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The Presidential Green Chemistry Challenge Awards Program

Summary of 1996 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 1996 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 the 1996 Awards and nationally recognized on July 11, 1996.

This document provides a collection of summaries of the entries received for the 1996 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 1996 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 that was 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

Monsanto Company

The Catalytic Dehydrogenation of Diethanolamine

Disodium iminodiacetate (DSIDA) is a key intermediate in the production of Monsanto's Roundup® herbicide, an environmentally friendly, nonselective herbicide. Traditionally, Monsanto and others have manufactured DSIDA using a well-known process (Strecker process) requiring ammonia, formaldehyde, hydrogen cyanide, and hydrochloric acid. Hydrogen cyanide is of particular concern because of its extreme acute toxicity, and its use requires special handling to minimize risk to workers, the community, and the environment. Furthermore, the chemistry involves the exothermic generation of potentially unstable intermediates, and special care must be taken to preclude the possibility of a runaway reaction. The overall process also generates up to one kilogram of waste for every seven kilograms of product. Much of this waste contains traces of cyanide and formaldehyde and must be treated prior to safe disposal.

In pursuit of safer and environmentally benign chemistry, Monsanto has developed and implemented an alternative DSIDA process that relies on the copper-catalyzed dehydrogenation of diethanolamine (DEA). The raw materials have low volatility and are less toxic than those of other processes. Process operation is inherently safer because the dehydrogenation reaction is endothermic and therefore does not present danger of runaway. Moreover, this "zero-waste" route to DSIDA produces a product stream that, after filtration of catalyst, is of such high quality that no purification or waste cut is necessary for subsequent use in the manufacture of Roundup®. The new technology represents a major breakthrough in the production of DSIDA because it avoids the use of cyanide and formaldehyde, is safer to operate, produces higher overall yield, and has fewer process steps.

The metal catalyzed conversion of aminoalcohols to amino acid salts was known since 1945. However, commercial application of this chemistry was not known until Monsanto developed a series of proprietary catalysts that make the chemistry commercially feasible. The original dehydrogenative approach to amino acid salts had apparently been impracticable because the catalysts, cadmium, nickel, and copper, are either too toxic, poorly selective, poorly active, and/or physically unstable to be commercially viable. The patented improvements on metallic copper catalysts made at Monsanto afford an active, easily recoverable, highly selective, and physically durable catalyst that has proven itself in large-scale use.

This catalysis technology also can be used in the production of other amino acids such as glycine. Moreover, it is a general method for conversion of primary alcohols to carboxylic acid salts and is potentially applicable to the preparation of many other agricultural, commodity, specialty, and pharmaceutical chemicals.

Alternative Solvents/Reaction Conditions Award

The Dow Chemical Company

The Development and Commercial Implementation of 100 Percent Carbon Dioxide as an Environmentally Friendly Blowing Agent for the Polystyrene Foam Sheet Packaging Market

In recent years the chlorofluorocarbon blowing agents used to manufacture polystyrene foam sheet have been associated with environmental concerns such as ozone depletion, global warming, and ground level smog. Due to these environmental concerns, the Dow Chemical Company has developed a novel process for the use of 100 percent carbon dioxide CO_2. Polystyrene foam sheet is a useful packaging material offering high stiffness to weight ratio, good thermal insulation value, moisture resistance, and recyclability. This combination of desirable properties has resulted in the growth of the polystyrene foam sheet market in the United States to over 700 million pounds in 1995. Current applications include thermoformed meat, poultry and produce trays, fast food containers, egg cartons, and serviceware.

The use of 100 percent CO_2 offers optimal environmental performance because CO_2 does not deplete the ozone layer, does not contribute to ground level smog, and will not contribute to global warming since CO_2 will be used from existing by-product commercial and natural sources. The use of CO_2 by-product from existing commercial and natural sources such as ammonia plants and natural gas wells, will ensure that no net increase in global CO_2 results from the use of this technology. Carbon dioxide is also non-flammable providing increased worker safety and is cost effective and readily available in food grade quality. Carbon dioxide also is used in such common applications as soft drink carbonation and food chilling and freezing.

The use of Dow 100 percent CO_2 technology eliminates the use of 3.5 million pounds per year of hard CFC-12 and/or soft HCFC-22. This technology has been scaled from pilot line to full scale commercial facilities. Dow has made the technology available through a commercial license covering both patented and know how technology. The U.S. Patent Office granted Dow two patents for this technology (5,250,577 and 5,266,605).

Designing Safer Chemicals Award

Rohm and Haas Company

Designing an Environmentally Safe Marine Antifoulant

Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry approximately $3 billion a year. A significant portion of this cost is the increased fuel consumption needed to overcome hydrodynamic drag. Increased fuel consumption also contributes to pollution, global warming, and acid rain.

The main compounds used worldwide to control fouling are the organotin antifoulants, such as tributyltin oxide (TBTO). They are effective at preventing fouling, but have widespread environmental problems due to their persistence in the environment and the toxic effects they cause, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish. These harmful effects led to an EPA special review of organotin antifoulants and to the Organotin Antifoulant Paint Control Act of 1988. This act mandated restrictions on the use of tin in the United States and charged the EPA and the U.S. Navy with conducting research on alternatives to organotins.

Based on the need for new antifoulants, Rohm and Haas Company began to search for an environmentally safe alternative to organotin compounds. The ideal antifoulant would prevent fouling from a wide variety of marine organisms without causing harm to non-target organisms. Compounds from the 3-isothiazolone class were chosen as likely candidates and over 140 were screened for antifouling activity in laboratory and field tests. The 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Sea-Nine™ anti-foulant) was chosen as the candidate for commercial development.

Extensive environmental testing was done comparing Sea-Nine™ antifoulant to TBTO, the current industry standard. Sea-Nine™ antifoulant degraded extremely rapidly with a half life of one day in seawater and one hour in sediment. TBTO, on the other hand, degraded much more slowly, with a half life in seawater of nine days and six to nine months in sediment. Tin bioaccumulated, with bioaccumulation factors as high as 10,000 X, while Sea-Nine™ antifoulant's bioaccumulation was essentially zero. Both TBTO and Sea-Nine™ were acutely toxic to marine organisms, but TBTO had widespread chronic toxicity, while Sea-Nine™ antifoulant showed no chronic toxicity. Thus the maximum allowable environmental concentration (MAEC) for Sea-Nine™ antifoulant was 0.63 parts per billion (ppb) while the MAEC for TBTO was 0.002 ppb. Sea-Nine™ antifoulant has been sold world-wide and hundreds of ships have been painted with coatings containing it. Rohm and Haas Company obtained EPA registration for the use of Sea-Nine™ antifoulant, the first new antifoulant registration in over a decade.

Small Business Award

Production and Use of Thermal Polyaspartic Acid

Donlar Corporation

Millions of pounds of anionic polymers are used each year in many industrial applications. Polyacrylic acid (PAC) is one important class of such polymers. In many uses, the polymers ultimately end up in a waste treatment facility. The ideal disposal for these polymers is via biodegradation by microorganisms because the degraded endproducts are innocuous. The disposal of PAC is problematic, however, because it is not biodegradable. An economically viable, effective, and biodegradable alternative is thermal polyaspartate (TPA).

Donlar invented two highly efficient processes to manufacture TPA; patents have either been granted or allowed. The first process involves a dry and solid polymerization converting aspartic acid to polysuccinimide. No organic solvents are involved during the conversion and the byproduct is condensated water. The process is extremely efficient – a yield of more than 97 percent of polysuccinimide is routinely achieved. The second step of this process, the base hydrolysis of polysuccinimide to polyaspartate, is also extremely efficient and waste free.

The second TPA production process involves using a catalyst during the polymerization, which allows a lower heating temperature to be used. The resulting product has improvements in performance characteristics, lower color, and biodegradability. The catalyst can be recovered from the process, thus minimizing waste.

Independent toxicity studies of commercially produced TPA have been conducted using mammalian and environmental models. Results indicate that TPA is non-toxic and environmentally safe. TPA biodegradability also has been tested using established OECD methodology, performed in an independent laboratory. Results indicate that TPA meets OECD guidelines for Intrinsic Biodegradability. PAC can not be classified as biodegradable when tested under the same conditions.

Many end uses of TPA have been discovered. In the agricultural sector, the use of high levels of fertilizer has been practiced to sustain crop yields. However, the efficiency of fertilizer usage is generally low and unused fertilizer can cause not only economic loss, but has an undesirable impact on the environment. Therefore, a better fertilizer management strategy is warranted to sustain crop yields and lessen the negative environmental impact of fertilizer runoff. TPA can be an ideal candidate to improve fertilizer or nutrient management because it increases the efficiency of plant nutrient uptake, which not only assists in sustaining the nutrient sources, but also protects the ecology of the agricultural land, while at the same time bringing economic benefits in the form of increased crop yields.

TPA also can be used in the water treatment industry. TPA can be used as mineral scale inhibitors for calcium carbonate, calcium sulfate and barium sulfate. The efficacy of TPA has been tested extensively and compared with PAC, the industry standard. Results indicate that TPA is as good as, and in many instances outperformed, PAC.

There are additional uses for TPA. In the detergent industry, TPA can be used as an anti-redeposition agent; its efficacy is again comparable to PAC. In the oil and gas production industry, TPA can serve as scale and corrosion inhibitors, reducing the need for toxic corrosion inhibitors and lessen the need for waste treatment.

TPA is an ideal candidate for use in water treatment, agriculture, and other industries. The processes to manufacture TPA are economically viable and TPA is proven to be biodegradable, non-toxic, and effective.

Academic Award

Conversion of Waste Biomass to Animal Feed, Chemicals, and Fuels

Professor Mark Holtzapple, Department of Chemical Engineering, Texas A&M University

A family of technologies has been developed at Texas A&M that converts waste biomass into animal feed, industrial chemicals and fuels. Waste biomass includes such resources as municipal solid waste, sewage sludge, manure, and agricultural residues. Currently these resources are under-utilized; in fact, many have a cost associated with their disposal. Waste biomass is treated with lime to render it more digestible. Lime-treated agricultural residues (e.g. straw, stover, bagasse) may be used as ruminant animal feeds. Alternatively, the lime-treated biomass can be fed to a large anaerobic fermentor in which rumen microorganisms convert the biomass into volatile fatty acid (VFA) salts such as calcium acetate, propionate, and butyrate. The VFA salts are concentrated and may be converted into chemicals or fuels via three routes. In one route, the VFA salts are acidified releasing acetic, propionic, and butyric acids. In a second route, the VFA salts are thermally converted to ketones such as acetone, methyl ethyl ketone, and diethyl ketone. In a third route, the ketones may be hydrogenated to their corresponding alcohols such as isopropanol, isobutanol, and isopentanol.

This family of technologies offers many benefits for human health and the environment. Lime-treated animal feed can replace feed corn, which is approximately 88 percent of corn production. Growing corn requires plowing, which exacerbates soil erosion; approximately two bushels of top soil are lost for each bushel of corn harvested. Also, corn requires intensive inputs of fertilizers, herbicides, and pesticides, all of which are contaminating ground water.

Chemicals (e.g. organic acids and ketones) may be produced economically from waste biomass that has a negative impact on the environment, such as municipal solid waste and sewage sludge. Typically, these wastes are landfilled or incinerated, which incurs a disposal cost while contributing to land or air pollution. By producing chemicals from biomass, nonrenewable resources such as petroleum and natural gas, are conserved for later generations. Because 50 percent of U.S. petroleum consumption is now imported, displacing foreign oil will help reduce the U.S. trade deficit.

Fuels (e.g. alcohols) produced from waste biomass have the benefits cited above, i.e., reduced environmental impact from waste disposal and reduced trade deficit. In addition, oxygenated fuels derived from biomass are cleaner burning and do not add net carbon dioxide to the environment, thereby reducing factors that contribute to global warming.

Entries from Academia

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

Professor
Stephen L. Buchwald,
Chemistry Department,
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 have 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 solvents are derivatives of solvents currently used in reaction and separation processes, tailored such that they are relatively non-volatile and non-water 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 higher alkanes. Polymeric or oligomeric solvents such as derivatized THF have been synthesized using macromonomers incorporating the desired functionality. These polymeric solvents are easily recovered using mechanical separations such as ultrafiltration rather than energy-intensive distillation processes. This new concept for solvent design and synthesis 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.

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

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

The development of effective carbon-carbon bond forming reactions in aqueous media is imperative for the future welfare and growth of the chemical industry. 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 non-toxic, very resistant to air oxidation, and easily recovered by simple electrochemical means, thus permitting its re-use and guaranteeing uncontaminated waste flow. In addition, protection-deprotection of functional groups and an inert atmosphere are not necessary when implementing this technology. Commercial application is immediately possible for this exciting new chemistry and may have been implemented already. As additional progress is made, adaption to existing procedures will undoubtedly come quickly.

Professor
Tomas Hudlicky,
Department of Chemistry,
University of Florida

Enzyme-Assisted Conversion of Aromatic Substances to Value-Added End Products. Exploration of Potential Routes to Biodegradable Materials and New Pharmaceuticals

The combination of enzymatic transformations performed in aqueous media with efficacious, brevity-based design has been shown to yield unprecedented efficiency in the attainment of important pharmaceuticals from metabolites of the arene *cis*-diol type, more than 200 of which are known. Such processes lead to pollution reduction at the manufacturing source by drastically shortening the synthetic process, thus requiring less reagent and solvent input. Because one or more steps are performed in water with whole cells of common soil bacteria, the residual mass of such steps is, after sterilization, judged suitable for disposal to municipal sewers, thus further reducing the amount of actual waste. This program has potentially global impact with attendant benefits to the health and economy of society at large through managed processing of aromatic waste.

Green Technology for the 21st Century: Ceramic Membranes

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

Advancing technology in the areas of remediation and such "green" engineering tools as ceramic membranes can make a significant contribution in terms of environmental clean-up and a healthier world. Ceramic membranes represent a relatively new class of materials that can be produced from a variety of starting materials and processed in different ways to yield products with a broad range of physical-chemical characteristics and an equally large range of applications. The robust character of ceramic membranes enables them to withstand broad pH and temperature ranges, elevated pressures, organic solvents, and chemical and heat sterilization. In addition, pore size can be controlled in these materials and is typically 5-100 Å in diameter. These characteristics indicate that ceramic membranes could replace their organic polymeric counterparts in many applications where conditions would otherwise preclude using an organic polymer membrane. These applications include separations, catalysis, photocatalysis and energy storage systems for solar cells and micromotor devices. Ceramic membranes are a cutting edge technology that could well provide economic growth for existing industries, in addition to facilitating new growth industries in environmental remediation. A market survey published in 1992 on the economic benefits from alternate applications of inorganic membrane technology indicated that active implementation of such technology could well result in a $2 billion per year sales market, a $16.6 billion increase in the national GDP, a $2 billion improvement in the balance of trade, and a decrease in energy use of 6 quads per year.

A Nontoxic Liquid Metal Composition for Use as a Mercury Substitute

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

Virginia Tech Intellectual Properties

Mercury is used extensively in switches and sensors, but 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 non-toxic 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, non-mercury 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 non-mercury material also can serve as a substitute for elemental mercury in a many of these applications.

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

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

Rational Design of Catalytic Reactions for Pollution Prevention

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. Yield 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 has been 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 formulate the catalyst. This strategy for the rational design of catalytic reactions has found wide acceptance worldwide and has been applied successfully to link surface science research to the development of industrially important catalytic chemical reactions. Industrial collaborations and/or applications include ammonia catalysis, the environmental de-NOx 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.

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

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

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

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. The technology is the first to show that free radical bromination of organics can be carried out in aqueous systems. A unique semi-continuous 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 VOC’s adds a major incentive for process modification.

Soapy CO_2

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

Air Products and Chemicals, Inc.

Carbon dioxide surfactant technology, or “soapy CO_2”, has demonstrated the utility of replacing less acceptable organic chemicals with liquid/supercritical CO_2 and thus can have a very positive environmental impact. Carbon dioxide represents an environmentally friendly alternative to the solvents currently used in a variety of applications. In order to expand the use of liquid and supercritical CO_2, its solvating power for large, hydrocarbon based molecules must be enhanced. The key to this technology is the development of surfactant systems for CO_2 as well as establishing the underlying principles involved with CO_2-surfactant combinations. In addition to polymerization processes, technology extensions of this project are relevant for CO_2 as a cleaning and extraction media (replacing halogenated hydrocarbons) as well as a solvent/media for organic reactions. In all of these applications, the production and emission of hazardous waste would be significantly reduced by replacing the current technology with carbon dioxide surfactant technology. It must be noted that CO_2 is readily available as a waste gas from various sources. Thus no new CO_2 will be produced due to the success of the technology – it will just be borrowed from the environment for an interim period of time.

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 the short alternative syntheses of any product from real starting materials in terms of both their cost and environmental impact.

Entries from Small Businesses

Molten Metal Technology, Inc.

Catalytic Extraction Processing

Catalytic Extraction Processing (CEP) is a proprietary technology that uses secondary materials and by-products (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 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 off-site, closed-loop process unit, CEP maximizes environmental performance for a broad spectrum of secondary materials and by-products through pollution prevention, waste minimization, and decreased demand on ever-diminishing natural resources.

Altus Biologics Inc.

Cross-Linked Enzyme Crystal Technology

Enzymes are proteins that can function as highly efficient and selective catalysts. They have evolved over billions of years to facilitate the myriad of biochemical reactions essential to life, and as such, they are compatible by definition with living organisms. The benefits of enzyme technology have long been recognized, but to date, the chemical and physical stability of enzymes has not approached that of conventional heterogeneous catalysis. Crosslinked Enzyme Crystals (CLEC) are novel catalysts that are suitable for chemical manufacturing, diagnostic instruments, therapeutics, and for the detoxification of hazardous materials. The concept of CLEC emerged from the realization that protein crystals grown for structural studies using X-ray diffraction were also macroscopic particles that, if properly stabilized, might present a new and robust class of immobilized enzymes. By extension of this simple idea, CLECs have been developed that circumvent many of the practical problems associated with enzyme use. In addition to being environmentally benign, enhanced properties of CLECs include superior catalytic performance, operating stability, storage stability, compactness, superior uniformity, and operational convenience.

Development of a Biodiversity Search and Enzyme Optimization Technology

Recombinant BioCatalysis, Inc. (RBI)

Biocatalysis is widely regarded as a promising new approach to source reduction of pollution associated with chemical manufacturing. It has not been widely adopted to date, however, due to the limited availability of process-compatible biological catalysis. Recombinant Biocatalysis, Inc. (RBI), has developed a whole new tool kit of biological catalysis for chemists. Catalysts are central to modern chemical manufacturing as well as to life. A good catalyst accelerates the rate of a desired reaction compared to unwanted, waste generating, side reactions. Enzymes are wonderfully selective and specific catalysts. Enzymes, however, evolved to work in living systems, and enzymes that work well in a chemical process plant have not been broadly available to chemists and chemical engineers. RBI has developed a new technology specifically to meet that unmet need. By turning state-of-the-art biotechnology to the problem of making useful enzymes for chemists, RBI has enabled a step change in the availability of useful protein-based catalysts for the chemical process industry. RBI has developed and applied a powerful, new biodiversity search technology to scan natural sources for new enzymes. Once the best enzyme that nature has to offer for a particular application is identified, RBI applies additional high throughput technology to optimize the enzyme to make it more useful in a chemical plant. This new technology already has produced more than 150 new, robust biological catalysts for the chemical process industry and will generate more than 3,000 by 1997.

Development of a Nickel Brightener Solution

Benchmark Products, Inc.

Historically, electroplaters of duplex nickel had to use formaldehyde and coumarin-bearing nickel plating solutions to obtain a non-sulfur 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 modern bright nickel plating baths known today, using 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 "semi-bright". Today, semi-bright 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 non-hazardous ingredients.

Zeller International

Enviroblock Technology

Using a new pulverization technology, all types of scrap glass can be ground into a useful aggregate with the consistency of beach sand or fine gravel. Any size or form of flat window glass, mirrors, windshields, light bulbs, bottles, neon tubing, or glass containers can be processed back into a usable form. Scrap glass is fed to an EVIROGRINDER pulverizing machine which delivers a controlled particle size material. A fine grind sand product is then fed to a blending machine, the ENVIROMIXER, which dry blends the two basic substances, ground glass and a reactive binder. These mixed materials are placed inside the ENVIROPACTOR machine to form blocks. Hard, dense, naturally insulative/smooth faced blocks are rapidly compacted at low cost and high volume with a yield of 400 to 600 blocks per hour. Walls built with glass blocks reduce heating and air conditioning because glass is a natural insulation source. Glass blocks are waterproof, fireproof, strong, and reduce energy consumption.

Stanson Corporation

National Conversion to Low Sudsing Hand Dish Detergents for Industrial, Institutional, and Especially Consumer Application

In the United States, almost all dish detergents or liquid detergents used for hand dish washing are anionic based, with specifically high foaming properties formulated purposely into the product to deliver a consumer aesthetic. To provide this sudsing characteristic, multiple anionic and foam boosters are used/needed to deliver the effect. The addition of all these extra chemicals is unnecessary to deliver actual cleaning performance and oily soil emulsification. This can be achieved by using nonionic surfactants, straight chain linear alcohol ethoxylates or APGs (alkyl polyglycosides) or other low foaming environmentally suitable alternatives to alkylbenzene sulfonate and foam boosters formulation types. Nationwide use of this technology in all dish detergents would reduce overall toxicity due to the discharge of high sudsing dish products in rivers and streams. In addition, overall water usage would decrease due to faster manufacturing and overall reduced energy consumption of operations providing this product category to all U.S. market sectors: consumer, industrial, and institutional. This formulation strategy can be available immediately nationwide and can be manufactured readily by all national brand companies.

Circuit Research Corporation

A Non-Toxic, Non-Flammable, Aqueous-Based Cleaner/Degreaser and Associated Parts Washing System Commonly Employed in Automotive Repair Industry

An aqueous based cleaner and associated parts washing system commonly employed in the automotive repair industry has been developed that eliminates the generation of hazardous waste associated with current parts wash systems. Currently, the majority of parts washers employ a "Stoddard Solvent" which, when spent, is manifested as a hazardous waste to a distillation facility which separates the solvent from the petroleum residue. The new technology employs a non-toxic, non-flammable, 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 and/or transportation and special treatment of spent cleaner material off-site. Testing results have shown that (i) 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 (ii) 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.

Entries from Industry and Government

Bayer Corporation

Aldimine-Isocyanate Chemistry: a Foundation for Environmentally-Friendly High Solids Coatings

The single greatest challenge that the chemical industry faces today is the design and manufacture of new chemicals that are not only efficacious, but just as importantly, environmentally friendly. Within the coatings industry, these new chemicals play the additional role of aiding in pollution prevention by reducing the amount of volatile organic compounds (VOCs) in the form of solvents, materials that traditionally have been used at high levels. The need for raw materials that reduce solvent demand and yet maintain or preferably improve coating performance is of primary importance. Commercial coatings systems based on aldimine-isocyanate chemistry have been developed and are finding widespread acceptance as a solution to VOC restrictions. Current applications exist in the automotive refinish business where aldimines are used to make coatings containing only 20 to 25 percent volatile solvents, replacing products that have 40 to 50 percent volatile solvents by weight. Since the introduction of this technology in 1995, old technology resin systems requiring more than 100,000 kilograms of additional organic solvent have been displaced. This volume will triple in 1996 and approach one million kilograms in 1997. More importantly, the volume of organic solvents displaced as other market areas adopt this technology is expected to increase dramatically. Additional benefits of this technology include: allowing low VOC coatings to be developed, resulting in large solvent savings for a given application without transferring environmental liability to production or use; it is already in significant commercial use, and will become a high volume product line by the end of the century, resulting in nontrivial source reduction of organic solvent emissions; it is compatible with existing and future coatings systems; it does not require significant capital investment to employ; and it increases productivity.

Henkel Corporation, Emery Group

Alkyl Polyglycoside Surfactants

Henkel Corporation's alkyl polyglycoside (APG®) surfactants are a class of non-ionic surfactants marketed to the detergent and personal care industries. APG® surfactants are manufactured from renewable resources: fatty alcohol, derived from coconut and palm oils, and glucose, derived from corn starch that is supplied from U.S. sources. APG® surfactants have very low ecotoxicity and are readily biodegradable and, therefore, are more innocuous to the environment than alternative petrochemical-based technologies. In addition to the environmental friendliness of the chemistry, APG® surfactants demonstrate the following benefits in detergent and personal care applications: reduction of overall chemical consumption by improving the cleaning efficiency in detergent formulations; reduction of formulated product packaging waste by permitting the formulation of concentrated cleaning products; reduction of formula stabilizing adjuncts (hydrotropes), such as sodium xylene sulfonate and ethanol, that do not contribute to cleaning performance and, in the case of ethanol, increase volatile organic emissions; and excellent cleaning performance with lower skin and eye irritation compared to other surfactants. APG® surfactants represent an important application of green chemistry that uses renewable resources. APG® surfactants are currently manufactured in a new plant producing 50 million pounds per year for use in the formulation of several hundred detergent and personal care products in the United States and worldwide.

The Alternative Feedstocks and Biological and Chemical Technologies Research Programs

U.S. Department of Energy, Office of Industrial Technologies Programs

The Alternative Feedstocks (AF) program supports development work that employs alternative, renewable feedstocks in the biological and/or chemical production of commodity or commodity-like chemicals. The Biological and Chemical Technologies Research (BCTR) program supports research and development efforts that provide evidence of the technical and economic feasibility of advanced chemical and biological concepts that improve energy utilization, operational efficiencies, and environmental soundness of current U.S. industry process operations. These two programs involve both the specific and broad utilization of "green chemistry" in the fulfillment of their missions. By definition, the AF program is green chemistry since it promotes the use of renewables in producing subsidy-free chemicals from feedstocks such as corn, lignocellulosics, and oil seed crops on scales that are or could be commodity chemicals. Many of the technology hurdles needed to employ biocatalysts as tools or biomass as a feedstock resource for the chemical processing industry have been addressed by the BCTR program. For example, efforts ranging from the development of molecular modeling tools to new, less toxic electrochemical hydrogenation processes have been undertaken and demonstrated for use in current processes. Within the federal sector, these two programs have an exceptional history of applying green chemistry to industrial needs.

An Alternative Solvent, Isomet

Bureau of Engraving and Printing, Office of Research and Technical Support

The Bureau of Engraving and Printing, the world's largest securities manufacturing establishment, produces currency, postage stamps, revenue stamps, United States Saving Bonds, and other government securities. Until 1990, the Bureau used Typewash for cleaning the typographic seals, serial number, numbering blocks of the Cop-Pack (overprinting presses) and postage stamp printing presses. Typewash is a solvent mixture of methylene chloride (55 percent), toluene (25 percent) and acetone (20 percent). As of September 1, 1990, this solvent is no longer in compliance with District of Columbia Environmental Law and Federal Air Toxic Law. An alternative solvent, Isomet was developed by the Bureau of Engraving and Printing to replace Typewash. Isomet is a mixture of synthetic isoparaffinic hydrocarbon (55 percent), propylene glycol monomethyl ether (10 percent), and isopropyl alcohol. Initial testing of Isomet found the solvent to be a highly successful replacement for Typewash and less costly than any commercially available solvent. Isomet was found to be acceptable in cleaning ability, solvent evaporation rate, solvent odor, environmental and safety compliances, and cost.

Isomet is currently used for cleaning all Bureau postage stamp and overprinting presses. Thus a solvent discharged at the rate of 5,000 gallons per year was made environmentally friendly.

Pharmacia and Upjohn, Inc.

An Alternative Synthesis of Bisnoraldehyde, an Intermediate to Progesterone and Corticosteroids

For the past 40 years, the steroidal intermediate bisnoraldehyde (BNA) has been made and used at Pharmacia and Upjohn to produce bulk pharmaceutical steroids like progesterone and corticosteroids. Recently, an entirely new route to BNA from waste soya bean residues was implemented due to the development of an environmentally acceptable and efficient chemical process for the oxidation of an intermediate, referred to as bisnoralcohol (BA), to bisnoraldehyde. The new process uses commercial strength bleach and a catalyst/co-factor system (4-hydroxy-TEMPO) and is run in a two-phase reaction medium. This new route to BNA has many human health and environmental benefits because it: avoids using heavy metal based oxidants such as hexavalent chromium salts and complexes, manganese oxides, or lead salts; does not produce noxious emissions unlike oxidations which use activated dimethylsulfoxide, dimethylsulfide, or complexes of sulfur trioxide; does not use toxic or hazardous materials like organic peroxides, organoselenium compounds, or chlorinated quinones; avoids potentially hazardous reaction mixtures like those used for ozonolysis, or oxidative dehydrogenation with metal oxides; increases utilization of soya sterol feedstock from 15 percent to 100 percent; produces non-toxic aqueous process waste streams and recoverable organic solvent waste streams; eliminates a process with a running, recycled inventory of 60,000 gallons of ethylene dichloride (EDC), a known carcinogen, and that needs up to 5,000 gallons of EDC input annually; produces the same product amount as the previous route with 89 percent less non-recoverable organic solvent waste and 79 percent less aqueous waste; and has the chemical selectivity required for high quality bulk pharmaceutical manufacture. In addition to being a new synthetic route for converting soya sterols to therapeutic steroids, this chemical process is also a general method for converting primary alcohols to aldehydes that is environmentally superior to currently available oxidation methods.

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 (resins or chelating agents, which in turn must be disposed as radioactive) are typically needed by 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 re-used or discarded as nonradioactive. FDT will drastically reduce the volume of radioactive wastes. Volume reductions greater than one thousand 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 has been investigated as an alternative to conventional operations, which are a significant source of air pollution. The bricks used in building many houses and offices buildings in Mexico and other parts of the third world are typically made by hand and fired in a small kiln using available fuels such as sawdust, treated wood, paper, trash, tires, plastic, and used motor oil. Although these bricks cost about 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 by-product of this brickmaking industry is a high level of air pollution–both particulates and toxic chemicals–that results from inefficient thermal design and 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 non-polluting fuels (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 have been 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 for the brickmakers of about 35 percent.

**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

Application of Microchemistry Technology to the Analysis of Environmental Samples

"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 have 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.

Asarco Incorporated

Asarco – West Fork Biotreatment Project

Asarco has developed a biotreatment system for removing metals from mine water prior to its discharge to surface waters. Asarco's West Fork Unit is an underground lead-zinc mine that discharges water from mine dewatering to the West Fork of the Black River under NPDES permit. Recent changes in the Water Quality Standards required Asarco to explore water treatment alternatives. Asarco initiated passive biotreatment investigations in 1993 which lead to the design and construction of an anaerobic pilot biotreatment cell (biocell) in February, 1994. The biocell (designed to treat 20 gallons of water per minute) was filled with a substrate mixture of 50 percent old sawdust, 33 percent mine tailings, 10 percent cow manure, 5 percent alfalfa hay, and 2 percent lime rock (all material used was obtained locally; other organic materials such as yard waste and sewage sludge can be substituted). Sulfate Reducing Bacteria (SRB) were cultivated within the anaerobic environment of the substrate. SRB are abundant in nature and are found predominately in bogs and swamps. SRB produce hydrogen sulfide gas as a by-product that acts as a sulfiding agent to precipitate dissolved lead and other metals from mine water. The pilot biocell has demonstrated continued success in reducing metals from mine water to below Missouri's Water Quality Standards. The biotreatment cell operated efficiently through extremes of ambient temperature, water flow rates, and metal loading. Unlike conventional chemical water treatment plants, a biotreatment cell does not require the introduction of chemicals into the water, does not produce sludges on a daily basis that must be disposed, does not require a full time operator, is not subject to mechanical malfunction, can operate at twice the design rate for short periods of time without a reduction in treatment efficiency, and can be constructed at a fraction of the cost.

The BHC Company Ibuprofen Process

BHC Company (Hoechst Celanese Corporation)

A new synthetic "green chemistry" process has been developed and commercialized by BHC Company to manufacture ibuprofen, a well known non-steroidal, anti-inflammatory pharmaceutical (painkiller) marketed under the names of Advil™, Motrin™, and others. The new process involves only 3 catalytic steps with approximately 80 percent atom utilization and replaces technology with 6 stoichiometric steps and less than 40 percent atom utilization. The use of anhydrous hydrogen fluoride as both catalyst and solvent offers important advantages in reaction selectivity and waste reduction. This chemistry (99 percent atom utilization when including the recovered by-product acetic acid) is a model of source reduction, the optimum waste minimization method topping the Environmental Protection Agency's waste management hierarchy. Virtually all starting materials are either converted to product, reclaimed as by-product, 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 has revolutionized bulk pharmaceutical manufacturing. Large volumes of aqueous waste (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 virtually complete atom utilization of this streamlined process makes it truly a waste minimizing, environmentally friendly, green technology.

CleanSystem^3 Gasoline

Texaco Inc.

Internal combustion engines produce considerable amounts of nitrogen oxides (NO_x) as a combustion by-product. Nitrogen oxides 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 nitrogen oxides (NO_x).

Lockheed Martin Tactical Aircraft Systems

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 (LMTAS) has developed and patented low vapor pressure organic solvents and has successfully implemented a low vapor pressure cleaning operations and waste cloth management and disposal system. The solvent blends and cleaning technology are being used by the aerospace industry, the military, and various other industries. Additionally, LMTAS has 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 significantly reduced solvent use and air emissions, eliminated ozone depleting compounds from cleaning during aircraft assembly, reduced costs, and improved chemical handling and usage practices. From 1986-1992, 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 (VOCs). The implementation of DS-104 has reduced wipe solvent VOC emissions to 7 tons per year in 1993 and 3 tons per year in 1994, with no CFC emissions. Other reductions documented and include: 68 to 71 percent reductions in solvent use by volume, 86 to 88 percent savings in solvent purchase cost, and 95 to 97 percent reductions in total air emissions.

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/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 that are 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 has been developed that are less toxic with reduced impacts to both people and the environment when compared to traditional products used for the same purpose. The chemistries incorporated into these products have 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 (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. These new "core" line of cleaners are an innovative approach to the formulation of an important series of products and are the safest yet developed in their fields.

Development of 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 processes being conducted at this site for their susceptibility to improvements in the utilization of solvents, to minimize the waste byproduct, and at the same time improve operating efficiency. One process in particular was identified that appeared to offer significant opportunities for such process restructuring. After two 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, 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 into 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 three 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.

Development of a New Sealant/Adhesive Chemistry for Automotive Windshields. A New Two Part Chemical System Using Acetoacetylated Polyol Prepolymers and Aminated Acetoacetylated Polyol Prepolymers.

BF Goodrich

Tremco, a BF Goodrich Company

Up until this year all automotive windshield adhesives, used when replacing windshields, have been made from unblocked isocyanate prepolymers. These products may contain one to three percent isocyanates, which pose a potential severe health hazard to the workers in the manufacture of these prepolymer adhesives. In addition to chemical workers, installers of these products and car owners can be exposed to the isocyanate prepolymers, which can pose a health risk. Tremco, a BF Goodrich Company, has been able to develop a new sealant/adhesive chemistry that is significantly better than isocyanate adhesives in many respects – it demonstrates more rapid cure rate, even at low temperatures and low humidity conditions, posses higher lap shear strengths, and is non-moisture sensitive. In addition, this product is nonhazardous, nontoxic, contains no isocyanates, and poses no health risks to chemical workers, installers, or consumers. This new two part chemical system uses acetoacetylated polyol prepolymers. These prepolymers are made by reacting di and triol polymers with tert-butylacetoacetate (tBAA). Some of these acetoacetylated polyols are aminated with low molecular weight diamines. These acetoacetylated polyol amines are then reacted with acetoacetylated polyols to achieve a cured polymer matrix. This system produces an extremely strong isocyanate type cure and allows for faster "drive away times" for the car owner and more productivity for the installer. In addition, an acetoacetylated roofing adhesive using the same technology is being field tested. This product is completely free of solvents, is 100 percent solid, and is environmentally friendly.

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 that are working on one of the world's most challenging environmental issues: Cold War legacy waste. Sampling and analytical technologies that minimize waste production have been 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.

The Dow Chemical Company's Novel INVERT™ Solvents

The Dow Chemical Company

The industrial cleaning industry, one of the largest consumers of organic solvents in North America, is an industry in transition. Customers, both end-users and formulators of cleaning products for the industrial cleaning industry, are seeking alternatives for methyl chloroform and other ozone depleting chemicals and for ways to reduce the total amount of volatile organic compounds (VOCs) used in their work processes. Any alternative solvents or solvent technology for industrial cleaners must meet specific physical characteristics that result in performance properties similar to what it is replacing. To meet industry needs, any new product should be easy to use, evaporate quickly, prevent any new health or worker safety concerns, and allow the user to meet emerging environmental regulations. INVERT™ solvents from the Oxygenated Solvents Business of the Dow Chemical Company are a remarkable advancement in solvent technology. These revolutionary new products maintain the performance properties of organic solvents but incorporate the environmental benefits of water. INVERT™ solvents are best described as the first practical development of solvent continuous microemulsions that can function as an alternative to traditional solvents. The unique properties of microemulsions have led to their use in a diverse range of applications that include enhanced oil recovery, environmental remediation, consumer products, pharmaceutical formulations and media for polymerization.

DryWash™

Hughes Environmental Systems, Inc.

All conventional dry-cleaning solvents present health risks, safety risks, or are detrimental to the environment. Currently, the dry-cleaning industry uses perchloroethylene (85 percent), petroleum based or Stoddard solvents (12 percent), CFC-113 (less than two percent), and 1,1,1-trichloroethane. Perchloroethylene 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 these cleaning solvents and the high costs of implementing and complying with safety and environmental restrictions and regulations, reduced dry-cleaning profit margins. Solvents are suspected of contaminating ground water, air, and food products. For these reasons, the dry-cleaning industry is engaged in an ongoing search for alternative, safe and environmentally friendly cleaning technologies, substitute solvents, and methods to control exposure to dry cleaning chemicals. DryWash™, a Hughes carbon dioxide technology, has been developed and marketed as a safe, ecologically acceptable and cost effective alternative to the current dry-cleaning process. Carbon dioxide is a readily available, inexpensive, and unlimited natural resource. It is chemically stable, non-corrosive, non-flammable, non-ozone depleting and non-smog producing. The DryWash™ system reuses a naturally occurring by-product with a multitude of sources. A dry-cleaning developmental prototype using liquid carbon dioxide has been built and demonstrated. Completion of a 10 kilogram commercial size cleaning unit is expected during the first quarter of 1996.

DuPont Company

The DuCare "Zero Effluent" Recycle Chemistry System

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 on-site treatment. The effluent contains hazardous chemicals (as defined by SARA Title III), very high BOD and COD, 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 which 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 wiring 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.

Advanced Micro Devices (AMD), Austin Environmental Department

The Emission Quantification Model

In the semiconductor manufacturing process, liquid and gaseous chemical mixtures are used to manufacture submicron devices. These chemicals are categorized into four general groups: corrosives, organics, toxics, and fluorinated compounds. Local, state, and federal environmental regulations governing these materials are becoming more stringent and facilities must ensure protection of human health and the environment. To help accomplish this, ADM developed the Emissions Quantification Model (EQM) as a method to identify and quantify the chemicals used in manufacturing processes and incorporate them into a comprehensive environmental management system. Based on a modified mass balance model, pollution prevention and control outcomes were used to develop a real-time measurement method. The EQM provides information such as toxicity, usage, and emission rates and is an invaluable tool for assessing human health and environmental impacts as well as identifying opportunities to optimize, reduce, reuse, recycle, and eliminate chemicals. The EQM has initiated many improvements at AMD's Austin site. For example, chemicals with potential teratogenic properties were identified and replaced with less toxic chemicals that still meet the specifications required to produce semiconductors. Methyl ethyl ketone, a hazardous air pollutant as well as a SARA

313 reportable chemical, was replaced by methyl propyl ketone, a much less hazardous substitute. Data from the EQM assessments identified chemicals used in large quantities, including sulfuric acid and isopropyl alcohol, that could be recycled. Currently, ADM is recycling 50 percent of the sulfuric acid used in these facilities and is evaluating isopropyl alcohol recycling. In the near future, all sulfuric acid used in these facilities will be recycled, and if the capital expenditure is justified, feasible, and approved, isopropyl alcohol reprocessing will be implemented.

U.S. Department of Defense,
Office of Munitions

U.S. Department of Energy,
Weapons Supported Research

Lawrence Livermore National Laboratory

Environmentally-Driven Preparation of Insensitive Energetic Materials

An innovative approach has been developed at Lawrence Livermore National Laboratory to the 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 a 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.

DuPont Company

The INFINITY Dyeing 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 multi-layer circuit boards per year in a manufacturing plant in north Austin. 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. Two areas were identified for their waste minimization potential: 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 solution and reducing developing solution reduces the carbonates in the waste water which precipitates 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), 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.

Rohm and Haas Company

Invention and Commercialization of CONFIRM™ Selective Caterpillar Control Agent

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. CONFIRM™ received full registration in the United States for codling moth control in walnuts in early 1995 and was used effectively in 1994/5, under emergency exemption, to combat severe beet armyworm outbreaks in cotton and vegetables in several southern states. CONFIRM™ insecticide controls caterpillars through an entirely new and inherently safer mode of action than current insecticides. It acts by strongly mimicking a natural substance found in the caterpillar's body, called 20-hydroxy ecdysone, which is the natural "trigger" that induces molting and regulates development in insects. CONFIRM™ disrupts the molting process in caterpillar pests, causing them to stop feeding within hours of exposure and to die soon thereafter. Although CONFIRM™ is a potent mimic of 20-hydroxy ecdysone in caterpillars, it is a surprisingly poor mimic in most other insects and arthropods, and therefore is remarkably safe to a wide range of key beneficial, predatory, and parasitic insects such as honeybees, ladybeetles, parasitic wasps, predatory bugs and lacewings. In addition to its novel and selective mode of action, CONFIRM™ does not bioaccumulate, volatilize, leach, or persist unreasonably long in the environment. All of these reasons make CONFIRM™ one of safest, most selective, and most useful caterpillar control agents ever discovered.

Praxair, Inc.

Liquid Oxidation Reactor

Praxair 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 and/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 and/or solvent to by-products 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-$20 million per plant per year have been projected

Magnetic Separation for Treatment of Radioactive Liquid Waste

Los Alamos National Laboratory

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 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 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.

A Microwave Oven Dissolution Procedure for a Ten Gram Sample of Soil Requiring Radiochemical Analysis

Los Alamos National Laboratory

A microwave soil dissolution procedure was incorporated into a standard analytical method for testing soils for americium and plutonium. This modification displaces several hot plate dissolution steps by incorporating a microwave oven with new commercially available products. The new procedure uses a commercially available microwave oven that has the capability to monitor and control the pressure and temperature of a control vessel using a feed back system. The ability to repeatedly obtain and control desired temperatures and pressures has resulted in improved analytical precision because the reaction conditions can be reproduced. This new procedure also reduces the consumption of hazardous substances, the amount of air pollution produced, worker exposure to hazardous substances, and sample preparation time. The use of closed vessels in this modified procedure also results in reduced hazardous reagents use. Less reagents means less hazardous waste and air pollution are produced, and reduced worker exposure to the reagents. In addition, the use of the microwave oven reduces the time requirements from two to three days for the hot plate procedure to eight hours.

DuPont Company

NAFION Membrane Technology

Membrane technology is now recognized as the state-of-the-art for chloralkali chemical production, which constitute 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

Nalco Fuel Tech NOxOUT® Process

Nalco Fuel Tech is a joint venture of Nalco Chemical Company and Fuel Tech formed to develop and market air pollution control technologies. Nalco Fuel Tech's flagship technology, NOxOUT®, selectively reduces harmful nitric oxide emissions from the flue gases of stationary combustion sources to yield nitrogen gas and water, leaving no solid residue requiring disposal. The NOxOUT® Process meets many of today's environmental challenges such as employing less toxic chemistries, reducing or eliminating toxic releases to the environment, converting wastes to more environmentally acceptable discharges, and by using these chemistries, enables reduced energy consumption. The NOxOUT® Process provides an economical solution for meeting the stringent regulatory requirements for NO_x reduction from fossil fuel and waste fuel combustion sources. NOxOUT® is capable of providing up to 75 percent reduction of NO_x emissions (existing combustion modification such as low NO_x burners, flue gas recirculation, and overfire air are effective, yet normally only provide NO_x reductions in the range of 20 to 50 percent). The process uses chemicals and sophisticated injection equipment to convert NO_x to harmless species – nitrogen and water. In the NOxOUT® Process, an aqueous solution of proprietary chemicals is introduced into the flue gas of the combustion equipment. The program is designed according to the type, size, and operating load of the boiler, and NO_x reduction required. The NOxOUT® Process is being used commercially and has been demonstrated in tests on a wide range of combustion processes and fuels. The process is well-suited to new combustion units of all sizes – from small industrial units to large utility installations. In addition, the system can be retrofitted to most existing units. The environmental benefits are: high NO_x reduction, no disposal by-products, no SARA Title III chemical reporting requirements, and increased energy efficiency due to the low cost per ton to remove NO_x.

Nalco NALMET®

Nalco Chemical Company

New, stricter NPDES discharge limits for effluent metals are impacting both metal and non-metal industries. Stringent NPDES plant effluent metal concentration limits focus on effluent toxicity reductions that impact both metal and non-metal industries. Traditional metal removal programs use multiple chemicals and toxic components such as dialkyldithiocarbamates, sodium sulfide, and ferrous sulfide. In addition, the concentration limits for heavy metals such as copper, lead, nickel and zinc often cannot be met by traditional metal precipitation processes. Nalco Chemical Company developed NALMET®, a patented, low-toxicity program for metal removal that includes a liquid polymer containing a metal chelating functional group that simultaneously precipitates metals and clarifies the waste stream. It is effective on soluble, mixed metal wastes and in many cases, reduces final sludge volumes by 30 to 75 percent. NALMET® also allows some RCRA hazardous sludges to be reclassified as non-hazardous. Automated chemical feed with patented sensor technology makes the NALMET® program easier to use, substantially decreases product overfeed, and assists with waste minimization. More significantly, this product offers a remedy to environmental management problems by helping Nalco customers consistently meet their extremely low NPDES metals discharge limits. NALMET® offers a realistic approach to "green" chemistry because the technology is based on high molecular weight polymers that express low toxicity, is easy to implement, does not require extensive changes in plant design or capital investment, and is broadly applicable and readily transferrable to other industry sectors.

Nalco PORTA-FEED® Advanced Chemical Handling Systems

Nalco Chemical Company

Nalco Chemical Company is a manufacturer and marketer of specialty chemicals for industrial water treatment and process applications. In the early 1980s, drum disposal and the associated chemical residue was becoming a health and environmental risk for Nalco customers and the general public. In response, Nalco developed the PORTA-FEED® Advanced Chemical Handling System consisting of returnable containers to help reduce chemical waste and the potential risks associated with non-returnable drums. The Nalco PORTA-FEED® System has more than 96,000 returnable, stainless steel containers of various sizes, ranging from 15 gallons to 800 gallons to accommodate all Nalco customers and applications. It is the largest fleet of returnable chemical containers in the world. All the units are owned, tracked and maintained by Nalco as a cradle-to-grave risk management process. Since it began, the PORTA-FEED® pollution prevention program has helped Nalco customers eliminate the need to dispose more than three million drums and more than 30 million pounds of chemical waste. In 1985, 33 percent of the Company's annual sales were shipped in non-returnable drums and required 500,000 drums. Ten years later, only 7 percent of sales are shipped in non-returnable drums and the number of drums has been reduced 80 percent. By the year 2000, Nalco expects to have eliminated the need to dispose of 10 million drums and 100 million pounds of chemical waste worldwide as a result of the PORTA-FEED® program. The PORTA-FEED® System provides several benefits both to users of Nalco chemicals and to the environment, which includes eliminating drums, the associated residual chemicals, and long-term environmental risk; reducing the likelihood of spills, leaks, and container damage during transportation and use; simplifying chemical handling, which enhances worker safety by reducing exposure; and reducing the need for on-site chemical inventory and chemical storage.

Nalco Chemical Company

Nalco TRASAR® Technology

Nalco Chemical Company is the largest water treatment specialty chemical company in the world. Customers range from water treatment plants in large industrial complexes that produce commodities such as steel, electricity, paper, gasoline, and fertilizer to smaller water facilities in hotels, hospitals, breweries, canneries, and public sewage treatment facilities. Nalco programs such as TRASAR® Technology, Diagnostic TRASAR®, and TRA-CIDE™ are impacting the way the world manages water by helping customers reduce pollution at its source and conserving energy. These applications are a complete cradle-to-grave approach to water management. TRASAR® Technology has several aspects that can be grouped in "stages" for discussion. In stage I, an inert fluorescent material "trace" is blended into TRASAR® treatment products. The signal from the "trace" is used to control the treatment chemical application and injection rate changes are made instantaneously and automatically. It is common to see a 20 to 30 percent reduction in total chemicals used when customers convert to a TRASAR® program. Stage II of TRASAR® Technology relies on the direct, automatic detection of the treatment chemical. Where stage I might be analogous to adding microscopic, glowing ping-pong balls to the chemical product, stage II is like putting a bar code on the active ingredient molecule. Nalco has taken fluorescent materials and chemically bonded them to the active ingredients. Stage II TRASAR® Technology allows Nalco to correlate variations in the consumption of the chemical with variations in the way the water system is operated. Stage III TRASAR® Technology is based on performance (e.g. corrosion protection, prevent foaming, etc.). Nalco monitors how well its products inhibit corrosion, disperse suspended solids, and prevent foaming. The dosage is further adjusted based on the performance measures.

Nalco ULTIMER™ Polymer Technology

Nalco Chemical Company

Most industrial processes use water as a raw material or as a processing aid. Typically, water taken from the environment must be conditioned to remove suspended solids, organic matter, and other materials that may be harmful to the industrial process before it is used. Water that has been used in industrial processes often must be treated to remove harmful wastes and contaminants before being reintroduced to the environment. Solids/liquids separation unit operations are critical to cost-effective and safe operation of most industrial operations. High molecular weight, water-soluble polyacrylamides are commonly used to assist solids/liquids separation in many industrial water and waste treatment applications. In 1995, shipments of polyacrylamides in the United States are expected to be over 200 million pounds. Worldwide, the market for polyacrylamides is presently at least one billion dollars. As flocculants, these polyacrylamides are extremely effective. The last major technical improvement in flocculant technology might be considered the invention and development of inverse emulsion polymers by Nalco Chemical Company in the late 1970's. In 1995, Nalco continued its technological innovation in this area by introducing the first major innovation in water treatment flocculants since the development of inverse emulsion cationic polyacrylamides–ULTIMER™ polymers. ULTIMER™ polymers are a new product line of high molecular weight cationic polyacrylamides that are formulated without oils or surfactants. ULTIMER™ Polymer technology is more effective in purifying industrial processes and wastewater than traditional technology and eliminates toxic components and has worldwide applicability in all industrial nations. Its toxic use reduction and pollution prevention is achieved by eliminating environmental discharges that present environmental hazards.

New Catalyst for Producing ULTEM® Thermoplastic Resin

GE Plastics (General Electric Corporation)

GE Plastics produces an engineering thermoplastic known as ULTEM® polyetherimide resin. The production of this resin involves several complicated synthetic conversions and generates both an aqueous waste stream containing organic materials and an organic waste stream. The key step in the process depends on a catalyst that has been a research "target of opportunity" for several years. Laboratory studies indicated that the amount of waste generated from this step could be significantly reduced using several members of a new catalyst class. A small plant trial verified the early findings. In 1995, the most promising member of this new catalyst class was streamlined, and a full plant trial was conducted in the ULTEM® manufacturing plant. Based on the full plant trial, the following pollution prevention benefits were demonstrated: the volume of organic waste stream for off-site disposal was reduced by 90 percent or 123,000 pounds a year; the water-based organic waste for on-site thermal oxidization was reduced by 60 percent or 300,000 pounds a year; 50 percent less catalyst was consumed due to greater effectiveness per pound of catalyst; the amount of waste from the manufacture of the catalyst itself was reduced by 75 percent or 39,000 pounds a year; the amount of energy required to produce each pound of the resin was reduced by 25 percent or 5 x 109 BTU/yr; and the amount of a workplace hazardous by-product was reduced by 90 percent. In addition to these health and environmental benefits, the new catalyst system also offers several significant economic advantages. This catalyst technology is the cornerstone of new process chemistry for manufacturing the ULTEM® resin that will eliminate completely the need for a thermal oxidizer.

CTS Corporation Resistor Networks

No-Clean Soldering

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. Soldering operations were a major source of hazardous waste generation at CTS's Berne facility. Oil on top of the solder, flux, and cleaning solvents to remove the oil after soldering, generated large quantities of hazardous waste. A solder process, new to CTS, was developed and implemented on all manufacturing lines. The No-Clean soldering process was implemented in March of 1993 and eliminated the use of wave oil, soldering fluxes, and cleaning solvent. Changing to a No-Clean soldering process involved installing hoods with an inert atmosphere over the solder pots, which eliminated the need for oil and flux. The parts are clean after solder and thus no solvent cleaning is needed. In 1992, waste generated from CTS's soldering operations included 21,767 pounds of wave oil; 15,792 pounds of flux; 9,900 pounds of 1,1,1-trichloroethane solvent (TCA); and 226,000 pounds of 1,1,2-trichloroethylene solvent (TCE). In 1995, waste oil, flux, TCA, and TCE from soldering operations was completely eliminated. The elimination of solvent-based cleaning operations also has resulted in a reduction in air emissions from 1992 levels of 99,000 pounds per year of TCA and 250,000 pounds per year to zero (estimated for 1996). By eliminating these chemicals from soldering operations, the hazards from releasing these chemicals to the environment is eliminated and workers are no longer exposed to fumes from fluxes, oils, and cleaning solvents that are typical of the solvent-based soldering operations. In addition, the product quality has improved.

Technic, Inc.

U.S. Department of Energy

Lawrence Livermore National Laboratory

Non-Cyanide Silver Electroplating

A proprietary, non-cyanide 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 fifty 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 and on a few occasions have resulted in death. Alternatives to cyanide-based solutions had been developed for all metals commercially electroplated except silver. The non-cyanide silver electroplating process developed by Technic provides an alternative that is noticeably less toxic than the cyanide process and one that is inherently safer with regard to accident potential. In addition, tests clearly show that the non-cyanide formulation is capable of producing sound, thick (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 non-cyanide chemistry, Technic has made it possible to operate an entire plating facility without having to use any cyanide compounds.

Eastman Kodak Company

Polycarbonate/Polydimethylsiloxane Copolymers for Thermal Print Media

The process to make polycarbonates using bischloroformates and bisphenols or diols was developed and commercialized in the early 1990's 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.

Mallinckrodt Chemical, Inc.

The Removal of Oxides of Nitrogen by In Situ Addition of Hydrogen Peroxide to a Metal Dissolving Process

An innovative technology for the removal of oxides of nitrogen (NO_x) in a metal dissolving process by adding hydrogen peroxide was developed and implemented by Mallinckrodt. Salts are produced by dissolving metals in nitric acid and during the dissolving process, approximately 30 tons per year of NO_x emissions are generated. A study was completed to determine the best method for reducing NO_x emissions from the process. While the literature suggests that NO_x is required to catalyze the dissolution reaction, this theory was challenged and it was proposed to oxidize the NO_x back to nitric acid by adding hydrogen peroxide directly to the process. Trial runs using this technology were completed and resulted in complete elimination of NO_x emissions. The full scale hydrogen peroxide addition process has eliminated the generation and evolution of approximately 30 tons per year of gaseous NO_x waste, while at the same time reducing nitric acid usage by approximately 109 tons per year. Further, approximately 13 million gallons of scrubber waste water were eliminated annually since the scrubber, traditionally used by the chemical industry to control the NO_x that is generated and released from reactions, is no longer needed. This technology can be used by any process in any industry that generates NO_x emissions when dissolving metals in nitric acid or pickling metals using nitric acid.

Monsanto Company

Roundup Ready™ Technology

The Roundup Ready™ Technology is the mechanism by which crop selectivity to Roundup®, the world's largest selling herbicide, has been introduced into crop plants. The technology is the result of the discovery of a unique set of genes and the introduction of these Roundup Ready™ genes into crop plants. These genes were identified following many years of research on the mode of action and environmental fate of the active ingredient of the Roundup® herbicide. The Roundup Ready™ Technology genes protect the crop plant from damage by inserting a new version of the enzyme, which is normally inhibited by the herbicide, so that the enzyme is now insensitive to the herbicide. In addition, the Roundup Ready™ Technology provides a mechanism for the plant to degrade the herbicide taken into the plant. Initial commercial launch will be in soybean, cotton, and corn in the United States in the 1996-1998 time frame. The technology is widely applicable to other crops. Potential applications include wheat, rice, forestry, and vegetable and salad crops. 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. The impacts will be seen in the shift in the spectrum of herbicides possible for in-crop use. Farmers who plant Roundup Ready™ soybeans in 1996, for example, will be able to reduce herbicide use in those soybean fields by up to one-third and still control weeds better. In addition, Roundup Ready™ technology is compatible with no-till crop production, a practice that is expanding in the United States and around the world.

Los Alamos National Laboratory

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

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 (BARF). 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.

Stepan Company PA Lites Polyester Polyol

Stepan Company

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 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 a cost effective alternative to traditional building construction products. Using the phthalic anhydride distillation by-product as a raw material for the polyol process eliminates an entire waste stream. In 1994, 235,300 pounds of Phthalic Anhydride Light Ends was used as a feedstock and 454,420 pounds were shipped out as a waste for fuel blending. In 1995, approximately 700,000 pounds of PA waste were used as a feedstock in the polyol process, thus eliminating an estimated 350 tons per year of organic waste material. Benefits from this product substitution go beyond eliminating a waste requiring disposal. With its substitution as a raw material, it has reduced the requirement for phthalic anhydride, the traditional raw material for the polyol product, and the air emissions associated with its manufacture. Since this previously categorized waste material is now used on-site to produce Polyester Polyol, potential exposure to the general public during off-site transportation to disposal facilities has been eliminated. This technology also provides significant cost savings. The savings associated with the transportation and disposal via fuel blending for energy recovery is expected to be $200,000 per year. The raw material savings due to the replacement of pure PA with PA lites material on a pound per pound basis is $20,000 per year.

Tetrakishydroxymethyl Phosphonium Sulfate (THPS) Biocides

Albright & Wilson Americas Inc.

The United States industrial water treatment market for non-oxidizing biocides is 40 million pounds per year and growing at six to eight percent annually. Tetrakishydroxymethyl phosphonium sulfate (THPS) biocides represent a completely new class of antimicrobial chemistry that combines superior antimicrobial activity with a relatively benign toxicology profile. THPS provides a reduced risk to both human health and the environment when substituted for more toxic biocides. The human and environmental health risks of THPS have been compared with other biocides that currently comprise an estimated 80 percent of the U.S. industrial water treatment market. THPS poses much less risk to the environment than many of the alternative products currently on the market. THPS biocides are aqueous solutions and do not contain VOCs; they are also halogen-free and do not contribute to dioxin or AOX formation. THPS does not bioaccumulate and can rapidly breakdown through hydrolysis, oxidation, biodegradation, and photo-degradation before it enters the environment. The degradation products have been shown to be non-toxic. THPS is also the only biocide, compared to high volume alternatives, for which the typical dose rate is below the LC^{50} for fish. Because of its low overall toxicity when compared to alternative products, THPS provides an opportunity to reduce the risk of health and safety incidents.

U.S. Department of Energy

Los Alamos National Laboratory

Professor Jonathan Phillips, Department of Chemical Engineering, Pennsylvania State University

Two-Stage Catalyst for NO_x Reduction, CO Oxidation, and Hydrocarbon Combustion in Oxygen Containing Exhaust Mixtures

A unique catalyst system has been developed for removing oxides of nitrogen from automobile exhaust. These catalysts operate in a lean burn environment (excess oxygen in the engine) and represent a significant improvement over existing technologies. Automobile manufactures prefer to operate engines with excess oxygen to completely combust the fuel, improve efficiency, and reduce pollution. The principle impediment to designing such an engine is the inability of existing exhaust system catalysts to reduce oxides of nitrogen in the presence of oxygen. Some progress has been made in resolving this problem, specifically, copper impregnated zeolites are found to reduce oxides of nitrogen in the presence of oxygen. This material is not, however, without problems, including, low conversion of the oxides of nitrogen. We have demonstrated a two stage catalysts system that significantly improves the conversion of oxides of nitrogen to environmentally acceptable gases. We have shown that a heterogeneous catalyst system consisting of two beds in sequence, each containing a different catalytic material, is superior for the removal of NO_x from exhaust streams containing oxygen, to the current generation of single stage catalysts. The character of each of the catalyst beds is fairly specific. The first bed consists of any high surface area refractory oxide such as silica, alumina, titania, zirconia, ceria, zeolite, etc. The second bed consists of any metal loaded catalytic material known to reduce NO_x species in the presence of oxygen such as copper exchanged zeolite (e.g. Cu-ZSM-5). Many other materials, including zeolites exchanged with other metals, high surface area silica or alumina impregnated with metals, also are known to reduce NO_x species in such environments, and thus also are candidates for second bed materials.

U.S. Department of the Navy, Office of Naval Research

U.S. Department of the Navy, Naval Surface Warfare Center

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

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.

Professor Joseph DeSimone, Department of Chemistry, University of North Carolina

Aerojet Propulsion

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

Alliance for Environmental Technology (AET)

The use of chlorine dioxide as part of 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 eco-systems 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, followed by increased substitution of chlorine by chlorine dioxide in 1990. In less than four years, downstream dioxin body burdens declined more than 90 percent. These indicators of progress toward broader eco-system integrity demonstrate the success of chlorine dioxide as "green chemistry."

Lockheed Martin Tactical Aircraft Systems

Use, Regeneration, and Analysis 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 and/or vapor degreasing with chlorinated solvents such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), both of which are toxic and ozone depleting compounds. These solvents have been successfully replaced with LMTAS' aqueous cleaning technology. Since May of 1994, 100 percent of both tubing and honeycomb core manufactured at LMTAS have been cleaned using the aqueous cleaning technology. Coulometric titration data indicates that the LMTAS aqueous cleaning technology is as effective or more effective than TCE vapor degreasing for cleaning aluminum tubing and honeycomb core. In addition, implementation of the aqueous cleaning technology at LMTAS has eliminated approximately 360 tons of air emissions per year and has resulted in a cost savings of $490,000 per year. LMTAS also has 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 contaminants. 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. Finally, LMTAS has demonstrated that ultrafiltration is a viable technology for the regeneration of aqueous cleaners for reuse. Regeneration of aqueous cleaners can greatly reduce replacement and disposal costs.

Merck & Co., Inc.

Waste Minimization in the Manufacture of an Antibiotic Produced by Chemical Synthesis

PRIMAXIN is an injectable, broad-spectrum antibiotic commercialized in 1985. Development and implementation of an effective manufacturing process for PRIMAXIN was an immense challenge due in part to the complexity of the imipenem molecule and instability. The manufacturing process initially proposed for PRIMAXIN involved 18 steps and would have created one ton of waste for every pound of product. While still in the development lab, however, Merck's chemists and engineers found a way to eliminate 500,000 gallons of annual toxic waste. After production began, Merck continued to improve the process by eliminating a mixture that prevented solvents from being reused, developing an innovative extractive hydrolysis technology that improved yield, and reducing use of another solvent. For example, one of the process steps involved the use of methyl isobutyl ketone (MIBK) and acetonitrile. Process development work indicated that MIBK could be eliminated. This allowed acetonitrile to be recycled, which previously was sent off-site for disposal. In a separation step, the number of cycles between regeneration of a chromatographic column using acetone/sulfuric acid was increased tenfold. These solvent recovery opportunities resulted in an annual savings of $50,000. Even after PRIMAXIN was in full scale manufacturing, several waste minimization process modifications were implemented that resulted in dramatic waste load reductions. The most significant is the 82 percent reduction in the use of methylene chloride by eliminating materials that made methylene chloride recovery impractical, modifying processes to allow the use of recovered material, and improving recovery techniques. This dramatic waste reduction resulted in an annual savings of over $1 million, and the process is still undergoing modification in order to further reduce waste generation. Development, implementation, and ongoing improvement of the process to manufacture PRIMAXIN (imipenem) is a prime example of Merck's contribution to the promotion of environmentally benign technology.

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

U.S. Department of the Navy, Office of Naval Research

U.S. Department of the Navy, Naval Surface Warfare Center

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

Los Alamos National Laboratory

Aerojet

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 life-cycle inventories on various munitions revealed that up to 50 percent of the life-cycle 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 greater than that of HMX, the most powerful military explosive in current use. Thus, TNAZ may offer 30-40 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 1200 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 Sulfopolyester for Reduced VOC Consumer Products

Eastman Chemical Company

The reduction of airborne emissions is a major focal point for legislation to safeguard public health. Volatile organic compounds (VOCs) are one of the major sources of air pollution that arise from both consumer and industrial products. Legislation proposed at the state level, particularly in

California, is targeting consumer and personal care products for VOC content reductions. One of the largest product areas is in hairsprays, which a very large, diverse segment of the population uses daily. Consumers, however, demand that "green" products have the same if not better performance characteristics. Eastman Chemical Company has developed a new product, known as EASTMAN AQ 48 Ultra, for this general need that not only reduces VOCs, but actually may improve performance. EASTMAN AQ 48 Ultra is a water-dispersible sulfopolyester that allows hairsprays to be formulated with 55 percent ethanol, which is significantly less than the current industry standard of 80 percent VOC. Switching all of the hairspray market from the current standard of 80 percent VOC to 45 percent VOC would result in a total reduction of VOC emissions around 55 million pounds per year. In general, sulfopolyester dispersions may be used as low VOC filmformers for a variety of cosmetic products in addition to hairsprays; therefore, an even larger potential for VOC emission reduction exists. Finally, the process chemistry is completed in the melt phase. There are no organic solvents used in the synthesis of sulfopolyesters at Eastman Chemical Company. The synthesis also does not release any toxic by-products.

The Green Chemistry Challenge is a voluntary program that operates through a broad consortium that includes members of the chemical industry, trade associations, scientific organizations, and representatives from academia. The program is open to all individuals, groups, and organizations involved in chemical design, manufacture and use.

Additional Information about the Green Chemistry Challenge is available from EPA's homepage on the internet (http://www.epa.gov; select "Offices," then "Prevention, Pesticides, and Toxic Substances," then "Toxics") and from EPA's Toxic Substance Control Act Assistance Information Service (202-554-1404; TDD: 202-554-0551), or call EPA's Industrial Chemistry Branch at 202-260-2659.

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