solvent is recovered and recycled with greater than 99.9 percent efficiency. No other solvent is needed in the process, simplifying product recovery and minimizing fugitive emissions. The nearly complete atom utilization of this streamlined process truly makes it a waste-minimizing, environmentally friendly technology.

Alternative Solvents/Reaction Conditions Award

Imation

DryView™ Imaging Systems

Photothermography is an imaging technology whereby a latent image, created by exposing a sensitized emulsion to appropriate light energy, is processed by the application of thermal energy. Photothermographic films are easily imaged by laser diode imaging systems, with the resultant exposed film processed by passing it over a heat roll. A heat roll operating at 250 °F in contact with the film will produce diagnostic-quality images in approximately 15 seconds. Based on photothermography technology, Imation's DryView™ Imaging Systems use no wet chemistry, create no effluent, and require no additional postprocess steps such as drying.

In contrast, silver halide photographic films are processed by bathing them in a chemical developer, soaking them in a fix solution, washing them with clean water, and finally drying them. The developer and fix solutions contain toxic chemicals such as hydroquinone, silver, and acetic acid. In the wash cycle, this chemistry, along with silver compounds, is flushed from the film and becomes part of the waste stream. The resulting effluent amounts to billions of gallons of liquid waste each year.

Significant developments in photothermographic image quality have been achieved that allow it to successfully compete with silver halide technology. During 1996, Imation placed more than 1,500 DryView™ medical laser imagers, which represent 6 percent of the world's installed base. These units alone have eliminated the annual disposal of 192,000 gallons of developer, 330,000 gallons of fixer, and 54.5 million gallons of contaminated water into the waste stream. As future systems are placed, the reductions will be even more dramatic.

DryView™ technology is applicable to all industries that process panchromatic film products. The largest of these industries are medical radiography, printing, industrial radiography, and military reconnaissance. DryView™ is valued by these industries because it supports pollution prevention through source reduction.

Designing Safer Chemicals Award

Albright & Wilson Americas

THPS Biocides: A New Class of Antimicrobial Chemistry

Conventional biocides, used to control the growth of bacteria, algae, and fungi in industrial cooling systems, oil fields, and process applications, are highly toxic to humans and aquatic life and often persist in the environment, leading to long-term damage. To address this problem, a new and relatively benign biocide, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), has been discovered by Albright & Wilson Americas. THPS biocides represent a completely new class of antimicrobial chemistry that combines superior antimicrobial activity with a relatively benign toxicology profile. THPS's benefits include low toxicity, low recommended treatment level, rapid breakdown in the environment, and no bioaccumulation. When substituted for more toxic biocides, THPS biocides provide reduced risks to both human health and the environment.

THPS is so effective as a biocide that, in most cases, the recommended treatment level is below that which would be toxic to fish. In addition, THPS rapidly breaks down in the environment through hydrolysis, oxidation, photodegradation, and biodegradation. In many cases, it substantially breaks down before the treated water enters the environment. The degradation products have been shown to possess a relatively benign toxicology profile. Furthermore, THPS does not bioaccumulate and, therefore, offers a much reduced risk to higher life forms.

THPS biocides are aqueous solutions and do not contain volatile organic compounds. Because THPS is halogen-free, it does not contribute to dioxin or AOX formation. Because of its low overall toxicity and easier handling when compared to alternative products, THPS provides an opportunity to reduce the risk of health and safety incidents.

THPS has been applied to a range of industrial water systems for the successful control of microorganisms. The U.S. industrial water treatment market for nonoxidizing biocides alone is 42 million pounds per year and growing at 6 to 8 percent annually. There are over 500,000 individual use sites in this industry category. Because of its excellent environmental profile, THPS has already been approved for use in environmentally sensitive areas around the world and is being used as a replacement for the higher risk alternatives.

Small Business Award

Coldstrip™, A Revolutionary Organic Removal and Wet Cleaning Technology

Legacy Systems, Inc.

For over 30 years, the removal of photoresists with Piranha solutions (sulfuric acid, hydrogen peroxide, or ashers) has been the standard in the semiconductor, flat panel display, and micromachining industries. Use of Piranha solutions has been associated with atmospheric, ground, and water pollution. Legacy Systems, Inc. (LSI) has developed a revolutionary wet processing technology, Coldstrip™, that removes photoresist and organic contaminants for the semiconductor, flat panel display, and micromachining industries. Coldstrip™ uses only water and oxygen as raw materials.

LSI's Coldstrip™ process is a chilled ozone process that uses only oxygen and water as the raw materials. The active product is ozone, that safely decomposes to oxygen in the presence of photoresist. Carbon dioxide, carbon monoxide, oxygen, and water are formed. There are no high temperatures, no sulfuric acid, no hydrogen peroxide, and no nitric acid, all of which cause environmental issues.

The equipment required for the chilled ozone process consists of a gas diffuser, an ozone generator, a recirculating pump, a water chiller, and a process vessel. The water solution remains clear and colorless throughout the entire process sequence. There are no particles or resist flakes shed from the wafer into the water; therefore, there are no requirements for particle filtration.

Using oxygen and water as raw materials replacing the Piranha solutions significantly benefits the environment. One benefit is the elimination of over 8,400 gallons of Piranha solutions used per year per silicon wet station and over 25,200 gallons used per year per flat panel display station. Additionally, the overall water consumption is reduced by over 3,355,800 gallons per year per silicon wafer wet station and over 5,033,700 gallons per year per flat panel display station. The corresponding water consumption in LSI's process is 4,200 gallons per year and there is no Piranha use.

In 1995, the U.S. Patent Office granted LSI patent 5,464,480 covering this technology. The system has the lowest environmental impact of any wet resist strip process, eliminating the need for thousands of gallons of Piranha chemicals and millions of gallons of water a year.

Academic Award

Professor Joseph M. DeSimone, University of North Carolina at Chapel Hill and North Carolina State University

Design and Application of Surfactants for Carbon Dioxide

One dilemma of modern industrial technology is that the solvents required to dissolve the environment's worst contaminants themselves have a contaminating effect. Now, new technologies for the design and application of surfactants for carbon dioxide (CO_2), developed at the University of North Carolina at Chapel Hill (UNC), promise to resolve this dilemma.

Over 30 billion pounds of organic and halogenated solvents are used worldwide each year as solvents, processing aids, cleaning agents, and dispersants. Solvent-intensive industries are considering alternatives that can reduce or eliminate the negative impact that solvent emissions can have in the workplace and in the environment. CO_2, in a solution state, has long been recognized as an ideal solvent, extractant, and separation aid. CO_2 solutions are nontoxic, nonflammable, safe to work with, energy-efficient, cost-effective, waste-minimizing, and reusable. Historically, the prime factor inhibiting the use of this solvent replacement has been the low solubility of most materials in CO_2, both in its liquid and supercritical (sc) states. With the discovery of CO_2 surfactant systems, Professor DeSimone and his students have dramatically advanced the solubility performance characteristics of CO_2 systems for several industries.

The design of broadly applicable surfactants for CO_2 relies on the identification of 'CO_2-philic' materials from which to build amphiphiles. Although CO_2 in both its liquid and supercritical states dissolves many small molecules readily, it is a very poor solvent at easily accessible conditions (e.g., T less than 100 °C and P less than 300 bar) for many substances. As an offshoot of Professor DeSimone's research program on polymer synthesis in CO_2, he and his researchers exploited the high solubility of a select few CO_2-philic polymeric segments to develop nonionic surfactants capable of dispersing high solids polymer latexes in both liquid and sc CO_2 phases. The design criteria they developed for surfactants, which were capable of stabilizing heterogeneous polymerizations in CO_2, have been expanded to include CO_2-insoluble compounds in general.

This development lays the foundation by which surfactant-modified CO_2 can be used to replace conventional (halogenated) organic solvent systems currently used in manufacturing and service industries such as precision cleaning, medical device fabrication, and garment care as well as in the chemical manufacturing and coating industries.

Entries From Academia

Biocatalysis/The Use of Genetically Manipulated Microbes as Synthetic Catalysts

Professor W. John Frost, Department of Chemistry, Michigan State University

Professor Karen M. Draths, Department of Chemistry, Michigan State University

Fundamentally changing chemical syntheses, as opposed to incremental changes in currently practiced syntheses, is one strategy for ensuring that environmental improvement does not occur at the expense of global, economic competitiveness. Examples of this design principle are found in the syntheses of adipic acid and catechol created by John W. Frost and Karen M. Draths as well as in this research team's elaboration of the antioxidant activity of 3-dehydroshikimic acid (DHS). In excess of 1.9 x 10^9 kg of adipic acid is annually produced and used in the manufacture of nylon 66. Most commercial syntheses of adipic acid use benzene as the starting material. Approximately 2.1 x 10^7 kg of catechol is globally produced each year. Catechol is an important chemical building block used to synthesize flavors, pharmaceuticals, agrochemicals, and polymerization inhibitors and antioxidants. Although some catechol is distilled from coal tar, petroleum-derived benzene is the starting material for most catechol production. The Frost-Draths syntheses of adipic acid and catechol rely on the use of genetically manipulated microbes as synthetic catalysts. Nontoxic glucose is employed as a starting material that, in turn, is derived from renewable feedstocks such as plant starch. In addition, water is used as the primary reaction solvent, and generation of toxic intermediates and environment-damaging byproducts is avoided.

Biomimetic Transition Metal Complexes for Homogeneous Catalytic Reductive Dechlorination of the PCBs/One-Step Extraction-Detoxification in Subcritical and Supercritical Fluids

Dr. Charles M. King, Department of Chemistry, University of Georgia

Dr. R. Bruce King, Department of Chemistry, University of Georgia

Polychlorinated biphenyls (PCBs) are ubiquitous in the global environment, toxic, and generally nonbiodegradable. A family of homogeneous catalysts has been developed at the University of Georgia for the conversion of PCBs to dechlorinated congeners and nontoxic biphenyl by a hydrogenolysis process known as reductive dechlorination (RD). This unique green chemistry has been demonstrated to occur at room temperature due to the high reactivity of the homogeneous transition metal catalysts used for activation of the carbon chlorine bond. The organophosphorus transition metal complexes used for catalysis also are extractable in subcritical solvents used for PCB extraction from soils, sediments, and animal and human tissue matrices. Hence, coextraction of PCBs and the transition metal catalyst has been demonstrated, leading to dechlorination and detoxification of the PCB mixture in one step. This process is compatible with chemical engineering unit operations for countercurrent continuous liquid extraction, as practiced in the chemical industry.

Professor Richard A. Gross, Department of Chemistry, University of Massachusetts—Lowell

Dr. David L. Kaplan, Department of Chemical Engineering, Tufts University

Biotechnological Routes to 'Tailored' Polymeric Products of Environmental and Industrial Importance

Microbial polymerizations offer the potential for the discovery of important new routes to polymers and materials from renewable resources that involve all aqueous, green chemical routes. A critical problem limiting the utility of such methods is the inability to control product structural variables that ultimately determine functional properties. The work of Richard A. Gross has led to the development of a family of technologies that demonstrated unprecedented levels of control for nonribosomal mediated microbial polymerizations. Lipoheteropolysaccharides have been prepared from renewable resources, and innovative methods were developed to control the product's fatty acid structure and the degree of substitution. This has led to a diverse family of new biodegradable bioemulsifiers that have wide applicability for the stabilization of oil/water emulsions in cleaning and degreasing formulations, biocosmetics, green coating technologies, and bioremediation of organic pollutants. A second technology area has used polyethylene glycols to regulate microbial polyester molecular weight, repeat unit composition, and alter repeat unit sequence distribution. Furthermore, this strategy can be used to form microbial polyester-polyethylene glycol diblock copolymers. It is now possible, therefore, to consider the in-vivo preparation of synthetic-natural diblocks. This technology created a number of opportunities for the preparation of completely biodegradable interfacial agents for blends, the termination of chains with reactive end-groups for coupling pharmacologically active molecules, and the engineering of surfactant molecules. A third technology area has been the development of new fermentation routes to anionic γ-poly(glutamic acid) from renewable resources such as glucose. These routes have the potential to replace millions of pounds of anionic polymers, such as polyacrylic acid, which is nonbiodegradable and persistent in nature.

Professor Alan T. Hatton, Department of Chemical Engineering, Massachusetts Institute of Technology

Professor Stephen L. Buchwald, Chemistry Department, Massachusetts Institute of Technology

Linda K. Molnar, Department of Chemical Engineering, Massachusetts Institute of Technology

Derivatized and Polymeric Solvents for Minimizing Pollution During the Synthesis of Pharmaceuticals

A new class of solvents has been developed that has solvation properties similar to those of solvents used conventionally in chemical synthesis, separations, and cleaning operations, but for which the potential for loss by environmentally unfavorable air emissions or aqueous discharge streams is minimized. These alternative solvents are derivatives of solvents currently used in reaction and separation processes, tailored so that they are relatively nonvolatile and nonwater soluble, thereby satisfying the criteria for pollution source reduction. The solvents can be used as neat reaction or separation media, or they can be diluted in an inert environment such as in higher alkanes. Polymeric or oligomeric solvents have been synthesized using macromonomers incorporating the desired solvent functionality. These polymeric solvents are easily recovered using mechanical separations such as ultrafiltration rather than energy-intensive distillation processes. This new concept for the design and synthesis of solvents offers the potential for significant source reductions in air and water pollution and can be considered to be widely applicable to fine chemical and pharmaceutical synthesis, separations, and cleaning operations. It is expected to reduce the complexity of downstream processing options considerably and lead to energy efficient reaction/separation sequences.

Environmental Advantages Offered by Indium-Promoted Carbon-Carbon Bond-Forming Reactions in Water

Dr. Leo A. Paquette, Department of Chemistry, Ohio State University

In view of increasing demands to reduce emissions during the production of chemical and pharmaceutical end-products, it is imperative to consider the development of effective carbon-carbon bond forming reactions in aqueous media. The work of Dr. Paquette demonstrates not only that the counter-intuitive notion of organometallic carbon-carbon bond-forming reactions performed in water is indeed workable but also that high levels of stereocontrol are attainable. The key to this safe, environmentally friendly technology is the utilization of metallic indium as the promoter. The metal indium, a relatively unexplored element, has recently been shown to offer intriguing advantages for promoting organic transformations in aqueous solution. The feasibility of performing organometallic/carbonyl condensations in water, for example, has been amply demonstrated for the metal indium. Indium is nontoxic, very resistant to air oxidation, and easily recovered by simple electrochemical means, thus permitting its reuse and guaranteeing uncontaminated waste flow. The power of the synthetic method, which often can exceed performance levels observed in purely organic solvents, includes no need for protecting groups, greatly enhanced ease of operation, and greatly reduced pollution risks.

Environmentally Benign Approach to Chemical Processing Using Microwave Irradiation Under Solvent-Free Conditions

Dr. Rajender S. Varma, Department of Chemistry and Texas Regional Institute for Environmental Studies, Sam Houston State University

An environmentally benign approach was developed by Rajender S. Varma that utilizes microwave activation of neat reactants either in the presence of a catalyst or catalyzed by the surfaces of recyclable support(s) such as alumina, silica, clay, and 'doped' surfaces, namely, $NaIO_4$-silica, iron(III)nitrate-clay (clayfen) and Envirocats® reagents under solvent-free 'dry' conditions, thus promoting 'at source' reduction of solvents and excess chemicals in manufacture. This pollution prevention strategy has been targeted to industrially significant cleavage, condensation, oxidation, and cyclisation reactions that currently employ toxic, corrosive, and irritant chemicals, and generate hazardous waste. This technology uses material science, molecular modeling and synthetic organic chemistry expertise, and addresses the needs of the broad chemical community (e.g., polymer, pharmaceutical, and fine chemical) by efficient production of valuable intermediates (e.g., enones, imines, enamines, nitroalkenes, oxidized sulfur species, and heterocycles). Further, the technology teaches the pollution prevention theme to younger generations of scientists and extends to in situ destruction of pollutants and hazardous waste.

Environmentally Benign Supramolecular Assemblies of Hydroquinones in Polaroid Instant Photography

Dr. John Warner, Department of Chemistry, University of Massachusetts—Boston

Polaroid Corporation

This technology represents the first example of supramolecular synthesis in a manufacturing system for pollution prevention. Using the concepts of molecular recognition and self-assembly, a new technique has been developed for the control of molecules within films and coatings. This process has a number of environmental benefits including reduced synthetic steps, reduced waste generation, reduced solvent usage, and the introduction of solventless or aqueous processing. Instead of performing several time consuming, solvent-based, chemical reactions in order to synthesize a series of candidate compounds for structure activity studies, this technique allows for the addition of simple, inexpensive, readily available 'complexing reagents.' For this to be successful as pollution prevention, these assemblies must significantly reduce the number of synthetic reactions carried out. Often the formation of these assemblies involve no organic solvents. The supramolecular structures can be constructed via solid state grinding or aqueous dispersing techniques.

Professor Marc A. Anderson, Water Chemistry Program, University of Wisconsin-Madison

Green Technology for the 21st Century: Microporous Ceramics

The Green Technology for the 21st Century: Microporous Ceramics program is dedicated to both the fundamental understanding and practical environmental applications of microporous ceramic materials. These materials are typically used as thin porous films on a variety of supports for numerous applications. Such films are composed of nano-particulate oxides (i.e., 0.5 to 10 nm in diameter) that are either randomly close-packed to form membranes (i.e., 30 percent porosity) or more loosely packed to form catalysts, photocatalysts, and thin film energy storage devices. Because the particle size, surface chemistry, and particle packing of these oxides can be controlled, so can the pore size, pore size distribution, and the physical-chemical properties of these materials. As a result, the properties of these materials can be tailored for given applications which include reverse osmosis and gas separation membranes; high temperature membrane reactors; size and shape selective photolysis membranes; low temperature deep-oxidation catalysts; room temperature photocatalysts; and energy storage devices such as thin film batteries, ultracapacitors, and fuel cells. The Green Technology for the 21st Century: Microporous Ceramics program is illustrated using three examples: an indoor air cleaner for the complete oxidation of volatile organic compounds; an inorganic photoreactor for the size and shape selective synthesis of desired compounds with a minimum of waste; and, finally, an inexpensive, thin film ultracapacitor which exceeds the U.S. Department of Energy's near-term goal for this type of energy storage device.

Professor Larry T. Taylor, Department of Chemistry, Virginia Tech

Virginia Tech Intellectual Properties

A Nontoxic Liquid Metal Composition for Use as a Mercury Substitute

Mercury is used extensively in switches and sensors, but it is toxic to humans and animals. In addition to being an excellent conductor of electricity, mercury has significant surface tension and, unlike any other metal known, remains fluid throughout a wide temperature range which encompasses 0 °C. Because of these properties, mercury is found in numerous commercial products such as automobiles, thermostats, steam irons, pumps, computers, and even in tennis shoes. In each of these cases, mercury functions as a liquid electrical switch. Since billions of mercury switches are made worldwide each year, a nontoxic replacement appears highly desirable. A nontoxic, cost-effective alternative to mercury that has comparable performance characteristics has been identified at Virginia Tech. This green technology provides a gallium alloy containing indium, zinc, and copper that conducts electricity, freezes below 0 °C, exhibits high surface tension, and possesses a very high boiling point and very low vapor pressure. In addition, nonmercury switches and sensors can replace mercury switches and sensors without modifying existing technology. Mercury also is used in temperature sensors, pressure activated switches, pumps and filters, slip rings, liquid mirror telescopes, fluid unions, dental amalgam, and in medical devices such as sphygmomanometers and bougies. The nonmercury material also can serve as a substitute for elemental mercury in a many of these applications.

Rational Design of Catalytic Reactions for Pollution Prevention

Professor James A. Dumesic, Chemical Engineering Department, University of Wisconsin at Madison

Dr. John C. Crittenden, National Center for Clean Industrial and Treatment Technologies, Michigan Technological University

Chemical products manufacturing is a major industrial source of toxic and hazardous chemicals. Catalytic technologies hold the key to the development of more environmentally benign chemical processes and for the continued improvement of existing processes. Historically, the design of chemical synthesis catalysts was extraordinarily empirical. Yields of desired products and operational characteristics were normally optimized based on suites of experiments run on catalysts made from various manufacturing conditions and blends. The ability to correlate catalyst behavior to catalyst surface features was extremely limited. Accordingly, predicting the desired catalyst features for a given application and, from that, formulating a catalyst manufacturing strategy, was essentially beyond reach. Moreover, the concept of redesigning catalysts so as to inhibit the formation of undesired coproducts, toxic materials, and wasteful pollutants was fanciful. A methodology for Rational Catalyst Technologies was developed at the University of Wisconsin that makes it possible to design and optimize catalysts by first understanding the nature of the desired catalyst surface and, from that, formulating the catalyst. This strategy for the rational design of catalytic reactions has found acceptance worldwide and has been applied successfully to link surface science research to the development of industrially important catalytic chemical reactions. Industrial collaborations or applications include ammonia catalysis, the environmental deNOx reaction, the water gas shift reaction on magnetite, titania surface species, molybdena and vanadia catalysts for clean partial oxidation of methane, and hydrocarbon cracking over acid Y-zeolite catalysts for the clean production of isobutylene.

The Replacement of Hazardous Organic Solvents with Water in the Manufacture of Chemicals and Pharmaceuticals

Dr. Henry Shaw, Chemistry and Environmental Science Department, New Jersey Institute of Technology

Dr. Daniel J. Watts, Center for Environmental Engineering and Science, New Jersey Institute of Technology

The use of water as the primary solvent is a realistic approach to green chemistry and is a very desirable approach for reducing hazardous organic solvents from plant inventories. Multiphase reactors have been developed at the New Jersey Institute of Technology and other universities that use water as the reaction medium in order to avoid the use of hazardous organic solvents in the manufacture of pharmaceuticals and specialty chemicals. This is the first technology to show that free radical bromination of organics can be carried out in aqueous systems. A unique semicontinuous droplet reactor also has been developed for epoxidations. Before pollution prevention became fashionable, organic chemists found that water-based reactions gave higher yields at faster rates under milder conditions than organic solvent-based reactions. This is incentive enough for process change. The fact that these methods offer a new 'non-end-of-pipe' method of eliminating volatile organic compounds adds a major incentive for process modification.

The SYNGEN Program for Generation of Alternative Syntheses

Professor James B. Hendrickson, Department of Chemistry, Brandeis University

The SYNGEN program attempts to survey all possible synthetic routes to a target molecule and reduce the vast number of these possibilities quickly and stringently to focus on only the shortest and cheapest routes. The program first focuses on minimizing steps and the central role of prior skeletal dissection to find the best assemblies of the target skeleton from available starting skeletons. It then presents the ideal synthesis, of construction reactions only, to create the target just by sequential constructions uniting these starting skeletons. Finally, the digital basis rigorously, but concisely, defines all possible molecular structures and their reactions. This basis allows the new SYNGEN program to propose all of the short alternative syntheses of any product from real starting materials, in terms of both their cost and environmental impact.

Professor Tomas Hudlicky, Department of Chemistry, University of Florida

Synthetic Methodology 'Without Reagents.' Tandem Enzymatic and Electrochemical Oxidations and Reductions in the Manufacture of Pharmaceuticals

The prevention of pollution at its source is addressed by the replacement of currently used methods of oxidation and reduction (all based on metal reagents) with enzymatic and electrochemical techniques (all performed in water, alcohols, or other environmentally acceptable solvents). The combination of enzymatic transformations with electrochemistry, along with efficient design, yields unprecedented brevity in the attainment of important pharmaceuticals from metabolites of 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. 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. The nomination describes the strategy, logic, execution, and future projection of this program, which has potential global impact with attendant benefits to the health and economy of society through managed processing of aromatic waste to valuable substances. Several patents have already been granted on more efficient synthesis of pharmaceutical entities.

Professor David E. Nikles, Department of Chemistry, University of Alabama

Professor J.W. Harrell, Department of Physics & Astronomy, University of Alabama

Professor Alan M. Lane, Department of Chemical Engineering, University of Alabama

Professor I.A. Jefcoat, Department of Chemical Engineering, University of Alabama

Waterborne Coating Applications for Video Tape Manufacture

Magnetic tape technology is an important component of the information age and maintaining a domestic tape manufacturing capability is important to the U.S. economy. Magnetic tape is manufactured by a continuous web coating process that uses organic solvents, including tetrahydrofuran, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), toluene and cyclohexanone. MEK, MIBK, and toluene are on the list of 189 hazardous air pollutants and on the list of 18 chemicals for the EPA's 33/50 voluntary pollution reduction program. Waterborne magnetic tape coating formulations were designed at the University of Alabama and used to prepare experimental magnetic tape samples in a pilot coating trial. The formulations contained a blend of a water-dispersed polyester and an ethylene/vinyl chloride copolymer emulsion. The coatings were thermally cured with a melamine-formaldehyde cross-linker to give tensile properties that were comparable to a standard solvent-based binder composition. The pilot tape trial used existing processing equipment, including calendering and slitting. The tape had good magnetic properties and excellent adhesion between the pigmented magnetic layer and the base film, easily exceeding the 8 mm helical scan tape standard of 0.96 N peel force. An economic impact analysis for the case of using the waterborne video tape coating process in a conventional tape manufacturing plant showed an 11 percent decrease in hourly operating costs. The solvent-based process generated almost 650 kg of organic solvent per hour operation, while the waterborne process generated less than 5 kg methanol (from the melamine-formaldehyde cross-linker) per hour. In addition to pollution prevention, there was a clear economic incentive to adopt the waterborne video tape manufacturing process.

Entries From Small Businesses

Catalytic Extraction Processing (CEP)

Molten Metal Technology, Inc.

Catalytic Extraction Processing (CEP) is a proprietary technology that uses secondary materials and byproducts (that might otherwise be considered 'wastes') as raw materials in a manufacturing process. CEP manufactures commercial products (i.e., industrial gases, alloys, and ceramics) from heterogeneous organic, organometallic, and inorganic materials using a molten metal bath as both a catalyst for elemental dissociation and a solution for reaction engineering. CEP feed materials go through two stages in the metal bath: dissociation and dissolution of molecular entities to their elements and reaction of these elemental intermediates to form products. The waste minimization and environmental performance of CEP is ensured by the separation of feed from product through elemental dissociation and the predictable partitioning afforded by the control of thermodynamic operating conditions. Employed as an offsite, closed-loop process unit, CEP maximizes environmental performance for a broad spectrum of secondary materials and byproducts through pollution prevention, waste minimization, and decreased demand on ever-diminishing natural resources.

Cross-Linked Enzyme Crystals (CLECs) as Robust and Broadly Applicable Industrial Catalysts

Altus Biologics Inc.

Enzymes are proteins that function as highly efficient and selective catalysts. Enzymes are responsible for the biochemical reactions that are essential to life, and as such, they are unique in their intrinsic compatibility with living organisms. Their potential as safe and efficient industrial catalysts has been long recognized, but to date, enzymes have not exhibited the chemical and physical stability associated with more conventional, small-molecule organic and inorganic heterogeneous catalysts. Altus Biologics has developed a conceptually simple and broadly applicable solution to this fundamental problem–the formulation of enzymes in a cross-linked crystalline form–that enables enzyme use under the harsh chemical, physical, and mechanical conditions that characterize most practical industrial processes. To date, more than 20 enzymes have been formulated as CLECs and have demonstrated their utility on a pilot scale: as industrial catalysts, in consumer products such as detergents and cosmetics, as medical and process biosensors, and in the decontamination of waste and hazardous chemicals including insecticides and nerve agents. Two applications out of this broad portfolio of uses are described–the CLEC-catalyzed syntheses of the dipeptide artificial sweetener aspartame and of the semi-synthetic b-lactam cephalosporin antibiotic cephalexin. In these applications, an enhancement in synthetic efficiency has been demonstrated, with dramatic source reductions in the waste streams associated with these processes. In addition to the potential broad impact of the crosslinked enzyme crystal technology on source reduction, widespread application of CLECs might also serve to leverage America's investment in the area of molecular biology beyond the preeminence already established in the biotechnology industry prototype. Novel, though otherwise impractical, enzymes derived from that technological base could, through their stabilization as CLECs, lead to a penetration and dominance of the much larger and employment-intensive commodity- and fine-chemical manufacturing industry; driven by the economic benefits derived from the implementation of more efficient, competitive, and 'greener' chemical manufacturing options.

Benchmark Products, Inc.

Development of a Nickel Brightener Solution

Historically, electroplaters of duplex nickel had to use formaldehyde and coumarin-bearing nickel plating solutions to obtain a nonsulfur nickel deposit, which is essential to the duplex nickel process, for maximum corrosion protection of external automotive trim and bumpers. The Watts' bath, introduced in 1916, made it possible to increase the speed of nickel deposit by a factor of ten by increasing the electrical current density. This development lead to the bright nickel plating baths known today, which use organic and inorganic additives. Organic aromatic sulfonic acid was later introduced to the Watts' bath to achieve the first practical bright nickel plating solution. In 1936, formaldehyde was added to the solution followed in rapid succession by other additives. Coumarin, along with formaldehyde, became the important ingredients in a variety of nickel plating baths referred to as 'semibright'. Today, semibright nickel plating occupies an important position in plating. Benchmark Products has developed a nickel brightener solution that, while improving the performance of electroplating, also significantly reduces the environmental impact by eliminating two toxic ingredients, formaldehyde and coumarin, and substituting nonhazardous ingredients.

Circuit Research Corporation

A Nontoxic, Nonflammable, Aqueous-Based Cleaner/Degreaser and Associated Parts Washing Systems Commonly Employed in the Automotive Repair Industry

Circuit Research Corporation developed an aqueous based cleaner and associated parts washing system commonly employed in the automotive repair industry that eliminates the generation of hazardous waste associated with current parts washing systems. Currently, the majority of parts washers employ a 'Stoddard Solvent,' which, when spent, is manifested as a hazardous waste to a distillation facility that separates the solvent from the petroleum residue. The new technology employs a nontoxic, nonflammable, aqueous-based cleaner/degreaser that can be recycled continuously on site by employing oil/water separation and standard combustion engine filters. Both the oil separation and filtration apparati are housed within a recently developed parts washer unit, such that the aqueous cleaner/degreaser is recycled in-situ, eliminating the removal or transportation and special treatment of spent cleaner material off site. Testing results have shown that: (1) the resulting oil skimmed from the cleaner can, under current hazardous waste definitions, be managed as a 'spent oil' and combined with spent engine oil for beneficial reuse as a secondary fuel, and (2) the filter can be managed under current methods used to recycle other used combustion engine oil filters. Circuit Research Corporation believes there are in excess of 7,000 parts washers in Minnesota generating approximately 1.5 million gallons of spent Stoddard Solvent annually. Circuit Research Corporation's alternative technology could significantly reduce the generation of this waste.

Radiance Services Company

The Radiance Process: A Quantum Leap in Green Chemistry

The Radiance Process, a new water- and chemical-free method of cleaning surfaces, is a powerful alternative to existing wet chemical processes that use detergents; organic solvents, including CFCs and their successors; and acid or alkaline reagents. The Radiance Process employs the quantum mechanical effects of laser light and an inert gas, ordinarily nitrogen, to clean surfaces. The light lifts the contaminant from the surface and the flowing gas sweeps it away. There is no pollution and no waste besides the removed contaminant itself. The Radiance Process will lead to significant human health and environmental benefits through source reduction by reducing toxicity, flammability, explosion potential, emissions, discharges, use of hazardous substances in reaction conditions, the transport of hazardous substances, and the creation of hazardous wastes. The process is inexpensive and readily adaptable to many manufacturing needs. The process has been demonstrated on a broad range of products including semiconductor materials, such as silicon wafers and chrome on quartz photomasks, and industrial metals such as tire molds, fuel injectors, brass fixtures, and metal beverage containers. *Semiconductor International* called Radiance a "breakthrough." *Advancing Microelectronics* called it "radical." *Futuretech* called it "indispensable." In December 1995, the Radiance Process was selected by *IndustryWeek* magazine as a Technology of the Year, one of only five, calling it "revolutionary." Radiance provides the ultimate Green Chemistry by completely eliminating the need for chemicals in cleaning while achieving equal or superior results at a lower cost.

SuperC™, The Use of Supercritical Carbon Dioxide

Materials Technology Limited

The process SuperC™ permanently consumes large quantities of carbon dioxide (CO_2) to make less-expensive, more durable, fully recyclable products from industrial wastes or ordinary cements. Even earth will serve as a material. SuperC™ is an economical answer to global warming and large-scale pollution. It employs simple reactions to sequester CO_2, preventing it from entering the atmosphere. It provides lower cost alternatives to forest products, steel, aluminum, plastics, composites, and ceramics by using industrial waste streams as feedstocks. It can lengthen the service life of new, and even restore existing, concrete structures and infrastructures. It can stabilize cemented mixed and high-level nuclear waste to facilitate long-term storage without further chemical evolution. Implementation/conversion requires minimal capital investment. The process uses supercritical CO_2 (at greater than 88.3 °F and greater than 1,071 PSI) to infiltrate fully formed products made from wastes like fly ash, blast furnace slag, dust, clay, or from common cements, to produce almost any desired properties or behaviors. In this state, CO_2 behaves as a super solvent. Products made this way cost less, are equal or superior in performance to those made in traditional ways, and are fully recyclable without manual segregation. They displace products made from higher energy or ecologically sensitive materials, and reduce environmental impact, health concerns, and fossil fuel consumption.

Utilization of High Performance, Environmentally Compliant Chemicals: GREEN LINE Adhesive, Sealant, and Coating Technologies

American Chemical Corporation

Astutely aware of the national strategy for protecting the environment and promoting energy efficiency in buildings, American Chemical Corporation developed the GREEN LINE, a complete stock of specialty adhesives, sealants, and coatings that utilize environmentally compliant polyvinyl acetate (PVA), acrylic, latex, and epoxy resins technologies. All methodologies meet Best Available Technology (BAT) standards for minimizing VOC exposure, health risks, and hazardous handling practices. Concurrent with the technical development of GREEN LINE products was the conceptualization of Cost Benefit Algorithms and Dynamic Labeling, which permit federal managers to determine the degree of 'green' compliance of the core materials used to manufacture the products and of the environmental improvements intended by use of such materials. Federal managers and their staffs are provided with reliable information that can help them make energy-saving, water-conserving, and maintenance improvements that solve environmental problems and provide for worker safety. GREEN LINE products have been successfully used to (1) reduce both energy use and the environmental impacts of HVAC and air handling distribution system repairs and upgrades, (2) conserve potable water resources by facilitating the repair and rehabilitation of treatment, storage, and distribution systems, and (3) repair U.S. Naval ship structures.

Klenzoid, Inc.

Zero Discharge System For Cooling Towers

The Zero Discharge system is a complete packaged water treatment system to control corrosion deposition and biological fouling with no water discharge (commonly known as 'bleed-off') from the system. This bleed-off is widely used by conventional water treatment programs to dilute the concentration of natural minerals in the water to prevent precipitation. In the Zero Discharge system, the recirculating cooling tower water is filtered by a side-stream filtration system to remove suspended solids. A microprocessor control monitors the prescribed characteristic of the recirculating water through sensors installed in a sample stream. The control maintains a programmed pH in the recirculating water along with prescribed levels of chemical treatment through actuation of chemical feed pumps. With these levels being maintained and monitored, the microprocessor, using stored tabular data, calculates the calcium content necessary to maintain a zero Langelier Saturation Index. The level of calcium is adjusted accordingly by regulating the flow of untreated raw water supplied to the tower as make-up through a bypass of a calcium removal (e.g., water softener or deionizer) system on the make-up water line. The health and environmental benefits of the Zero Discharge system are the result of the water saved and the significant reduction of chemicals discharged to the environment. The Zero Discharge system was patented in the early 1990s and has since been extensively applied in the metropolitan Philadelphia area. In total, about 30,000 tons of cooling water are being treated by the Zero Discharge system, which saves about 132 million gallons of water in the Philadelphia area annually.

Entries From Industry and Government

AGROTAIN® *N-(n-butyl) Thiophosphoric Triamide*

IMC-Agrico Company

Urea is now the favored form of solid nitrogen-containing fertilizer and is rapidly displacing anhydrous ammonia in the nitrogen fertilizer market. The market share of world nitrogen consumption has risen from 5 percent in 1962 to 37 percent in 1986 for urea. There are many reasons for this increase. Urea is a source of nitrogen for crop fertilization that is easily handled and transported, higher in nitrogen content than other common solid nitrogen fertilizers, and can be readily bulk blended with other fertilizer components, such as potassium chloride, diammonium phosphate, and other materials, to prepare multinutrient fertilizers. While urea has many advantages over other nitrogen sources and has already captured a greatly increasing market share, a major drawback to the use of urea is its tendency to lose a substantial portion of the nitrogen values by ammonia volatilization. These losses can easily exceed 30 percent of the available nitrogen in urea under certain climatic and soil conditions. AGROTAIN® is a formulation containing N-(n-butyl) thiophosphoric triamide (NBPT) as the active ingredient, or, more correctly, the precursor to the active ingredient, which is the oxygen analog of NBPT. NBPT is a urease enzyme inhibitor that inhibits the hydrolysis of urea by inhibiting the activity of the urease enzyme that catalyzes the hydrolysis of urea. This activity is the result of an interaction between the urease enzyme and the urease inhibitor. There is no interaction with soil microbes that generate the urease enzyme. Moreover, the recommended NBPT treatment rate is only 0.4 lbs/acre, and NBPT is relatively unstable and presents no problems with long-term buildup in the soil. The use of NBPT with urea also is ideally suited for no-till agriculture applications. No-till agriculture is an environmentally friendly approach that involves little or no disturbance of the topsoil, resulting in less soil erosion and less energy intensive operation. Urea, however, has not been well suited for use with surface-applied no-till applications until the advent of NBPT because of the possibility of substantial ammonia volatilization losses.

Alkyl Polyglycoside Surfactants

Henkel Corporation

Henkel Corporation's alkyl polyglycoside (APG®) surfactants are a class of nonionic surfactants that have been pioneered and marketed to the detergent and personal care industries under the Glucopon® and Plantaren® trade names since 1992 and 1990, respectively. APG® surfactants are manufactured from renewable resources including fatty alcohol, derived from coconut and palm oils, and glucose, derived from corn starch. APG® surfactants are more innocuous to the environment than petrochemical-based technologies, are readily biodegradable, and have very low ecotoxicity. APG® surfactants are highly efficient cleaners and have led to a significant reduction in overall chemical consumption in cleaner formulations and ultimately the amount of chemicals released to the environment. APG® surfactants also permit the formulation of concentrated cleaners that require less consumer product packaging and consequently reduce packaging waste. APG® surfactants are considerably less toxic and safer to humans and the environment than other major surfactants. APG® surfactants permit the formulation of less irritating and safer consumer products and significantly reduce the possible environmental impact associated with an accidental spill. Henkel Corporation's 50 million pound per year APG® surfactant plant has been operating in Cincinnati, Ohio, since 1992. A second plant was started up in Dusseldorf, Germany, in 1995, by Henkel Corporations's parent company, Henkel KGaA.

U.S. Department of the Treasury, Bureau of Engraving and Printing

An Alternative Solvent, Isomet

The U.S. Bureau of Engraving and Printing (the Bureau), the world's largest security manufacturing establishment, produces currency, postage stamps, revenue stamps, naturalization certificates, U.S. savings bonds, and other government securities and documents. Until 1991, Typewash, a solvent mixture, was used by the Bureau for cleaning typographic seals and serial numbers of the COPE-Pack (overprinting presses) and for cleaning of sleeves of postage stamp presses. Typewash is a solvent mixture composed of methylene chloride (55 percent), toluene (25 percent), and acetone (20 percent). The use of Typewash was no longer in compliance with the District of Columbia Environmental Law and the Federal Air Toxic Law. An alternative solvent, Isomet, was designed and developed to replace Typewash. Isomet is a mixture of isoparaffinic hydrocarbon (55 percent), propylene glycol monomethyl ether (10 percent), and isopropyl alcohol (35 percent). Isomet is less toxic, less polluting, and environmentally friendly. Isomet was found to be acceptable in the areas of (1) cleaning ability, (2) solvent evaporation rate, (3) solvent odor, (4) environmental and safety compliance, and (5) cost. Thus, a solvent discharged at the rate of 7,500 gallons per year was made environmentally friendly. The performance of Isomet is excellent and it has been used for cleaning all postage stamp and overprinting presses in the Bureau.

Los Alamos National Laboratory

Application of Freeze Drying Technology to the Separation of Complex Nuclear Waste

The nuclear industry must comply with increasingly stringent standards for radioactive material levels present in liquid effluents. Current conventional methods of decontamination include distillation, ion exchange, precipitation reactions, or chelating agents. Freeze drying technology (FDT) has been applied to the decontamination of radioactive liquids and shown to be thousands of times more effective than conventional methods. Distillation, ion exchange, and chelating agents often require multiple passes, and because additional components (e.g., resins or chelating agents, which in turn must be disposed of as radioactive) are typically required for these methods, reductions in the volume of radioactive waste are rarely realized. FDT will efficiently separate solvents and volatile acids from complex waste solutions and process liquids. The separated liquids will be virtually free of radioactive contamination and can be reused or discarded as nonradioactive. FDT will drastically reduce the volume of radioactive wastes. Volume reductions greater than 1,000 times have been achieved in aqueous solutions, but the exact volume reduction of nuclear waste will depend on its moisture content. FDT will eliminate the need for storage or destruction of the liquid component and will lower transportation costs because of volume and weight reductions. In addition, this technology can be considered safe; no high temperatures or pressures are used. The process occurs in a vacuum, so the failure of a component would lead to an inward leak and the potential for contamination outside the system is significantly reduced. Finally, the refrigerant used in this technology is environmentally friendly liquid nitrogen.

Application of Green Chemistry Principles to Eliminate Air Pollution From the Mexican Brickmaking Microindustry

Los Alamos National Laboratory

A new recirculating design for small brickmaking kilns was investigated as an alternative to conventional operations, which are a significant source of air pollution. The bricks used in building many houses and office buildings in Mexico and other parts of the third world are typically made by hand and fired in small kilns using available fuels such as sawdust, treated wood, paper, trash, tires, plastic, and used motor oil. Although these bricks cost about half of standard high-fired construction bricks, they do not meet the minimum strength requirements for commercial construction in the United States. In addition, a major byproduct of this brickmaking industry is a high level of air pollution—both particulates and toxic chemicals—that results from inefficient thermal design of the kilns and the use of cheap but readily available fuels. This industry is the third leading cause of air pollution in the El Paso-Juárez area. Redesign of the kilns to allow efficient energy recovery and to eliminate waste from over- and under-firing makes the use of nonpolluting fuels (e.g., natural gas) economically attractive. The design challenge is to use inexpensive, readily available materials and equipment to avoid significant capital outlay. Laboratory investigations and process modeling were performed at the Los Alamos National Laboratory, and field tests are being performed at ECOTEC in Ciudad Juárez, Mexico, in cooperation with FEMAP, a private foundation in Mexico, and with the El Paso Natural Gas Company. The direct benefits of these improvements in the brickmaking process are reduced air pollution, safer operating conditions, and better bricks. In addition, process modeling indicates that fuel consumption can be reduced by approximately 55 percent and cost analyses project that this will result in an increase in profit of about 35 percent for the brickmakers.

Application of Microchemistry Technology to the Analysis of Environmental Samples

U.S. Department of Energy, Office of Pollution Prevention

U.S. Department of Energy, Office of Energy Research

U.S. Department of Energy, Chicago Operations Office

U.S. Department of Energy, Argonne Group

Argonne National Laboratory

'Green' chemistry is an umbrella term addressing such related concepts as waste minimization, pollution prevention, solvent substitution, environmentally conscious manufacturing, maximum atom utilization, technologies for a sustainable future, environmental security, and industrial ecology. Another applicable concept, microscale chemistry (or microchemistry), is the application of chemical principles and apparatus at a scale much smaller than currently employed by most bench chemists, thus reducing the volume of reagents and product by several orders of magnitude. Microscale and green chemistries both incorporate waste minimization, pollution prevention, and solvent substitution. Adoption of green and microscale methods is increasingly essential for the environmental analytical community as regulations tighten, the costs of waste disposal escalate, and public scrutiny increases. By applying green chemistry principles and using advances in separation science, instrumentation, microscale techniques, and solvent substitution, chemists at Argonne National Laboratory developed trace environmental analysis methods that incorporate source reduction. The techniques reduce or eliminate the use of hazardous solvents, decrease analysis turnaround time, and significantly reduce the generation of secondary wastes associated with analytical processing. The success of these methods exemplifies the opportunities to reduce waste generation at analytical laboratories across the country. With appropriate institutional advocacy, these principles can be applied broadly to this large chemical sector.

Eastman Chemical Company

Biodegradable Copolyester

An integrated resource management approach to the use of materials such as paper, metals, and plastics considers the entire life of a product from raw materials to final disposition. After the useful life of some products, the final disposition depends on various options. The products can enter the municipal solid waste (MSW) stream to a landfill, an incinerator, or an incinerator with electricity/steam production. They also can be discarded on land or at sea, be recycled by industry, or be reused for another purpose by the consumer. One growing option, which Eastman Biodegradable Copolyester 14766 is designed to complement, is composting. This is a process that essentially mimics nature's biodegradation process (i.e., carbon cycle) and has been used over the ages to various degrees. The process is now recognized to have various benefits, one of which is the reduction of the amount of waste to landfills or incinerators (both of which are expensive to build and maintain, not to mention the problems inherent with siting a new one). In addition, the compost resulting from biodegradation is a soil amendment that adds water retention and other benefits to soils. In fact, such a compost is more beneficial to agricultural soil regeneration than chemical fertilizers. Eastman Biodegradable Copolyester 14766, a patented aliphatic/aromatic copolyester of adipic acid, terephthalic acid, and 1,4-butanediol, was engineered to decompose under proper conditions into water, carbon dioxide, and biomass. This innovative new product also exhibits such features as low cost, tensile properties similar to low density polyethylene (LDPE), and a soft feel, and is blendable with natural polymers such as starch. Extensive biodegradation and toxicity evaluations demonstrated definitively that Eastman's new product biodegrades completely at rates comparable to paper without negatively impacting the ecosystem. The material can be extruded into blown film, extrusion coated, and spun into fiber. A plethora of applications is envisioned for Eastman Biodegradable Copolyester 14766 including compost bags, personal hygiene items, medical products, and coated paper and board.

Eastman Chemical Company

Biofiltration Technology

Biofiltration has been used for decades in the United States in towns and cities for odor control, and has also been used in Europe. American companies, however, have been hesitant to consider the natural process because it is so different from the widely accepted conventional control technologies. As part of Tennessee Eastman Division's (TED) Odor Identification and Control Program, a 1,400 cubic feet per minute gas stream was determined to be a ‘priority’ odor source. Though the vent was, at the time, treated by a 12C-20 caustic scrubber, a hydrogen sulfide odor was detected. One obvious solution to the odor problem was to increase the frequency of the caustic changeouts. This increased frequency would greatly increase the operation expenses for the scrubber as well as expose operations to greater risks of caustic burns resulting from the increased handling requirements. As an alternative to caustic treatment, biofiltration was investigated as a possible solution. In biofiltration, micro-organisms supported on a stationary porous media bed are used to destroy pollutants from waste gases flowing through the bed. The micro-organisms commonly occur in nature, and various media are excellent candidates for sustaining the micro-organisms and harboring their nutrients. In July 1993, a pilot biofilter was set up to test its effectiveness on hydrogen sulfide removal. The pilot biofilter proved that biofiltration was a technically feasible and economically attractive alternative to the 12C-20 caustic scrubber for hydrogen sulfide removal from the vent gas stream. Due to this success, a full-scale biofilter, 12C-1022, was installed in December 1995 to replace the 12C-20 caustic scrubber.

CleanSystem[3] Gasoline

Texaco, Inc.

Internal combustion engines produce considerable amounts of nitrogen oxides (NO_x) as a combustion byproduct. NO_x are an air pollutant in their own right and react with atmospheric organic compounds in the presence of sunlight to form ozone, a powerful respiratory irritant. Despite a 76 percent reduction in allowable NO_x emissions from light-duty gasoline vehicles over the past 25 years, U.S. motor vehicles still emit 3 million tons of NO_x each year. Source reduction in the context of vehicular NO_x means less NO_x generated in the engine. Steps in this direction have been few (primarily exhaust gas recirculation) and, being a design feature, are not applicable to older vehicles. There is, therefore, a genuine opportunity for technology which can reduce the NO_x generated in vehicle engines on the road today. Texaco has developed and introduced a patented additive technology based on novel chemistry which reduces NO_x formation in gasoline engines. This additive is present in all CleanSystem[3] gasoline sold in the United States. Controlled vehicle testing has demonstrated reductions in tailpipe NO_x up to 22 percent. This additive fulfills the role of traditional deposit control ('detergent') additives in keeping fuel system components clean, and provides additional performance in the area of preventing and removing combustion chamber deposits. Cleaner combustion chambers retain less combustion heat from one engine cycle to the next, and the resulting lower temperature leads to the formation of fewer NO_x.

Development and Implementation of Low Vapor Pressure Cleaning Solvent Blends and Waste Cloth Management Systems to Capture Cleaning Solvent Emissions

Lockheed Martin Tactical Aircraft Systems

Lockheed Martin Tactical Aircraft Systems (LMTAS) (formerly General Dynamics Fort Worth Division) has developed low vapor pressure organic solvents. LMTAS patented these solvent blends and the technology is being used by the aerospace industry, the military, and various industries. Additionally LMTAS substituted one of the new solvent blends (DS-104) for a CFC-113 based general purpose cleaning solvent used in the surface wiping of aircraft parts, components, and assemblies in all aspects of aircraft manufacturing. The substitution resulted in major reductions in solvent use and air emissions, the elimination of ozone depleting compounds from cleaning during aircraft assembly, cost reductions, and improved chemical handling and usage practices. From 1986 to 1992, LMTAS produced mainly F-16 fighter aircraft at a rate of 220 to 350 aircraft per year. Throughout the 6 years, LMTAS used a general purpose wipe solvent containing 85 percent CFC-113 by weight throughout the manufacturing process. The use of the CFC-113 solvent blend resulted in the emission of approximately 255 tons per year of CFC-113 and 45 tons per year of volatile organic compounds (VOC). The implementation of DS-104 at LMTAS has reduced wipe solvent VOC emissions to 7 tons per year in 1993, 3 tons per year in 1994, and 2 tons per year in 1995, with no CFC emissions. After the LMTAS implementation, other companies and military operations throughout the United States have implemented this technology. Additionally, this technology has been implemented in several countries, such as Australia, Canada, Greece, Israel, Mexico, the Netherlands, South Korea, Taiwan, and Turkey. Several other European countries will implement this technology in 1997. This technology was developed primarily for aerospace; however, it has found applications in many other industries such as automotive, various prison manufacturing operations, postal operations, electronics, building maintenance, steel, and nondestructive testing methods.

Rochester Midland Corporation

Development of a New 'Core' Line of Cleaners

Cleaning is an important practice and necessity of modern civilization. An effective cleaner must be able to penetrate through soil to disrupt and destroy the complicated types of bonding that cause it to adhere to the surface being cleaned. Most modern cleaners are comprised of surface active agents derived from petrochemical resources. While these components are effective, they tend to be environmentally harsh and depend upon a natural resource whose supply is finite and limited. The market for these products is estimated to be in the range of $5 billion, which equates to approximately 5 billion pounds of product annually. The impact of developing chemistries that are less polluting during the extraction, manufacturing, use, and disposal of these products is, therefore, quite significant, as are the human health and safety impacts. During the past few years a new family of cleaners was developed that are less toxic and have reduced impacts to both people and the environment when compared to traditional products used for the same purpose. The chemistries incorporated into these products resulted in products that are readily biodegradable, comprised of zero to very low volatile organic components and ozone depleting substances, effective in their intended purpose (i.e., cleaning), and economically competitive. In addition, these products have low human and aquatic toxicity and low corrosivity. Main molecular components of these products are derived from renewable, bio-based resources that are lower polluting and typically less toxic than their petrochemical alternatives. This new 'core' line of cleaners is an innovative approach to the formulation of an important series of products and is the safest yet developed in its field.

U.S. Department of Energy

Pacific Northwest National Laboratory

DOE Methods for Evaluating Environmental and Waste Management Samples

DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods) is a document that provides new technology and consolidated methods to analytical chemistry laboratories around the country. These laboratories are working on one of the world's most challenging environmental issues: Cold War legacy waste. Sampling and analytical technologies that minimize waste production are given priority over traditional methods. It has been demonstrated, for example, that some of the technologies produce 60 to 70 percent less hazardous and radioactive waste than other available technologies. The guidance information in *DOE Methods* also helps minimize the number of analyses and saves time and money. Guidelines are provided on how to (1) efficiently develop a sampling and analysis program, (2) effectively and efficiently sample waste, (3) handle radioactive samples safely, and (4) select appropriate analytical methods. Cross references allow the users to select from currently available standard methodologies. *DOE Methods* has been available for both DOE and commercial use since 1992. It is updated every 6 months, thereby accelerating the release of new technology to speed EM operations. The significance of the document is in its unique application to the analysis of radioactive components and highly radioactive mixed waste. The document currently contains about 65 sampling and analytical methods, many of which are focused on the mixed-waste issue. The highly challenging world of environmental problems cannot be solved without effective sampling and analytical methods. *DOE Methods* takes a major step in the resolution of this problem.

DryWash™
Carbon Dioxide Dry Cleaning Technology

Hughes Environmental Systems, Inc.

DryWash™ is a patented, Hughes-specific liquid carbon dioxide garment dry cleaning technology and is a safe, ecologically acceptable, and cost effective alternative dry cleaning process. Currently, the dry cleaning industry uses perchloroethylene (PCE) (85 percent of establishments), petroleum-based or stoddard solvents (12 percent of establishments), CFC-113 (less than 2 percent of establishments), and 1,1,1 trichloroethane. All conventional dry cleaning solvents present health risks, safety risks, or are environmentally detrimental. PCE is a suspected carcinogen, petroleum-based solvents are flammable and smog producing, and CFC-113 is an ozone depletor and targeted to be phased out by the end of 1995. Health risks due to exposure to cleaning solvents and the high costs of implementing and complying with safety and environmental restrictions and regulations, have made dry cleaning a much more difficult business in which to achieve profitability. Solvents are suspected of contaminating ground water, air, and food products (i.e., in nearby markets). For these reasons, there is an ongoing search for alternative, safe, and environmentally friendly cleaning technologies, substitute solvents, and methods to control exposure to dry cleaning chemicals. DryWash™ reuses carbon dioxide, a naturally occurring byproduct of combustion that is a readily available, inexpensive, and unlimited natural resource. It is also chemically stable, noncorrosive, nonflammable, nonozone depleting, and nonsmog producing. Performance has been demonstrated to major dry cleaning equipment manufacturers worldwide and to the EPA. Actual garments, along with International Fabricare Institute (IFI) standardized cleaning test fabrics, were used for the demonstrations. The performance of the DryWash™ cleaning process was quantified favorably against commercial perchloroethylene cleaning by Los Alamos National Laboratory, using IFI standards.

The DUCARE 'Zero Effluent' Recycle Chemistry System

DuPont Company

The printing and publishing pre-press industry is undergoing a revolutionary change driven by advances in imaging technology from a craft-based industry to one relying far more on digital imaging and printing technology. From a user perspective, this new technology is more environmentally benign than the process it replaces. Several iterations of improvements in hardware and software will be required before digital imaging completely replaces conventional chemical imaging. The DUCARE system is a 'bridge' between the current and developing systems. It is designed as a 'drop in' for conventional processing and enables the customer to continue utilizing their current equipment, thus avoiding a financial burden while still eliminating the adverse environmental impact. DUCARE is an environmentally proactive way for customers to prevent any film processor effluent from going down their drain. Typically, customers discharge the effluent to the drain, pay to have it hauled away and disposed, or use expensive high maintenance equipment for onsite treatment. The effluent contains hazardous chemicals (as defined by SARA Title III), very high BOD and COD, and high silver and pH extremes. DUCARE, offered only by DuPont, solves these problems using several industry firsts. A new developer was invented which has no SARA Title III chemicals and is based on a vitamin C isomer. The chemistry is designed to use 25 to 40 percent less product than conventional chemistry and is recycled at its manufacturing sites to insure high quality and 'like new' performance. The wash-water recirculating unit reduces water use up to 99 percent. This system can be used worldwide, wherever a cost effective reverse distribution system can be set up.

California-Pacific Lab & Consulting

The ECO Funnel

The ECO Funnel and Container is a new product designed to prevent volatile toxic air contaminants from evaporating into the laboratory work environment and into the atmosphere through the laboratory fume hood system. Typically, a simple funnel is used in pouring waste solvent into a waste bottle or carboy. In most cases, the funnel is left on top of the bottle permanently during the day, resulting in significant emission due to evaporation of volatile organic compounds (VOCs) from the bottle into the laboratory environment or fume hood. It may seem that contamination of the atmosphere from such sources may not be large enough to be important or significant; however, exact measurements have proven the contrary. For example, an 8-liter carboy filled with 8 liters of dichloromethane will emit 500 mL (1.5 pounds) of this solvent into the atmosphere in 5 days. The emission will vary depending on the type of solvents used. The fume hood face velocity also can affect the evaporation rate. However, for a typical fume hood at 700 cubic feet per minute and a typical 4 liter waste bottle with a regular funnel containing 1000 mL tetrahydrofuran, 1000 mL acetone, and 1500 mL dichloromethane, the emission rate was 0.09 pounds per 8 hours or 33 pounds per year. California-Pacific Lab and Consulting designed and patented a new funnel that has a lid connected to a shut-off ball that double seals the system. The funnel stem is also longer and sealed to the bottle cap in order to prevent emission from the side of the stem. Under the same conditions as described above for the 4-liter waste bottle with a standard funnel, the ECO Funnel and Container resulted in zero emissions.

IBM-Austin

Elimination of Ozone-Depleting Chemicals in the Printed Wire Board and Electronic Assembly and Test Processes

IBM-Austin is a manufacturing and development facility. Operations include the manufacture of printed wire board (PWB) in the Panel Plant facility and electronic circuit cards in the Electronic Card Assembly and Test (ECAT) facility. In 1992, IBM-Austin completely eliminated the use of CFCs and other ozone depleting substances from its PWB and ECAT processes. This elimination program resulted in 100 percent reduction of CFC-113 (1988 peak usage of approximately 432,000 pounds) and 100 percent reduction of methyl chloroform (1988 peak usage of approximately 308,000 pounds) from IBM-Austin's PWB and ECAT processes. These accomplishments were achieved by converting to an aqueous-based photolithographic process in the PWB facility in 1989, an interim aqueous cleaning process in the ECAT facility in 1991 and 1992, and a final No-Clean process (eliminating the aqueous cleaning process) in the ECAT facility. Changing from a solvent-based photolithographic process to an aqueous-based process eliminated methyl chloroform (MCF) from PWB panel manufacturing (1988 usage of 181,000 pounds). The interim process changes to aqueous cleaning eliminated MCF from manufacturing processes in ECAT (1989 peak usage of 196,000 pounds) and were largely responsible for eliminating CFC-113 from all manufacturing processes at the IBM site. Although CFC-113 was eliminated from the site in 1991 and MCF was eliminated in 1992, ECAT's ultimate goal was to convert all ECAT processes to No-Clean manufacturing processes. This conversion was completed in 1993.

Environmental Improvements From Redesigning the Commercial Manufacture of Progesterone

Pharmacia & Upjohn

For more than 40 years, the steroid bisnoraldehyde (BNA) has been produced at Pharmacia & Upjohn because it is a key intermediate for the commercial synthesis of progesterone and corticosteroid classes of pharmaceuticals. Recently, a redesigned route to BNA was implemented. This new synthetic route to progesterone is founded on both the development of a new fermentation process which improves the utilization of a renewable, naturally derived feedstock from 15 to 100 percent, and the development of a chemical oxidation process that offers high selectivity and reduced waste streams. The fermentation employs a genetically modified bacterium to convert soya sterols directly to a new synthetic intermediate, bisnoralcohol. The new chemical process oxidizes bisnoralcohol to bisnoraldehyde, a key intermediate for the registered, commercial manufacture of progesterone. Contrary to standard chemical methods for oxidizing alcohols to aldehydes, the nominated process does not use hazardous or noxious materials and does not generate toxic waste streams. The new bisnoralcohol route exemplifies the synergism possible between biochemical and chemical process development. It eliminated a process with a running, recycled inventory of 60,000 gallons of ethylene dichloride (EDC), a known carcinogen, which needed up to 5,000 gallons of EDC input annually. The new route produces the same amount of product as the previous route with 89 percent less nonrecoverable organic solvent waste and 79 percent less aqueous waste. The new route also has the chemical selectivity required for high quality bulk pharmaceutical manufacture and can be applied to the oxidation of other primary alcohols. By implementing this redesigned, commercial synthesis of BNA, Pharmacia & Upjohn has substantially reduced the chemical waste associated with manufacturing progesterone, while simultaneously improving process economics through a dramatic increase in feedstock utilization.

Environmentally-Driven Preparation of Insensitive Energetic Materials

U.S. Department of Defense, Office of Munitions

U.S. Department of Energy, Weapons Supported Research

Lawrence Livermore National Laboratory

An innovative approach was developed at Lawrence Livermore National Laboratory to synthesize 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and other insensitive energetic materials through the use of Vicarious Nucleophilic Substitution chemistry (VNS). TATB is a reasonably powerful insensitive high explosive (IHE), whose thermal and shock stability is considerably greater than that of any other known material of comparable energy. The high cost of TATB ($100 per pound) has precluded its use for civilian applications such as deep-hole oil explorations. TATB is manufactured in the United States by nitration of the relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), which is then aminated to yield TATB. The new VNS method developed at Lawrence Livermore National Laboratory for the synthesis of TATB has many 'environmentally friendly' advantages over the current method of synthesis of TATB. Most significantly, it allows the elimination of chlorinated species from the synthesis of insensitive energetic materials. The new synthesis of TATB uses unsymmetrical dimethylhydrazine (UDMH), a surplus propellant from the former Soviet Union, and ammonium picrate (Explosive D), a high explosive, as starting materials in lieu of the chlorinated species, TCB. Several million pounds of Explosive D are targeted for disposal in the United States; 30,000 metric tons of UDMH also await disposal in a safe and environmentally responsible manner. The use of these surplus energetic materials as feedstocks in the new VNS method of synthesizing TATB allows an improved method of demilitarization of conventional munitions that also should offer significant savings in production, thereby making this IHE more accessible for civilian applications.

Lockheed Martin Tactical Aircraft Systems

Implementation and Verification of Aqueous Alkaline Cleaners

Lockheed Martin Tactical Aircraft Systems (LMTAS) was the first aerospace company to implement innovative aqueous cleaning technology for cleaning tubing and honeycomb core. Tubing is used in the aerospace industry for transferring pressurized oxygen within an aerospace vehicle. Honeycomb core is used in the aerospace industry for producing bonded structural parts. Both applications require that the parts meet stringent cleanliness requirements. These requirements were previously met by using cold cleaning or vapor degreasing with chlorinated solvents. These solvents included 1,1,1-trichloethane (TCA) and trichloroethylene (TCE). These chlorinated solvents are toxic, and TCA is an ozone depleting compound. The use of chlorinated solvents posed a threat to the environment because the solvents were commonly released into the air during cleaning operations and because the likelihood of a spill during their use was significant. These solvents were successfully replaced with aqueous cleaning technology. As of November 1993, 100 percent of tubing manufactured at LMTAS (including oxygen tubing) is being cleaned in an aqueous cleaning system. As of May 1994, 100 percent of all honeycomb core used at LMTAS is also being cleaned in an aqueous cleaning system. Implementation of aqueous cleaning technology at LMTAS eliminated approximately 360 tons of air emissions per year and resulted in a cost savings of $490,000 per year. In addition to replacing chlorinated solvents with the innovative aqueous cleaning technology, LMTAS also explored the use of environmentally safe methods for quantifying surface contaminants on parts cleaned by various cleaning technologies. Traditionally, extraction with CFC-113 followed by gravimetric or FTIR analysis has been used for quantifying surface contaminants. The use of CFC-113 is undesirable due to its ozone depleting potential. LMTAS has demonstrated the usefulness of carbon dioxide coulometry for determining the amount of residue remaining on a surface after cleaning and has used this technique for comparing the cleaning effectiveness of various cleaning technologies.

DuPont Company

The INFINITY Process

The INFINITY dyeing process was developed as an alternative method to manage the dyeing cycle for nylon textiles. Over 8 billion pounds of nylon textiles are consumed each year and most are dyed to meet aesthetic and functional demands. In the United States alone, consumption of dyes for nylon exceeds 30 million pounds, much of which is left in the spent dye bath after the fabric is dyed. This waste must be treated to avoid pollution of downstream waterways. Mills are meeting regulatory requirements through conventional process control techniques and end-of-pipe treatment. The INFINITY dyeing process lets mills reduce their consumption of dyes and other chemicals by 25 percent, and, in some applications, water and steam use per dye cycle is cut in half. Conventional methods use up to 4,000 gallons of water, 20 pounds of dye, and 10 pounds of dye assist chemicals per 1,000 pounds of fabric. The INFINITY dyeing process uses only 75 percent of the dye previously required, half the water, and less dye assist chemicals to get the same fabric color. In addition, dye discharge into mill effluent streams can be reduced as much as tenfold. A mill with a 90 percent exhaust rate may discharge 500 pounds of unused dye into the mill's wastewater treatment stream each week. With INFINITY, the same mill can move to 99 percent exhaust, reducing the amount of dye discharged to 50 pounds per week; a significant step toward attacking waste at the source. The process is currently being used at nylon textile mills in the United States, and work has begun on the feasibility of using the process on wool, cotton, and polyester blend fabrics. Cost savings by most mills using this process could easily exceed $100,000 per year.

Innovative Techniques for Chemical and Waste Reductions in the Printed Wire Board Circuitize Process

IBM-Austin

IBM produces 1.7 million square feet of multilayer circuit boards per year in a manufacturing plant in north Austin, Texas. Aqueous chemical baths and rinse water are processed at a pretreatment plant where acidity is neutralized and dissolved copper is removed prior to discharge to a sanitary sewer for further treatment in a POTW. In 1991, the treatment process produced 1,417 tons of metal hydroxide sludge, a RCRA F006 hazardous waste. In 1992, a team of environmental engineers, manufacturing engineers, and laboratory personnel was formed to reduce hazardous waste sludge generation at the water treatment plant by minimizing waste generation in the imaging line. Areas of key importance to sludge reduction were identified as acid used in cleaning operations and developing solutions used prior to etching operations. Minimizing acid in the waste water reduces the amount of lime needed to neutralize the waste water. Reducing the developing solution reduces the carbonates in the waste water that precipitate as calcium carbonate in the presence of lime. By 1994, the team accomplished a 90 percent reduction in hydrochloric acid used in cleaning for an annual savings of approximately $340,000 in chemical cost. Additional work allowed for a 40 percent reduction of developing and stripping solutions used in the imaging area, for an annual savings of approximately $75,000. These changes resulted in an approximately 75 percent decrease in use of lime at the pretreatment plant. This decrease, in combination with reduced carbonate usage in developing solutions, resulted in a decrease in sludge production of over 670 tons per year (based on first half 1994 results) and a 47 percent reduction from 1991 sludge generation, for an additional savings of $250,000 in sludge disposal costs. This project has shown that waste minimization through chemical source reduction can reduce expenses as well as reduce waste.

INVERT Solvents in Aircraft Paint Stripping

The Dow Chemical Company

Recent changes in regulations affecting the aircraft stripping industry have resulted in increased research into new, more environmentally and toxicologically friendly formulations. The Dow Chemical Company has developed a new line of solvent continuous microemulsions, which have merit in aircraft paint stripping, to aid in the reduction of regulated chemicals as well as lower flammability and volatile organic compound (VOC) levels. These solvent products are marketed under the INVERT trademark. Formulating with INVERT solvents allows for the inclusion of greater than 40 percent water in aircraft paint strippers so that worker exposure to chemicals, flammability, and VOC levels can be reduced. INVERT solvents are solvent continuous microemulsions that contain approximately 50 percent water, low surfactant levels (i.e., less than 5 percent), and approximately 45 percent solvents and cosolvents. Paint stripping formulations can easily be prepared, using INVERT as a base, through the addition of active stripping solvents along with performance enhancing ingredients such as thickeners, activators, and evaporation retardants. Hydrocarbon-based stripper formulations often have low flash points and high VOC levels. The incorporation of water significantly increases fire point, and water addition reduces VOC levels. INVERT solvents offer an economical and effective way to incorporate water into hydrocarbon-based strippers to reduce flammability and VOC concerns without sacrificing performance. When methylene chloride is used as a stripping solvent, exposure and regulatory issues may call for a reduction in use level. The use of INVERT solvent technology allows preparation of solvent continuous microemulsions with low methylene chloride content (i.e., less than 20 percent), while maintaining an excellent level of performance. The use of INVERT solvents in the aircraft stripping industry allows users to reduce worker exposure to regulated chemicals and to reduce emissions of volatile chemicals, while maintaining a high standard of performance and economic benefit.

Praxair, Inc.

Liquid Oxidation Reactor (LOR)

Praxair, Inc. has developed a unique process that allows the safe oxidation of organic chemicals with pure or nearly pure oxygen. This technology, known as the Liquid Oxidation Reactor (LOR), provides significant environmental advantages compared to conventional, air-based oxidation processes. The use of oxygen in place of air reduces the total gas throughput to the reactor, thereby reducing the compression energy and the amount of vent gas that must be treated prior to atmospheric release. In addition, the oxygen use can positively affect the chemistry of the reaction, allowing the operation of the process at lower temperatures or pressures, thereby improving selectivity without sacrificing production rate. The use of the Praxair LOR increases the overall rate of reaction and volumetric productivity of hydrocarbon oxidations while increasing selectivity and reducing the loss of solvent and reactant to carbon oxides. The increased chemical efficiency with oxygen results in substantial raw materials cost saving, and a 96 percent reduction in the quantity of waste gases. The cost of product purification and waste disposal is reduced substantially. In addition, the lower temperature operations afforded by the LOR process reduces the loss of reactant or solvent to byproducts and to waste streams that also can contribute to environmental problems and must be treated prior to release. The LOR will enable a large and important segment of the U.S. chemical industry to realize more efficient use of raw materials, reduced environmental emissions, and energy savings. Because the LOR also allows for higher productivity, lower capital costs, and, consequently, improves competitiveness, there are significant incentives for the implementation of the technology. Average operating-cost savings and productivity gains worth $5 to $20 million per plant per year have been projected.

Los Alamos National Laboratory

Magnetic Separation for Treatment of Radioactive Liquid Waste

High Gradient Magnetic Separation (HGMS) is the application of intense magnetic fields to selectively separate solids from other solids, liquids, or gases. The HGMS process has demonstrated promise for the treatment of waste streams containing actinide at Los Alamos National Laboratory (LANL). The caustic liquid waste generated by operations in the LANL Plutonium Processing Facility (TA-55) can produce up to 30,000 L of liquid effluent annually, with an average alpha activity of 10^{10} dpm/L. Treatment and disposal of the liquid effluents at the LANL Waste Water Treatment Facility (TA-50) can ultimately produce up to 15 tons of TRU solid waste per year. In order to avoid the TA-50 treatment, the goal at TA-55 is to reduce the radioactivity in the waste streams to less than 5.8×10^5 dpm/L. Physical separation processes, such as HGMS, are particularly attractive because no additional waste is generated during processing. HGMS is capable of concentrating the actinides in process waste streams to form a low volume, actinide-rich stream for recycling, and a high-volume, actinide-lean stream for direct discard. The proposed technology has been demonstrated successfully on a laboratory scale at TA-55 where results from screening experiments on radioactive caustic liquid waste water indicate that over 99.9 percent extraction of Pu activity can be achieved using HGMS (represents decontamination levels of three orders of magnitude to about 4.4×10^5 dpm/L). The application of this technology to radioactive liquid waste effluents would eliminate radioactivity from the source, in addition to reducing the volume of transuranic solid waste that is produced with the current treatment technologies. The hazard of pumping radioactive liquid waste to offsite facilities would also be eliminated because treatment of TA-55 effluent would occur prior to transportation.

NAFION Membrane Technology

DuPont Company

Membrane technology is now recognized as state-of-the-art for chloralkali chemical production, which constitutes the second largest commodity chemical volume produced globally. NAFION membranes are acknowledged as the world leader in bringing about a technology 'revolution,' which has made the membrane electrolyzer system the technology of choice over the incumbent mercury amalgam cells and asbestos diaphragm electrolyzers. While significantly reducing the environmental impact of the old technologies, membrane systems confer the advantages of a new electrolysis process with lower investment and lower operating costs. Before NAFION and membrane technology, the production of chloralkali chemicals was dependent on either mercury amalgam cells or asbestos diaphragm systems. While these systems may be operated safely, they pose health and environmental concerns in use and disposal. Membranes, such as NAFION, now offer a more environmentally friendly and economically attractive alternative, which accounts for the rapid global adoption of membrane technology. Another rapidly emerging application of NAFION is in the area of alternative energy, where electricity is produced from the 'combustionless burning' of hydrogen with oxygen in air via a membrane fuel cell. Fuel cell technology, with hydrogen as a fuel, is pollution-free. NAFION membranes often are cited in the many commercial developments of membrane fuel cell systems. As membrane fuel cells mature in the commercial mass market, more global energy needs will be served by renewable, sustainable, and environmentally friendly sources of power.

Nalco Fuel Tech NOxOUT® Process

Nalco Fuel Tech

Nalco Fuel Tech develops and markets air pollution control technologies worldwide. Nalco Fuel Tech's flagship technology, NOxOUT®, reduces harmful nitric oxide emissions of stationary combustion sources to yield nitrogen gas and water, leaving no disposal solids. The NOxOUT® process meets today's environmental challenges by using less toxic chemistry, reducing or eliminating toxic releases to the environment, converting wastes to more environmentally acceptable discharges, and reducing energy consumption. The NOxOUT® process provides an economical solution for complying with the stringent regulatory requirements for NO_x reduction from fuel combustion sources. NOxOUT® can reduce NO_x emissions by 75 percent, compared to the 20 to 50 percent reduction from existing treatment. The NOxOUT® process is being used commercially. It can be used on new combustion units for small industrial units to large utility installations or it can be retrofitted to existing units. The environmental benefits are significant NO_x reduction, elimination of byproduct disposal, toxic use elimination of SARA Title III chemicals, and increased energy efficiency.

Nalco TRASAR® Technology

Nalco Chemical Company

Nalco's TRASAR® Technology is impacting the way the world manages water by helping customers reduce pollution at its source and conserve energy. These applications are a complete cradle-to-grave approach to water management. The initial process consists of adding low levels of inert fluorescent 'trace' to Nalco's products. The trace allows controlled chemical application instantaneously and automatically. Chemical treatment reductions of 20 to 30 percent have resulted from this process. The second stage of the process consists of the direct, automatic detection of the treatment chemical. By fluorescent tagging of the treatment chemical, users can detect the chemical's presence in systems where low-level detection was not possible. This stage allows correlation to the variations in treatment consumption and to the variations in the water system's operation. The processes' final stage is based on the desired performance, such as corrosion protection or the prevention of foaming in the process system. Monitoring of the desired performance allows further chemical adjustment. This technology allows less consumption and more effective use of industrial process water, reduced chemical usage, energy conservation, the measurement of the fate of the chemical additives, the detection of industrial and biocide treatment for enhanced risk management, and the minimization of environmental release.

Nalco Chemical Company

Nalco ULTIMER™ Polymer Technology

Industrial processes require water as a raw material or processing aid. This water must be treated to remove harmful waste and contamination prior to discharge to the environment. High molecular weight, water soluble polymers are used to accomplish the solid/liquid separation in industrial water and waste treatment applications. A class of polymers, known as polyacrylamides, performs this separation. In 1996, shipments of polyacrylamides in the United States exceeded 200 million pounds. The worldwide market is $1 billion. In 1995, Nalco continued its technological innovation by introducing to the marketplace the first major innovation in water treatment flocculants since the development of inverse emulsion polymers. These new ULTIMER™ polymers of high molecular weight polyacrylamides are environmentally responsible since they eliminate oils and surfactants yielding oil-free sludge. ULTIMER™ polymers contribute nearly zero volatile organic content as compared to oil emulsion polymers. This technology is more effective than existing technology and eliminates potential human health and environmental hazards in worldwide use. Toxic use reduction and pollution prevention are achieved by eliminating environmental discharges that present environmental hazards and by reducing the amount of solid waste disposed to landfills.

Rohm and Haas Company

A New Chemical Family of Insecticides Exemplified by CONFIRM™ Selective Caterpillar Control Agent and the Related Selective Insect Control Agents MACH 2™ and INTREPID™

The value of crops destroyed worldwide by insects exceeds tens of billions of dollars. Over the past 50 years, only a handful of classes of insecticides have been discovered to combat this destruction. Rohm and Haas Company's invention of a new class of chemistry, the diacylhydrazines, is a significant new addition to the tools available to growers. Three members of this family have been or are in the process of being commercialized to date: CONFIRM™, MACH 2™, and INTREPID™. Not only are these materials effective in controlling target pests, but, in addition, they present the grower with significantly safer alternatives than those currently available. EPA recognized these unique features by classifying the first two members of this family as reduced risk pesticides. CONFIRM™ is a breakthrough in caterpillar control. It is chemically, biologically, and mechanistically novel. It effectively and selectively controls important caterpillar pests in agriculture without posing significant risk to the applicator, the consumer, or the ecosystem. It will replace many older, less effective, more hazardous insecticides. MACH 2™ is chemically and mechanistically related to CONFIRM™, but, unlike CONFIRM™, it is used to control an entirely different type of insect in an entirely different setting, namely turf grubs in soil. MACH 2™ is a low use rate product that is substantially safer to humans and to nontarget organisms (e.g., earthworms, birds, and fish) than other currently employed turf and lawn insecticides. INTREPID™ is the newest member of the diacylhydrazine class. It shares all the desirable attributes of CONFIRM™ (i.e., extraordinary caterpillar selectivity as well as excellent safety to humans, nontarget organisms, and the ecosystem) and has the additional advantage of significantly greater caterpillar potency, which translates into a wider range of use.

A New Process for the Manufacture of Pharmaceuticals

Sandoz Pharmaceutical Corporation

In an effort to reduce the amount of waste generated at its East Hanover site, Sandoz Pharmaceutical Corporation has evaluated all site processes in order to make improvements in the utilization of solvents and minimize the waste byproduct while also improving operating efficiency. One process in particular was identified that appeared to offer significant opportunities for such process restructuring. After 2 years of research, all the essential elements of the new process have now been demonstrated. The new process uses a single new solvent for both reaction medium and separation, which significantly reduces the overall solvent requirements and permits recycling of the used solvent by simple distillation. As a result, the process waste index is reduced from the current 17.5 pounds of waste generated per pound of product to 1.5 pounds, resulting in a projected reduction of 170,000 pounds per year in waste generation. Furthermore, the amount of solvent used per batch is cut in half, thereby significantly reducing the usage of solvent with attendant lower risks of worker exposure and accidental releases to the environment. The decision to proceed with development of a new process, despite the potential problem of obtaining FDA approval of the process changes, is due primarily to the favorable economics of the new process. Conservative estimates of annual savings are around $775,000, compared to an investment of $2.1 million to develop and implement the new process, which is equivalent to a return on investment of 36.7 percent and less than a 3 year pay-back time. It is estimated that over 75 percent of the manufacturing savings are due to process improvements rather than disposal costs of unused solvent, illustrating the process optimization benefits characteristic for pollution prevention innovations.

No-Clean Soldering

CTS Corporation Resistor Networks

CTS Corporation Resistor Networks produces solid ceramic resistor networks in various single in-line, dual in-line, surface mount, and through-hole packages with standard or custom circuit designs. Through CTS Corporation's commitment to a responsible environmental policy, many of its manufacturing methods have been modified with the goal of reducing or eliminating hazardous waste byproducts. One such method to reduce waste was the implementation of a No-Clean soldering process. This No-Clean soldering process, which began in March of 1993, has eliminated the use of wave oil, soldering fluxes, and solvent cleaning. Changing to the No-Clean soldering process involved installing hoods over the solder pots. Using the hoods, an inert atmosphere is maintained over the molten solder. By using the inert atmosphere, oil and flux are no longer required. The parts are clean after solder and thus no solvent cleaning is needed. Previously, TCA (1-1-1 Trichloroethane) and TCE (1,1,2 Trichloroethylene) were used as part of a post-solder cleaning operation to remove flux and wave oil residues. Due to the elimination of flux and wave oil, these cleaning operations became unnecessary. Therefore, the amounts of waste TCA and TCE from soldering operations were reduced from 9,900 pounds and 226,000 pounds in 1992, respectively, to zero in 1995. As an added benefit of eliminating solvent-based cleaning operations, air emissions due to the use of these chemicals have dramatically decreased. From 1992 through 1995, TCA and TCE related air emissions from soldering operations have been reduced from 99,000 pounds and 250,000 pounds, respectively, to zero. A cleaning operation, not related to soldering, generated a small amount of TCE air emissions in 1995. This operation was eliminated in June of 1995. The No-Clean soldering process has eliminated the generation of waste oil, flux, and cleaning solvents at the solder operation. Workers are no longer exposed to fumes from fluxes, oils, and cleaning solvents, which are typical of soldering operations. The product quality also has been improved.

Technic, Inc.

Lawrence Livermore National Laboratory

Noncyanide Silver Electroplating

A proprietary, noncyanide silver electroplating process, Techni-Silver Cy-Less L, was developed by Technic. Cyanide based processes for electroplating have been extensively used in the United States for the last 50 years. Due to the hazardous nature of cyanide, extensive safety precautions must be incorporated when manufacturing electroplating chemicals, transporting the solutions to user sites, using the electroplating process, and disposing waste solutions. For example, if cyanide based solutions become too acidic, large amounts of poisonous cyanide gas are created. Historically, the electroplating industry has suffered many accidents due to the use of cyanide, which on a few occasions have resulted in death. Alternatives to cyanide-based solutions had been developed for all metals commercially electroplated except silver. The noncyanide silver electroplating process developed by Technic provides an alternative that is noticeably less toxic than the cyanide process and inherently safer with regard to accident potential. In addition, tests clearly show that the noncyanide formulation is capable of producing sound, thick (i.e., around 125 µm) silver deposits that are extremely fine-grained and exhibit properties comparable to those produced in silver cyanide formulations. With the success of the noncyanide chemistry, Technic has made it possible to operate an entire plating facility without having to use any cyanide compounds.

DuPont Films

Petretec^{sm} Polyester Regeneration Technology

Polyethylene terephthalate (PET) is the fastest growing polymer. Becuase of their inherent thermal stability, PET-type thermoplastics lend themselves to direct recycling and serve as a raw material for the production of a number of products. For example, the success of PET bottle recycling is well known. This process annually diverts more than 600 million pounds of PET bottles per year from landfills. This technology requires waste with a high purity content and can only be used for carpeting or pillows. It usually cannot be reused to make new bottles. Additionally, there are a large number of uses for PET in which the material is dyed, coated, or mixed with a copolymer. The bulk of these materials are not suitable for direct recycling, so they are typically landfilled. However, the patented DuPont Petretec^{sm} polyester regeneration technology provides an environmental alternative to landfills. The DuPont Petretec^{sm} process unzips the PET molecule and breaks it down into its raw materials, dimethyl terephthalate (DMT) and ethylene glycol (EG). The process allows the monomers to retain their original properties so they can be reused over and over again in any first-quality application. The process accepts polyester with a variety of contaminants at higher levels than other processes. The process reduces dependence on oil-derived feedstocks and diverts polyester from the solid waste stream. In the Petretec^{sm} process, scrap PET reacts with methanol vapor at an elevated temperature (i.e., greater than 260 °C) to produce a vapor stream of DMT, EG, and excess methanol. A glycol azeotroping agent, methyl p-toluate (MPT), is added, and the components are separated. Purification is accomplished by extensive fractional vacuum distillation. The products are then shipped back to PET fiber, film, and resin producers. Each kilogram of DMT made by the Petretec^{sm} process reduces the demand for about 0.5 Kg of the traditional raw material known as paraxylene, an oil-derived basic petrochemical. The Petretec^{sm} process is FDA approved and provides an economical way to reuse materials with higher contaminant levels than other recycling methods. DuPont converted its Cape Fear facility, near Wilmington, North Carolina, to a methanolysis plant. The new plant can handle more than 100 million pounds of scrap PET and 30 million pounds of EG annually, and is easily expandable.

Polycarbonate/Polydimethylsiloxane Copolymers for Thermal Print Media

Eastman Kodak Company

The process to make polycarbonates using bischloroformates and bisphenols or diols was developed and commercialized in the early 1990s by the Polymer Products Unit of the Eastman Kodak Company in Rochester, New York. The original process to produce the polycarbonate of bisphenol A, diethylene glycol, and bisaminopropyl polydimethyl-siloxane was developed in 1992 and commercialized in 1993 for use in a new thermal print media product. Concerns over waste and air emissions, as well as cost and capacity issues, prompted a research and development effort to replace this polymer before production volumes increased to forecasted high levels. The new process to produce a similar polycarbonate/polydimethylsiloxane copolymer was certified early in 1994. Improvements include the following: (1) the new process is made in the solvent in which the polymer is coated, and is delivered to the manufacturing department dissolved in that solvent, eliminating the methanol precipitation, methanol washing, and vacuum drying steps; (2) in the new process, triethylamine is used as the acid acceptor instead of pyridine, making the water wash waste streams less hazardous; (3) the new process uses the commercially available diethylene glycol bischloroformate, eliminating the need to manufacture the bisphenol A bischloroformate at Kodak in Rochester (the bisphenol A bischloroformate synthesis uses phosgene as a key reactant, and its purification produces large quantities of hazardous waste containing heptane and silica gel). The new process will yield over 1.2 million pounds of hazardous waste reductions and more than 3,000 pounds of air emissions reductions from 1994 to year end 1996.

PORTA-FEED® Advanced Chemical Handling Systems

Nalco Chemical Company

During the 1980s, disposal of chemical residues and their containers was a potential human health and environmental risk for chemical users and the public. In 1985, Nalco developed the PORTA-FEED® Advanced Chemical Handling system for chemical applications worldwide. It is the largest private fleet of returnable containers in the world at a capital cost of $220 million. These 101,000 units are owned, monitored, maintained, and cleaned by Nalco as a cradle-to-grave risk management process. The program consists of the units, a computerized tracking system, a zero defect delivery system, and a systematic maintenance and cleaning program. This pollution prevention program has prevented the disposal of more than 3 million drums and 30 million pounds of chemical waste. In 1985, 33 percent of Nalco's annual sales of $659 million were shipped in 500,000 nonreturnable drums. Seven percent of 1995 annual sales of $1.2 billion were shipped in nonreturnable drums. By the year 2000, Nalco expects to have eliminated the disposal concerns from 10 million drums and 100 million pounds of chemical waste worldwide. The system benefits are the reduction of human and environmental risk from transportation to disposal, reduced chemical inventory, and renewable resource implementation.

The Production of Cumene with Zeolite Catalyst: Mobil/Badger Cumene Process

Mobil Technology Company

Cumene is manufactured in very large volumes for subsequent conversion to phenol and acetone. The existing worldwide demand for cumene is about 7 million metric tons per year. The production of cumene by alkylation of benzene with propylene has, in the past, been carried out commercially over two catalyst systems: solid phosphoric acid (SPA) or aluminum chloride ($AlCl_3$). Both SPA and $AlCl_3$ present severe environmental problems; SPA catalyst is wet, corrosive, and might contain hydrocarbons, while waste $AlCl_3$ is a corrosive liquor that also might contain hydrocarbons. Both are classified as hazardous wastes. The Mobil/Badger Cumene process uses a new zeolite catalyst developed by Mobil, tested by Badger, and first commercialized in 1996. The environmental features of this process are many. The catalyst is environmentally inert, requires no special packaging or handling, and can be returned to Mobil at the end of its useful life. Very high yields are achieved; this results in less byproducts and waste streams and in reduced consumption of raw materials. Byproducts are LPG and a small residue stream useful as a high value fuel; neither presents an environmental hazard. High product purity results in improved yield and greater throughput in downstream phenol units, with lower production of byproducts and waste streams. Lower consumption of utilities leads to environmental improvement in their generation. Existing cumene facilities can, with retrofit, derive the environmental benefits of a new facility. By the middle of 1998, approximately 85 percent of the demand for cumene in the United States will be met by new and upgraded facilities using this technology.

DuPont Company

Reduction of Carbon Tetrachloride Emissions at the Source by the Development of a New Catalyst

Phosgene is an important intermediate in the synthesis of polycarbonate plastics, high performance polymers, agrichemical intermediates, and urethane foams. Current global production is about 10 billion pounds per year. Although the process chemistry is selective, the byproduct carbon tetrachloride (CCl_4) is generated at a rate of 300 to 500 ppm, amounting to 5 million pounds per year globally. Since carbon tetrachloride is a carcinogen, an ozone depleting chemical, and a greenhouse gas, it was desirable to reduce or eliminate this undesirable byproduct. A DuPont team discovered a new catalyst that was produced in Siberia, Russia. After much laboratory work, it was decided to try a plant test, a scaleup of greater than 250,000 times. The catalyst was purchased, shipped from Siberia, and implemented in less than 1 year after the start of the program. After 1.5 years of commercial production, the new catalyst has consistently demonstrated high phosgene production rates and achieved a 90 percent reduction in the level of carbon tetrachloride generation (i.e., to less than 50 ppm, apparently a new global record). By conceptualizing, identifying, testing, securing from Russia, and implementing a novel phosgene production catalyst (well within the proposed 18 month deadline), the team saved the business a cost of $2 million associated with the installation of a new abatement furnace, which would have been the only other alternative. Furthermore, the resulting need for fewer catalyst changes in the reactor, as well as the prevention of maintenance costs that would have been associated with the abatement furnace, will save approximately an additional $400,000 per year. The catalyst technology is being offered for license globally, which could reduce emissions of CCl_4 by up to 5 million pounds per year.

Monsanto Company

Roundup Ready™ Technology

Roundup Ready™ technology is the mechanism by which crop selectivity to Roundup® herbicide has been introduced into crop plants. Roundup®, the world's largest selling herbicide, controls almost all weeds but shows little selectivity in crops. Roundup® has excellent environmental characteristics and the active ingredient of glyphosphate has been given a category E status (evidence for not being a carcinogen) by EPA. The mode of action of the herbicide is also known precisely. A set of unique genes (Roundup Ready™) were discovered and introduced into crop plants to protect them from damage by the herbicide. Commercial launch began in 1996 with soybeans in the United States and will be followed by cotton and corn in 1997 to 1998. Current research and development programs will soon thereafter lead to commercialization in other oilseed crops, such as rape seed, and in sugarbeet. Additional potential applications include wheat, rice, forestry, and vegetable and salad crops. Roundup Ready™ Technology has changed the spectrum of herbicides used. Farmers who planted Roundup Ready™ soybeans in 1996 reduced herbicide use by 10 to 35 percent with better weed control and generally did not use a preemergent or residual, post-emergent herbicide. Roundup® herbicide has no 'carry-over' in the soil, does not limit crop rotations, and is compatible with no-till crop production (a practice that is expanding in the United States and elsewhere). This technology extends to a wider aspect of agriculture and food production the ability to use one of the most beneficial and environmentally benign farm chemicals ever discovered.

Solvent Replacement and Improved Selectivity in Asymmetric Catalysis Using Supercritical Carbon Dioxide

Los Alamos National Laboratory

The use of supercritical carbon dioxide as a substitute for organic solvents already represents an important tool for waste reduction in the chemical industry and related areas. Coffee decaffeination, hops extraction, and essential oil production as well as waste extraction/recycling, and a number of analytical procedures already use this nontoxic, nonflammable, renewable, and inexpensive compound as a solvent. The extension of this approach to chemical production, using CO_2 as a reaction medium, is a promising approach to pollution prevention. Of the wide range supercritical carbon dioxide reactions that have been explored, one class of reactions has shown exceptional promise. Los Alamos National Laboratory has found that asymmetric catalytic reductions, particularly hydrogenations and hydrogen transfer reactions, can be carried out in supercritical carbon dioxide with selectivities comparable or superior to those observed in conventional organic solvents. Los Alamos has discovered, for example, that asymmetric hydrogen transfer reduction of enamides using ruthenium catalysts proceeds with enantioselectivities that exceed those in conventional solvents. The success of asymmetric catalytic reductions in CO_2 is due in part to several unique properties of CO_2 including tuneable solvent strength, gas miscibility, high diffusivity, and ease of separation. In addition, the insolubility of salts, a significant limitation of CO_2 as a reaction solvent, has been overcome by using lipophilic anions, particularly tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. These discoveries demonstrate an environmentally benign and potentially economically viable alternative for the synthesis of a wide range of specialty chemicals such as pharmaceuticals and agrochemicals.

Splittable Surfactants, A New Class of Surfactants Developed by Union Carbide Corporation

Union Carbide Corporation

Union Carbide has developed a new class of surfactants, 'Splittable Surfactants,' that will provide a substantial reduction in emulsified organics discharged in wastewater streams generated by a wide variety of industries. The new surfactants exhibit superior end use performance, as compared to current waste treatable surfactants and other proposed treatment schemes, which have not gained widespread use due to limitations in performance. Waste streams containing Union Carbide's 'Splittable Surfactants' are quickly, easily, thoroughly, and irreversibly 'split' and deactivated, via a chemical trigger, into nonsurface active components, allowing separation of the oily waste components from the water stream. A more concentrated oily waste is generated, facilitating incineration for fuel value and a highly biodegradable, essentially nontoxic water stream is discharged to treatment facilities. Before splitting and deactivation, 'Splittable Surfactants' have an environmental profile comparable to conventional nonionic surfactants. Upon deactivation, both the hydrophilic and hydrophobic components biodegrade rapidly; the hydrophilic component that remains in the wastewater is essentially nontoxic to aquatic life. The Splittable Surfactant technology is the focus of the first industry partnership under the U.S. Environmental Protection Agency's Environmental Technology Initiative for Chemicals.

Stepan Company

Stepan Company PA Lites Polyester Polyol

Stepan Company's Polyester Polyol product, manufactured using the Phthalic Anhydride Process Light Ends (PA Lites), uses a previously categorized waste as a raw material in its manufacture, thereby eliminating the material's disposal via incineration. This Polyester Polyol is the basic raw material for the manufacture of various types of insulating wallboard used in the home construction and commercial building industry. By substituting traditional raw materials with PA Lites, Stepan Company is providing the construction industry and consumer with a cost effective alternative to traditional building construction products. Benefits from this product substitution go beyond the elimination of a waste requiring disposal. With its substitution as a raw material, it has reduced the requirement for phtalic anhydride, the traditional raw material for the polyol product, and the air emissions associated with its manufacture. As part of the development of this process, the distillation operation in the phtalic anhydride facility was also improved. An estimated 350 tons per year of organic waste material has been eliminated with the development and implementation of this technology. This not only represents a significant reduction in waste requiring disposal by incineration, but also the air emissions associated with these processes. Since this previously categorized waste material is now used on site to produce Polyester Polyol, potential exposure to the general public during offsite transportation to disposal facilities has been eliminated. This project resulted in two economic benefits. The first is the savings associated with the transportation and disposal via fuel blending for energy recovery. On an annual basis the expected savings is \$200,000. The second economic benefit is the raw material savings due to the replacement of the Pure PA with the PA Lites material on a pound for pound basis. This results in additional savings of \$20,000 annually.

Stepan Company

STEPANFOAM® Water-Blown Polyurethane Foam HCFC-Free, Environmentally Friendly, Rigid Polyurethane Foam

STEPANFOAM® Water-Blown Polyurethane Foam is a product that replaces CFCs and HCFCs with water as the blowing agent in rigid polyurethane foam. Due to its unique and innovative chemistry, U.S. patent applications are pending for this product. Rigid polyurethane foam is a plastic material that provides a unique combination of insulation value and structural rigidity for common products such as picnic coolers, entry doors, and water heaters. Historically, polyurethane foams used in insulating applications incorporated trichlorofluoroethane (CFC-11) as the blowing agent. However, CFCs, such as trichlorofluoroethane, have been demonstrated to play a large role in the chemical destruction of Earth's stratospheric ozone layer, which acts as a filter for harmful ultraviolet radiation. Today, most polyurethane foams have replaced trichlorofluoroethane with HCFC-141b as the blowing agent. Although it has an ozone depletion potential that is lower than that of CFC-11, HCFC-141b is also considered an ozone-depleter. The Stepan Company has remained committed to addressing these issues through the development of a lower cost, technologically advanced polyurethane foam, which replaces environmentally unfriendly and potentially hazardous blowing agents with water. STEPANFOAM® Water-Blown Foam eliminates emissions of CFCs and HCFCs into the environment; it ultimately reduces the mass of solid waste requiring disposal, and it offers a safer alternative blowing agent than other technologies are currently offering. The final, and perhaps most important, property considered in the development of STEPANFOAM® Water-Blown Foam as an alternative to HCFC-blown products is its insulative capacity. Outstanding flow characteristics, combined with a fine cellular structure, maximize the insulation capability of STEPANFOAM® Water-Blown Foam. At the same core density, the physical properties of the two systems are nearly identical. By replacing CFC and HCFC with water in its formulations, Stephan has eliminated its use of as much as 2 million pounds per year of CFCs and will eliminate as much as 1 million pounds per year of HCFCs.

Synergy CCS™ Precision Cleaning Solvent: A Government/Industry Solution to a Complex Environmental Problem

Allied Signal Federal Manufacturing and Technologies

Synergy CCS™ had its beginnings at the Department of Energy's Kansas City Plant (managed and operated by AlliedSignal Inc.) when the plant began an effort focused on the elimination of toxic, restricted, or environmentally damaging solvents. Experience derived from this solvent substitution and elimination effort proved beneficial when, through its Technology Transfer Program, Kansas City Plant personnel were asked for help by a small manufacturer needing a safe, one-step cleaning solvent. Synergy CCS™ Precision Cleaning Agent was formulated to meet this need. Synergy CCS™ is a blend of environmentally derived products that forms a safe, powerful, yet distillable precision cleaning solvent capable of being heavily loaded with contaminants. Synergy CCS™ is comprised of natural components that have been in industrial use for over 45 years: d-limoene, a solvent derived from citrus byproducts, and tetrahydrofurfuryl alcohol, a solvent produced from the waste products of corn, oats, and sugar production. Individually, these materials are already used for cleaners, paint stripping formulations, and agricultural applications. The solvent was further developed and adopted by a Hewlett-Packard Co. division, patented, and licensed to Petroferm, Inc., a worldwide leader in sales and technical support for alternative solvents and cleaning technologies. This partnership demonstrates how government and private industry can work together to develop safe chemical alternatives to solve environmental problems while simultaneously improving America's industrial competitiveness.

Use of Carbon Dioxide as an Alternative Green Solvent for the Synthesis of Energetic Thermoplastic Elastomers

U.S. Navy, Office of Naval Research

U.S. Navy, Naval Surface Warfare Center

Aerojet Propulsion

Professor Joseph M. DeSimone, Department of Chemistry, University of North Carolina at Chapel Hill

Thermoplastic elastomers based on triblock oxetane copolymers containing azido functional groups offer an improved binding material for solid, high-energy formulations. Current technology uses chemically cross-linked energetic prepolymer mixes that introduce the problems of thermally labile chemical linkages, high end-of-mix viscosities, and vulnerability to premature detonation. These materials are also nonrecyclable and generate large amounts of pollution during disposal. The use of energetic thermoplastic elastomers eliminates the need for chemical cross-linking agents, makes processing easier due to their low melt viscosities, and eliminates the need for solvents during casting. Their superior processing qualities and the ease of demilitarization and recycling make these materials a much more environmentally sound choice for energetic binders. However, their synthesis still involves the use of large quantities of toxic chemicals, such as methylene chloride, as solvents. Carbon dioxide has been proven to be a viable, environmentally responsible replacement solvent for many synthetic and processing applications. It is cheap, easily recyclable, and available from current sources. Research at the University of North Carolina has shown that carbon dioxide is a viable solvent for the polymerization of vinyl ether monomers. Furthermore, polyoxetanes can be polymerized in carbon dioxide with molecular weight, molecular weight distribution, and functionality maintained. The University of North Carolina has demonstrated the synthesis of both nonenergetic and energetic homopolymers and random copolymers.

Alliance for Environmental Technology (AET)

The Use of Chloride Oxide, the Foundation of Elemental Chlorine-Free (ECF) Bleaching for Pulp and Paper, as a Pollution Prevention Process

The use of chlorine dioxide as a pollution prevention process to substantially or completely replace chlorine in the first stage of chemical pulp bleaching is a unique implementation of chlorine dioxide chemistry. It can be applied to the entire bleached chemical pulp and paper industry, both in the United States and abroad. By employing raw material substitution and process modifications, this technology has allowed the pulp and paper industry to meet the source reduction objectives of the Pollution Prevention Act of 1990. With this new application of sophisticated chlorine dioxide chemistry, the pulp and paper industry virtually eliminated dioxin from mill waste waters and our nation's water bodies. This technology has answered the industry's calls for a more benign chemical pulp bleaching agent. Virtual elimination of dioxin from mill waste waters and continuing nationwide ecosystem recovery provide a strong measure of chlorine dioxide's success and the industry's environmental progress. In fact, downstream of U.S. pulp mills bleaching with chlorine dioxide, fish dioxin body burdens have declined rapidly and aquatic ecosystems continue to recover. For example, the Mead Paper Company's Escanaba Mill, in Michigan, implemented pollution prevention strategies beginning with the use of low precursor defoamers in 1989. In 1990, the mill increased chlorine dioxide substitution. These process modifications decreased dioxin in final mill effluent to nondetectable levels. Consequently, dioxin body burdens declined more than 90 percent in less than 4 years. These indicators of progress toward broader ecosystem integrity demonstrate the success of chlorine dioxide as 'green chemistry.'

U.S. Navy, Office of Naval Research

U.S. Navy, Naval Surface Warfare Center

U.S. Army Armament Research, Development and Engineering Center

Los Alamos National Laboratory

Aerojet

Waste Reduction in the Production of an Energetic Material by Development of an Alternative Synthesis

1,3,3-Trinitroazetidine (TNAZ) is a promising new melt-castable explosive that has significant potential for providing environmental benefits and capability improvements in a wide variety of defense and industrial applications. Initial lifecycle inventories on various munitions revealed that up to 50 percent of the lifecycle pollution burden was associated with the demilitarization of the munitions, and in particular, the use of thermoset polymeric binders that require removal with water jet cutting. TNAZ is the only energetic material other than trinitrotoluene (TNT) that can be melt-cast in existing TNT loading plants. Demilitarization of TNAZ simply requires heating the device above the melting point and pouring the liquid out, rather than the complicated and destructive methods used for RDX- and HMX-based plastic-bonded explosives. The stability of TNAZ in the melt allows it to be easily recycled. TNAZ has performance slightly better than that of HMX, the most powerful military explosive in current use. Thus, TNAZ may offer 30 to 40 percent improvements in performance as a replacement for TNT-based formulations such as Composition-B. The alternative synthesis of TNAZ, developed at the Los Alamos National Laboratory, allows TNAZ to be produced in a waste-free process that also eliminates the use of halogenated solvents. This alternative synthesis produces 5.3 pounds of waste per pound of product compared to the original synthesis of TNAZ, which produces 1,200 pounds of waste per pound of product. The alternate technology has been transferred to industry, where it has been scaled up to production-plant quantities. Further improvements in waste reduction have been demonstrated in the laboratory that may eventually lead to a process giving little more waste than one pound of salt per pound of TNAZ.

Water-Dispersible Hot-Melt Adhesive Raw Material

Eastman Chemical Company

Current technologies make recycling and disposal of paper products difficult. The hot-melt adhesive industry has been searching for an answer in the form of a water-dispersible raw material. Previous attempts to satisfy this need were often deficient in both critical performance requirements and cost. Government regulations are not yet directly mandating improved adhesive raw materials, but the needs are real and urgent just the same. The lack of regulatory changes does not encourage adhesive manufacturers to introduce products based on expensive raw materials. Eastman AQ 1350 water-dispersible hot-melt adhesive raw material represents the best of both worlds. The water dispersibility of Eastman AQ 1350 is due to the random incorporation of sodiosulfonate groups along with polymer backbone. These ionic functionalities also facilitate the excellent adhesion of Eastman AQ 1350 to a variety of substrates. Some of the key features of Eastman's new product are low cost, 100 percent water-dispersible in ordinary tap water, nondispersible in ionic solutions, superior adhesion to polyolefin films, and comparable key physical properties to conventional formulations. Eastman AQ 1350 is part of a new family of water-dispersible polymers that provide the hot-melt adhesive industry with an innovation that addresses long-standing needs in very large, applicable areas. These products not only overcome the lack of water-dispersibility inherent to the current generation of technology but also are differentiated from the competitive generation of technologies by their ability to be dispersed into water coupled with insolubility in saline solutions. This tunable solubility mechanism also can be employed as a method for product recovery; thus, it is legitimate to call Eastman AQ 1350 an advanced technology of a 'smart material.'

West Fork Biotreatment Project

Asarco Incorporated

Asarco has developed a biotreatment system for removing metals from mine water prior to its discharge to the waters of the state. Asarco owns and operates two lead mines and a lead smelter and refinery in southeast Missouri. Recent changes in the Water Quality Standards required Asarco to explore water treatment alternatives. One of the alternatives considered was biotreatment. Preliminary results from a tank test and proof-of-principle test conducted in 1993, were very encouraging and plans were made for a scale size operation to be built. In early 1994 a pilot plant biocell was constructed and filled with a substrate mixture of sawdust from an abandoned sawmill, alfalfa hay, cow manure from a dairy, mine tailings, and lime rock. All material used was acquired locally. Sulfate Reducing Bacteria (SRB) were cultivated within the anaerobic environment of the substrate. SRB are abundant in nature and are found predominantly in bogs and swamps. The SRB produce hydrogen sulfide gas as a byproduct that acts as a sulfiding agent to precipitate the dissolved metals from the mine water. The system also removes significant amounts of nitrates. The pilot plant reduced metals to below the Water Quality Standards set by the State of Missouri for protection of aquatic life. Different operation scenarios were implemented to explore the limits of the system. For 2 years, through extremes of ambient temperature, water flow rates, and metals loadings, the biotreatment system operated efficiently. The system reverses the process which put the lead in the dissolved form and returns it to a lead sulfide (PbS), an original inert form of lead ore. The PbS remains in the substrate for the life of the plant which is estimated, based on carbon consumption, to be in excess of 30 years. No chemicals were used, therefore, no chemicals must be transported on highways at risk of spilling. No daily sludges are generated that have to be disposed of in landfills, and water quality is improved. Construction of a full-scale plant was completed in July 1996. Start-up was completed in November and the full-scale plant is currently treating 1,500 GPM and is allowing West Fork Mine to comply with the NPDES permit limits.

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