



The Presidential Green Chemistry Challenge Awards Program

Summary of 1998 Award Entries and Recipients



The Presidential Green Chemistry Challenge Awards Program

Contents

Summary of 1998 Award Entries and Recipients	1
Awards	2
<i>Academic Awards</i>	2
<i>Small Business Award</i>	4
<i>Alternative Synthetic Pathways Award</i>	5
<i>Alternative Solvents/Reaction Conditions Award</i>	6
<i>Designing Safer Chemicals Award</i>	7
Entries From Academia	8
Entries From Small Businesses	27
Entries From Industry and Government	38
Index	70

The Presidential Green Chemistry Challenge Awards Program

Summary of 1998 Award Entries and Recipients

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 1998 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. Six projects that best met the scope of the program and the criteria for judging were selected for 1998 awards and nationally recognized on June 29, 1998.

This document provides summaries of the entries received for the 1998 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 1998 Presidential Green Chemistry Challenge Awards. They were edited for space, stylistic consistency, and clarity, but they were not written by nor are officially endorsed by EPA. In many cases, these summaries represent only a fraction of the information provided in the entries received and, as such, are intended to highlight the nominated projects, not describe them fully. These summaries were not used in the judging process; judging was conducted on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.

Academic Awards

The Development of the Concept of Atom Economy

The general area of chemical synthesis covers virtually all segments of the chemical industry—oil refining, bulk or commodity chemicals, fine chemicals including agrochemicals, flavors, fragrances etc., and pharmaceuticals. Economics generally dictates the feasibility of processes that are “practical.” A criterion that traditionally has not been explicitly recognized relates to the total quantity of raw materials required for the process compared to the quantity of product produced or, simply put, “how much of what you put into your pot ends up in your product.” In considering the question of what constitutes synthetic efficiency, Professor Barry M. Trost has explicitly enunciated a new set of criteria by which chemical processes should be evaluated. They fall under two categories—selectivity and atom economy.

Selectivity and atom economy evolve from two basic considerations. First, the vast majority of the synthetic organic chemicals in production derive from non-renewable resources. It is self-evident that such resources should be used as sparingly as possible. Second, all waste streams should be minimized. This requires employment of reactions that produce minimal byproducts, either through the intrinsic stoichiometry of a reaction or as a result of minimizing competing undesirable reactions, i.e., making reactions more selective.

The issues of selectivity can be categorized under four headings—chemoselectivity (differentiation among various functional groups in a polyfunctional molecule), regioselectivity (orientational control), diastereoselectivity (control of relative stereochemistry), and enantioselectivity (control of absolute stereochemistry). These considerations have been readily accepted by the chemical community at large. In approaching these goals, little attention traditionally has been paid to the question of what is required. In too many cases, efforts to achieve the goal of selectivity led to reactions requiring multiple components in stoichiometric quantities that are not incorporated in the product or reagents, thus intrinsically creating significant amounts of byproducts. Consideration of how much of the reactants end up in the product, i.e., atom economy, traditionally has been ignored. When Professor Trost's first paper on atom economy appeared in the literature, the idea generally was not adopted by both academia and industry. Many in industry, however, were practicing this concept without explicitly enunciating it. Others in industry did not consider the concept since it did not appear to have any economic consequence. Today, all of the chemical industry explicitly acknowledges the importance of atom economy.

Achieving the objectives of selectivity and atom economy encompass the entire spectrum of chemical activities—from basic research to commercial processes. In enunciating these principles, Professor Trost has set a challenge for those involved in basic research to create new chemical processes that meet the objectives. Professor Trost's efforts to meet this challenge involve the rational invention of new chemical reactions that are either simple additions or, at most, produce low molecular weight innocuous byproducts. A major application of these reactions is in the synthesis of fine chemicals and pharmaceuticals which in general utilize very atom uneconomical reactions. Professor Trost's research involves catalysis, largely focused on transition metal catalysis but also main group catalysis. The major purpose of his research is to increase the toolbox of available reactions to serve these industries for problems they encounter in the future. However, even today, there are applications for which such methodology may offer more efficient syntheses.

Use of Microbes as Environmentally-Benign Synthetic Catalysis

Fundamental change in chemical synthesis can be achieved by elaboration of new, environmentally benign routes to existing chemicals. Alternatively, fundamental change can follow from characterization and environmentally benign synthesis of chemicals that can replace those chemicals currently manufactured by environmentally problematic routes. Examples of these design principles are illustrated by the syntheses of adipic acid and catechol developed by Dr. Karen M. Draths and Professor John W. Frost. The Draths-Frost syntheses of adipic acid and catechol use biocatalysis and renewable feedstocks to create alternative synthetic routes to chemicals of major industrial importance. These syntheses rely on the use of genetically manipulated microbes as synthetic catalysts. Nontoxic glucose is employed as a starting material which, in turn, is derived from renewable carbohydrate feedstocks such as starch, hemicellulose, and cellulose. In addition, water is used as the primary reaction solvent, and the generation of toxic intermediates and environment-damaging byproducts is avoided.

In excess of 1.9 billion kg of adipic acid is produced annually and used in the manufacture of nylon 66. Most commercial syntheses of adipic acid use benzene, derived from the benzene/toluene/xylene (BTX) fraction of petroleum refining, as the starting material. In addition, the last step in the current manufacture of adipic acid employs a nitric acid oxidation resulting in the formation of nitrous oxide as a byproduct. Due to the massive scale on which it is industrially synthesized, adipic acid manufacture has been estimated to account for some 10 percent of the annual increase in atmospheric nitrous oxide levels. The Draths-Frost synthesis of adipic acid begins with the conversion of glucose into *cis,cis*-muconic acid using a single, genetically-engineered microbe expressing a biosynthetic pathway which does not exist in nature. This novel biosynthetic pathway was assembled by isolating and amplifying the expression of genes from different microbes including *Klebsiella pneumoniae*, *Acinetobacter calcoaceticus*, and *Escherichia coli*. The *cis,cis*-muconic acid which accumulates extracellularly is hydrogenated to afford adipic acid.

Yet another example of the Draths-Frost strategy for synthesizing industrial chemicals using biocatalysis and renewable feedstocks is their synthesis of catechol. Approximately 21 million kg of catechol are produced globally each year. Catechol is an important chemical building block used to synthesize flavors (e.g., vanillin, eugenol, isoeugenol), pharmaceuticals (e.g., L-DOPA, adrenaline, papaverine), agrochemicals (e.g., carbofuran, propoxur) and polymerization inhibitors and antioxidants (e.g., 4-*t*-butylcatechol, veratrol). Although some catechol is distilled from coal tar, petroleum-derived benzene is the starting material for most catechol production. The Draths-Frost synthesis of catechol uses a single, genetically engineered microbe to catalyze the conversion of glucose into catechol which accumulates extracellularly. As mentioned previously, plant-derived starch, hemicellulose, and cellulose can serve as the renewable feedstocks from which glucose starting material is derived.

In contrast to the traditional syntheses of adipic acid and catechol, the Draths-Frost syntheses are based on the use of renewable feedstocks, carbohydrate starting materials, and microbial biocatalysis. As the world moves to national limits on carbon dioxide emissions, each molecule of a chemical made from a carbohydrate may well be counted as a credit due to the carbon dioxide which is fixed by plants to form the carbohydrate. Biocatalysis using intact microbes also allows the Draths-Frost syntheses to utilize water as a reaction solvent, near-ambient pressures, and temperatures that typically do not exceed human body temperature.

Dr. Karen M. Draths and Professor John W. Frost, Department of Chemistry, Michigan State University

Small Business Award

Technology for the Third Millennium: The Development and Commercial Introduction of an Environmentally Responsible Fire Extinguishment and Cooling Agent

Advances in chemical technology have greatly benefited firefighting in this century. From the limitation of having only local water supplies at their disposal, firefighters have been presented over the years with a wide variety of chemical agents, as additives or alternatives to water, to assist them. These advances in chemical extinguishment agents, however, have themselves created, in actual use, potential long term environmental and health problems which tend to outweigh their firefighting benefits. PYROCOOL Technologies, Inc developed PYROCOOL F.E.F. (Fire Extinguishing Foam) as an alternative formulation of highly biodegradable surfactants designed for use in very small quantities as a universal fire extinguishment and cooling agent.

Halon gases, hailed as a tremendous advance when introduced, have since proven to be particularly destructive to the ozone layer, having an ozone depletion potential (ODP) value of 10-16 times that of common refrigerants. Aqueous film forming foams (AFFF's), developed by the U.S. Navy in the 1960's to combat pooled surface volatile hydrocarbon fires, release both toxic hydrofluoric acid and fluorocarbons when used. The fluorosurfactants compounds that make these agents so effective against certain types of fires render anaerobic bacteria unable to metabolize their residue, often leading to contamination of ground water supplies and failure of waste water treatment systems.

In 1993, PYROCOOL Technologies initiated a project to create a fire extinguishment and cooling agent that would be effective in extinguishing fires and that would greatly reduce the potential long-term environmental and health problems associated with traditionally used products. To achieve this objective, it was first determined that the product (when finally developed) would contain no glycol ethers or fluorosurfactants. In addition, it was decided that the ultimate formulation must be an effective fire extinguishment and cooling agent at very low mixing ratios. PYROCOOL F.E.F. is a formulation of highly biodegradable nonionic surfactants, anionic surfactants, and amphoteric surfactants with a mixing ratio (with water) of 0.4 percent. In initial fire tests at the world's largest fire-testing facility in The Netherlands, PYROCOOL F.E.F. was demonstrated to be effective against a broad range of combustibles.

Since its development in 1993, PYROCOOL F.E.F. has been employed successfully against numerous fires both in America and abroad, and carries the distinction of extinguishing the last large oil tanker fire at sea (a fire estimated by Lloyd's of London to require 10 days to extinguish) on board the Nassia tanker in the Bosphorous Straits in just 12.5 minutes, saving 80 percent of the ship's cargo and preventing the spillage of 78,000 tons of crude oil into the sea.

As demonstrated by the PYROCOOL F.E.F. technology, selective employment of rapidly biodegradable substances dramatically enhances the effectiveness of simple water, while at the same time eliminating the environmental and toxic impact of other traditionally used fire extinguishment agents. Because PYROCOOL F.E.F. is mixed with water at only 0.4 percent, an 87 to 93 percent reduction in product usage is realized compared to conventional extinguishment agents typically used at 3 to 6 percent. Fire affects all elements of industry and society and no one is immune from its dangers. PYROCOOL F.E.F. provides an innovative, highly effective, and 'green' alternative for firefighters.

Alternative Synthetic Pathways Award

Elimination of Chlorine in the Synthesis of 4-Aminodiphenylamine: A New Process Which Utilizes Nucleophilic Aromatic Substitution for Hydrogen

**Flexsys
America L.P.**

The development of new environmentally favorable routes for the production of chemical intermediates and products is an area of considerable interest to the chemical processing industry. Recently, the use of chlorine in large scale chemical syntheses has come under intense scrutiny. Solutia, Inc. (formerly Monsanto Chemical Company), one of the world's largest producers of chlorinated aromatics, has funded research over the years to explore alternative synthetic reactions for manufacturing processes that do not require the use of chlorine. It was clear that replacing chlorine in a process would require the discovery of new atomically efficient chemical reactions. Ultimately, it was Monsanto's goal to incorporate fundamentally new chemical reactions into innovative processes that would focus on the elimination of waste at the source. In view of these emerging requirements, Monsanto's Rubber Chemicals Division (now Flexsys), in collaboration with Monsanto Corporate Research, began to explore new routes to a variety of aromatic amines which would not rely on the use of halogenated intermediates or reagents. Of particular interest was the identification of novel synthetic strategies to 4-aminodiphenylamine (4-ADPA) a key intermediate in the Rubber Chemicals family of antidegradants. The total world volume of antidegradants based on 4-ADPA and related materials is approximately 300 million lbs/year, of which Flexsys is the worlds largest producer (Flexsys is a joint venture of Monsanto's and Akzo Nobel's rubber chemicals operations)

Flexsys's current process to 4-ADPA is based on the chlorination of benzene. Since none of the chlorine used in the process ultimately resides in the final product, the pounds of waste generated in the process per pound of product produced from the process is highly unfavorable. A significant portion of the waste is in the form of an aqueous stream which contains high levels of inorganic salts contaminated with organics that are difficult and expensive to treat. Furthermore, the process also requires the storage and handling of large quantities of chlorine gas. Flexsys found a solution to this problem in a class of reactions known as nucleophilic aromatic substitution for hydrogen (NASH). Through a series of experiments designed to probe the mechanism of NASH reactions, Flexsys realized a breakthrough in understanding of this chemistry that has lead to the development of a new process to 4-ADPA that utilizes the base-promoted, direct coupling of aniline and nitrobenzene.

The environmental benefits of this process are significant and include a dramatic reduction in waste generated. In comparison to the process traditionally used to synthesize 4-ADPA, the Flexsys process generates 74 percent less organic waste, 99 percent less inorganic waste, 97 percent less waste water. In global terms, if just 30 percent of the worlds capacity to produce 4-ADPA and related materials were converted to the Flexsys process, 74 million lb/year less chemical waste would be generated and 1.4 billion lb/year less waste water would be generated. The discovery of the new route to 4-ADPA and the elucidation of the mechanism of the reaction between aniline and nitrobenzene has been recognized throughout the scientific community as a breakthrough in the area of nucleophilic aromatic substitution chemistry.

This new process for the production of 4-ADPA has achieved the goal for which all green chemistry endeavors strive, the elimination of waste at the source via the discovery of new chemical reactions which can be implemented into innovative and environmentally safe chemical processes.

Alternative Solvents/Reaction Conditions Award

Novel Membrane-Based Process for Producing Lactate Esters—Nontoxic Replacements for Halogenated and Toxic Solvents

ANL has developed a process based on selective membranes that permits low-cost synthesis of high-purity ethyl lactate and other lactate esters from carbohydrate feedstock. The process requires little energy input, is highly efficient and selective, and eliminates the large volumes of salt waste produced by conventional processes. Argonne's novel process uses pervaporation membranes and catalysts. In the process, ammonium lactate is thermally and catalytically cracked to produce the acid, which, with the addition of alcohol, is converted to the ester. The selective membranes pass the ammonia and water with high efficiency while retaining the alcohol, acid, and ester. The ammonia is recovered and reused in the fermentation to make ammonium lactate, eliminating the formation of waste salt. The innovation overcomes major technical hurdles that had made current production processes for lactate esters technically and economically noncompetitive. The innovation will enable the replacement of toxic solvents widely used by industry and consumers, expand the use of renewable carbohydrate feedstocks, and reduce pollution and emissions.

Ethyl lactate has a good temperature performance range (boiling point: 154°C, melting point: 40°C), is compatible with both aqueous and organic systems, is easily biodegradable, and has been approved by the U.S. Food and Drug Administration for food. Lactate esters (primarily ethyl lactate) can replace most halogenated solvents (including ozone-depleting CFCs, carcinogenic methylene chloride, toxic ethylene glycol ethers, perchloroethylene, and chloroform) on a 1:1 basis. At current prices (\$1.60-\$2.00 per pound), the market for ethyl lactate is about 20 million-pounds-per-year for a wide variety of specialty applications. The novel and efficient ANL membrane process will reduce the selling price of ethyl lactate to \$0.85-\$1.00 per pound and enable ethyl lactate to compete directly with petroleum-derived toxic solvents currently used. The favorable economics of the ANL membrane process therefore can lead to the widespread substitution of petroleum-derived toxic solvents by ethyl lactate in electronics manufacturing, paints and coatings, textiles, cleaners and degreasers, adhesives, printing, de-inking, and many other industrial, commercial, and household applications. More than 80 percent of the applications requiring the use of more than 3.8 million tons of solvents in the U.S. each year are suitable for reformulation with environmentally friendly lactate esters.

The ANL process has been patented for producing esters from all fermentation-derived organic acids and their salts. Organic acids and their esters, at the purity achieved by this process, offer great potential as intermediates for synthesizing polymers, biodegradable plastics, oxygenated chemicals (e.g., propylene glycol and acrylic acid), and specialty products. By improving purity and lowering costs, the ANL process promises to make fermentation-derived organic acids an economically viable alternative to many chemicals and products derived from petroleum feedstocks.

A U.S. patent on this technology has been allowed, and international patents have been filed. NTEC, Inc. has licensed the technology for lactate esters and provided the resources for a pilot-scale demonstration of the integrated process at ANL. The pilot-scale demonstration has produced a high-purity ethyl lactate product that meets or exceeds all the process performance objectives. A 10 million pounds-per-year demonstration plant is being planned for early 1999, followed by a 100 million pounds-per-year full-scale plant.

Designing Safer Chemicals Award

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

Rohm and Haas Company

The value of crops destroyed worldwide by insects exceeds tens of billions of dollars. Over the past fifty years, only a handful of classes of insecticides have been discovered to combat this destruction. Rohm and Haas Company has discovered a new class of chemistry, the diacylhydrazines, that offers farmers, consumers and society a safer, effective technology for insect control in turf and a variety of agronomic crops. One member of this family, 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, and the ecosystem. It will replace many older, less effective, more hazardous insecticides and has been classified by EPA as a Reduced Risk Pesticide.

CONFIRM™ controls target insects through an entirely new and inherently safer mode of action than current insecticides. The product acts by strongly mimicking a natural substance found within the insect's body called 20-hydroxy ecdysone, which is the natural "trigger" that induces molting and regulates development in insects. Because of this "ecdysonoid" mode of action, CONFIRM™ powerfully disrupts the molting process in target insects, causing them to stop feeding shortly after exposure and to die soon thereafter.

Since 20-hydroxy ecdysone neither occurs nor has any biological function in most nonarthropods, CONFIRM™ is inherently safer than other insecticides to a wide range of non-target organisms such as mammals, birds, earthworms, plants, and various aquatic organisms. CONFIRM™ is also remarkably safe to a wide range of key beneficial, predatory, and parasitic insects such as honeybees, lady beetles, parasitic wasps, predatory bugs, beetles, flies and lacewings, as well as other predatory arthropods such as spiders and predatory mites. Because of this unusual level of safety, the use of these products will not create an outbreak of target or secondary pests due to destruction of key natural predators/parasites in the local ecosystem. This should reduce the need for repeat applications of additional insecticides and reduce the overall chemical "load" on both the target crop and the local environment.

CONFIRM™ has low toxicity to mammals by ingestion, inhalation and/or topical application and has been shown to be completely non-oncogenic, non-mutagenic, and without adverse reproductive effects. Because of its high apparent safety and their relatively low use rates, CONFIRM™ poses no significant hazard to the applicator or the food chain and does not present a significant spill hazard. CONFIRM™ has proven to be an outstanding tool for control of caterpillar pests in many integrated pest management (IPM) and resistance management situations. All of these attributes make CONFIRM™ among the safest, most selective, and most useful insect control agent ever discovered.

Professor Michael R. Ladisch, Laboratory of Renewable Resources Engineering and Department of Agricultural and Biological Engineering, Purdue University

Entries from Academia

Biobased Adsorbents for Desiccant Coolers

Revised standards for acceptable indoor air quality have doubled ventilation requirements for commercial buildings and retail establishments. The need to dehumidify the additional air flow, combined with concerns about the phase-out of freons and the need to control costs of dehumidifying and cooling air, have led to an increase in the use of desiccant wheels. When combined with heating, ventilation, and air conditioning systems, desiccant wheels save both capital and operating costs, according to a Gas Research Institute funded study. An installation at the Johns Hopkins School of Medicine processes 300,000 cubic feet of air per minute (cfm) for a laboratory facility that requires 10 air changes per hour using all outdoor air. A desiccant wheel system using an inorganic adsorbent was proposed due to its energy efficiency and was installed at a cost of \$3 million in 1991. After 4 years of monitoring its operation, the Director of Maintenance Operations reported energy savings of \$650,000 per year over a conventional heating and air conditioning system.

Since desiccant wheel systems can dry and cool large volumes of air, they have the potential to supplant CFC and HFC refrigerants associated with compression-type air conditioning systems. The current production of desiccants is about 180 million pounds per year. Approximately half of this is attributed to molecular sieves, and 25 percent are silica gels. The potential of starch and cellulose as drying agents for fuel alcohol was reported in *Science* in 1979, and scaled up for industrial use by 1984. Ground corn is used in an adsorption process that replaces azeotropic distillation to dry approximately 750 million gallons of fuel ethanol, annually. The corn based adsorbent proved to save energy while avoiding the need to use benzene as the drying agent.

The fundamental research, and demonstration of the potential of starch and cellulose based adsorbents for desiccant air coolers, is an on-going research project at Purdue University that evolved from the first application of corn grits to the drying of fuel alcohol. Cross-disciplinary research at Purdue University has shown that starch, cellulose, and corn-based materials are potentially suitable for desiccant wheels. These adsorbents are biologically based and are given the abbreviation--biobased. Unlike silica gels and other inorganic adsorbents, biobased desiccants are less expensive, biodegradable and are derived from a renewable resource. Their low cost and wide availability could hasten adaptation of environmentally friendly air conditioning systems for residential as well as commercial uses.

Bioconversion of Carbon Dioxide into Organic Feedstocks

It has been established that emissions of carbon dioxide gas is responsible for about half of the increase in global warming. Efforts to decrease the consumption of fossil fuel are limited by increasing human population and industrialization and the fact that alternatives to fossil fuel all have important limitations. It is a matter of considerable urgency not only to conserve fossil fuel reserves, but also to search for means to recycle their main combustion product, which is carbon dioxide. In this regards, a unique bioprocess has been developed which is capable of converting waste carbon dioxide gas into algae, which is subsequently fermented into a variety of organic feedstocks, such as methane and acetic acid. Previous attempts to utilize phototrophic bacteria for fixation of carbon dioxide gas were limited by the following facts: photosynthesis by phototrophic bacteria require anaerobic conditions, which requires that carbon dioxide gas has to be separated from oxygen and is an expensive

Dr. Rakesh Govind and Rajit Singh, Department of Chemical Engineering, University of Cincinnati

process; unlike algae, phototropic bacteria require a wide spectrum of light, which limits their light source to sunlight.

In the work of Dr. Rakesh Govind and Rajit Singh at the University of Cincinnati, a marine algae, *Tetraselmis Suecica*, has been used successfully in a photobioreactor using light emitting diodes (LEDs) with a specific wavelength of 680 nm and a gas residence time of a few seconds. More than 98 percent removal efficiency of carbon dioxide gas from typical coal fired power plant stack gases was achieved experimentally at 3 seconds gas residence time at ambient temperature and pressure. The algae was separated from the aqueous phase by settling in a clarifier, and then converted under anaerobic conditions using electro-dialytic fermentation to acetic acid and methane in a batch reactor with yields of over 85 percent to acetic acid and 89 percent to methane gas. Catalytic conversion of methane gas to methanol and other organic feedstocks has been established in the literature. Thus, this process offers several advantages: bioconversion of waste carbon dioxide gas to useful organic feedstocks at ambient temperature and pressure; high conversion efficiencies of carbon dioxide gas to algae and subsequently to acetic acid and methane; and rapid reaction rate in the photobioreactor to produce algae. Economic estimates of the technology have shown that this technology can be easily implemented at power plant sites and acetic acid can be manufactured at less than half the current costs of manufacturing acetic acid from natural gas or crude oil resources.

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

Biodegradable polymers are attracting much public and industrial interest since they represent an important strategy to ease current problems in solid waste disposal. The surfactant and emulsifier industry in the U.S., for example, has grown nearly 300 percent during the last decade. In 1989, the U.S. production was estimated to be 15.5 billion pounds and the value of U.S. shipments in 1989 was approximately \$3.7 billion. Many of the applications of surfactants and emulsifiers either involve human contact or release into the environment. Therefore, there is a critical need for a new generation of low toxicity fully biodegradable products.

The work of Richard A. Gross at the University of Massachusetts Lowell on emulsion analogs, γ -poly(glutamic acid) and the preparation of low molecular weight polyester-polyethylene glycol diblocks have provided important new products from microbial syntheses. These products meet the need for biodegradability and low toxicity and, therefore, provide considerable human health and environmental benefits. Microbial polymerizations offer the potential for the discovery of important new routes to polymers and materials from renewable resources that involve all aqueous, green chemical routes. A critical problem limiting the utility of such methods, however, is the inability to control product structural variables that ultimately determine functional properties. The work of Professor Gross has led to the development of a family of technologies which has demonstrated unprecedented levels of control for nonribosomal mediated microbial polymerizations. Lipoheteropolysaccharides have been prepared from renewable resources, and innovative methods were developed to control the product's fatty acid structure and the degree of substitution. This has led to a diverse family of new biodegradable bioemulsifiers that have wide applicability for the stabilization of oil/water emulsions in cleaning and degreasing formulations, biocosmetics, green coating technologies, and bioremediation of organic pollutants.

A second technology area has used polyethylene glycols to regulate microbial polyester molecular weight, repeat unit composition, and alter repeat unit sequence distribution. Furthermore, this strategy can be used to form microbial polyester-polyethylene glycol

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

diblock copolymers. It is now possible to consider the in-vivo preparation of synthetic-natural diblocks. This technology has therefore created a number of opportunities for the preparation of completely biodegradable interfacial agents for blends, the termination of chains with reactive end-groups for coupling pharmacologically active molecules, and the engineering of surfactant molecules. A third technology area has been the development of new fermentation routes to anionic γ -poly (glutamic acid) from renewable resources such as glucose. γ -poly (glutamic acid) has the potential to replace millions of pounds of anionic polymers such as polyacrylic acid, which is nonbiodegradable and persistent in nature.

**Dr. Chhiu-Tsu Lin,
Department of
Chemistry and
Biochemistry, Northern
Illinois University**

Chrome-Free Single-Step In-Situ Phosphatizing Coatings

Economic losses resulting from corrosion of metals have been said to amount to billions of dollars per year and to be of the magnitude of 4 percent of the Gross National Product. In commercial practice, organic polymer coatings have been used in both commercial coating industries and the military to protect metal substrates against corrosion. The current organic coating on metals involves a multi-step process and considerable energy, labor, and control. The traditional phosphate treatment process for preparing metal prior to painting is a costly and error-prone process. For example, information provided by Caterpillar Tractor's Montgomery, Illinois, plant for the cost per year of its hydraulic tube phosphating line is \$330,000 (water/wastewater treatment = \$70,000, chemicals = \$36,000, labor = \$166,000, steam = \$50,000, and electricity = \$8,000). In addition, the use of corrosion inhibitors, the phosphating line baths, and the chromate sealing process in the current multi-step coating practice generates toxic wastes such as chlorinated solvents, cyanide, cadmium, lead, and carcinogenic chromates.

The innovative green chemistry technology of chrome-free single-step *in-situ* phosphatizing coatings (ISPCs) is a one-step self-phosphating process. The unique chemical principle of ISPCs is that an optimum amount of *in-situ* phosphatizing reagents (ISPRs) are pre-dispersed in the desired paint systems to form a stable and compatible one-pack coating formulation. The formation of a metal phosphate layer *in-situ* will essentially eliminate the surface pre-treatment step of employing a phosphating line/bath. The ISPRs form chemical bonds with polymer resin that act to seal and minimize the porosity of the *in-situ* phosphated substrate. The use of chemical bondings to seal the pores of metal phosphate *in-situ* should enhance coating adhesion and suppress substrate corrosion without a post-treatment of final rinses containing chromium (Cr^{6+}).

Design of CO₂-Soluble Ligands for Affinity Extraction Using CO₂

Carbon dioxide has elicited significant interest among the academic and industrial community over the previous decade in that it exhibits properties which render it a relatively "green" solvent. Carbon dioxide is an inexpensive, non-toxic solvent whose use in chemical processes is not limited by either FDA or EPA regulations. Use of CO_2 in extractions from water (or in biphasic reaction systems) is particularly advantageous in that, unlike the analogous situation using conventional organic solvents, one needn't worry about contamination of the aqueous phase when using CO_2 . Unfortunately, because CO_2 is a low dielectric fluid, extraction of polar materials from aqueous solution using CO_2 has been heretofore technically infeasible.

The work of Professor Eric J. Beckman at the University of Pittsburgh has shown that design and use of highly CO_2 -soluble ligands allows one to employ carbon dioxide in extrac-

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

tions of polar materials from water which were previously thought to be untenable. Using fluoroether-functional affinity ligands, for example, Professor Beckman has shown that one can extract proteins from aqueous solution into CO₂ with retention of activity following recovery by depressurization. Analogous chelating agents have been used to extract metals into CO₂ as well. While initial work has targeted primarily extractions, the described CO₂ soluble ligands can also be used to solubilize catalysts in CO₂ (enzymes and metals are examples) for use in carrying out reactions either in CO₂ or in CO₂ water biphasic mixtures.

Design of Rubberized Concrete From Recycled Rubber Tires

The United States produces about 279 million scrap tires per year. In addition, about 3 billion used tires are currently stored in waste piles throughout the country. Solid waste management experts recognize the need to recycle, reuse, or reduce the waste rubber tires, since this would lead to a direct diminution of waste tires in landfills. A number of processes have been suggested for reusing the waste rubber. Using tires as fuel and as asphalt material has provided only limited success. The work of Dr. Dharmaraj Raghavan at Howard University has led to the development of a technology that mixes rubber particles from scrap tires into portland cement resulting in a lighter material with improved performance of mortar and probably concrete.

The worldwide production of cement exceeds 1 billion tons annually, with the possibility of it nearly doubling in the next 14 years. Cement based materials are inexpensive, easy to produce, and possess valuable engineering properties such as high durability and compressive strength. One of the major shortcomings of cement based material is the vulnerability of concrete to catastrophic failure and to plastic shrinkage cracking. An encouraging finding was that plastic shrinkage cracking can be reduced significantly and the vulnerability of concrete to catastrophic failure can be greatly diminished by the addition of sufficient fibrous rubber. Chemical tests of the rubber retrieved from rubberized concrete showed no evidence of rubber undergoing any degradation and consequently no threat of released chemicals from the leached rubber into the environment. Possible uses of the rubberized concrete would be in subbases for highway pavements, highway medians, sound barriers, and other transportation structures. Currently the United States spends \$250 billion annually on infrastructure projects. Even if rubberized concrete replaced only a small fraction of the conventional infrastructural material, the ramifications to the civil and composite industries will be substantial. While the technology to reuse rubber tires into cement system yields value-added infrastructural material, it eliminates the imminent threat of health hazard and explosion potential because of the flammable nature of rubber tires.

The Determination of Alternative Solvents Quantifying and Qualifying Green Chemistries in Industrial Surface Cleaning

The Massachusetts Toxics Use Reduction Institute (TURI) was established by the state legislature with the passage of the Toxics Use Reduction Act (TURA) of 1989. TURI is a multi-disciplinary research, education, and technical support center at the University of Massachusetts, Lowell created to promote reduction in the use of toxic chemicals and/or the generation of toxic byproducts in Massachusetts industry and commerce. Because traditional organic and chlorinated solvents have known serious health and environmental effects,

Dr. Dharmaraj Raghavan, Department of Chemistry, Howard University

Carole LeBlanc, The Massachusetts Toxics Use Reduction Institute, University of Massachusetts, Lowell

Professor Terrence J. Collins, Department of Chemistry, Carnegie Mellon University

TURI maintains a Surface Cleaning Laboratory (SCL) with the capability to evaluate the effectiveness of different cleaning chemistries and equipment on a variety of substrates and contaminants. The objective of the Lab is to develop and promote safer alternatives to hazardous cleaning solvents. In this way, the Lab practices input substitution, one of six program-defined toxics use reduction (TUR) techniques. The Laboratory is designed with a special focus on aqueous/semi-aqueous cleaners and state-of-the-art surface cleanliness analyses. In full operation since 1994, SCL has served a wide range of businesses, including the electronics, metalworking, automotive, plastics, and paper and pulp sectors. The Institute's comprehensive appraisal of the tests conducted thus far will assist other companies with solvent substitution in many applications throughout the nation and the world.

Efficient, Selective, Totally Chlorine Free (TCF) Wood Pulp Bleaching Technology

The Pulp and Paper Industry is the eighth largest industry in the United States. In 1991, the value of shipments from the U.S. paper and allied products industry was \$129 billion. The 1994 global capacity of bleached pulp for paper making was 93.3 million tons; 58.7 millions tons was produced in the United States. Oxidative bleaching is essential for removing residual lignin from the pulp to produce bright white fiber. Dominant U.S. bleaching technologies have employed chlorine-based oxidants since the inception of the industry. Today, approximately 40 million tons of chlorine is produced annually; ca. 17 percent is used in paper making. The annual U.S. chlorine dioxide production has been estimated to be more than 10^5 metric tons.

In recent decades the environmental significance of chlorine-based bleaching has become well-recognized. Chlorine-containing organics are produced as byproducts of widely-practiced bleaching technologies, some of which are highly toxic. November 14, 1997, EPA signed a Cluster Rule requiring the industry to reduce chlorinated organics production. Enormous incentive exists to find cost-effective totally chlorine free (TCF) methodologies for bleaching pulp that meet environmental, health, and industrial needs. Professor Terrance J. Collins at Carnegie Mellon University has developed robust ligands that support iron catalysts for peroxide activation. This P_{Fe} technology is remarkable in possessing significant environmental and technological advantages. P_{Fe} catalyst lifetimes can be controlled in an unprecedented fashion because deep understanding has been achieved concerning how the catalyst ligands degrade upon oxidation and how such degradation can be blocked. The P_{Fe} catalysts consist of nontoxic elements. At micromolar concentrations, they activate peroxide efficiently for pulp bleaching from 0 to 90°C in water from neutral to basic pH; bleaching performance is best at room temperature, but remains excellent at 50°C. The all-important selectivity for lignin over cellulose oxidation is greater with the P_{Fe} technology than any existing TCF technology.

Engineered Baker's Yeast as a Means to Incorporate Biocatalysis Early in Process Design: Application to the Asymmetric Baeyer-Villiger Oxidation

While enzymes provide many advantages over traditional chemical reagents, they are generally applied to processes only during scale-up stages. It would make better economic and environmental sense to include biocatalytic methods during the initial discovery phase; however, this would require making biocatalysis accessible to bench chemists who often have no background in biochemistry or microbiology. Dr. Jon D. Stewart at the University of Florida

Dr. Jon D. Stewart, Department of Chemistry, University of Florida

has developed designer yeast, ordinary baker's yeast cells that have been engineered to express one or more foreign proteins. Whole cells of these engineered yeast can be used directly as a biocatalyst for organic synthesis. As proof of principle, Dr. Stewart's group has created a yeast strain that catalyzes a broad array of enantioselective Baeyer-Villiger oxidations. While this reaction plays an important role in laboratory-scale syntheses, the severe environmental and safety problems associated with current reagents prohibit its large scale use. *Acinetobacter* cyclohexanone monooxygenase was expressed in *Saccharomyces cerevisiae* and whole cells of the engineered yeast were used to oxidize several ketones in good yields and with high enantioselectivities. This process uses atmospheric O₂ as the oxidant and produces water as the only byproduct. Cell biomass and spent culture medium can be discarded in sanitary sewers after heat inactivation.

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

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

Environmentally Benign Solvent-Free Chemical Processing

An environmentally benign solvent-free synthetic approach was developed by Dr. Rajender S. Varma at Sam Houston State University. This approach utilizes neat reactants either in the presence of a catalyst or catalyzed by the surfaces of recyclable support(s) such as alumina, silica, clay, and 'doped' surfaces such as NaIO₄-silica, iron(III) nitrate-clay (clayfen), and persulfate-clay. This occurs under microwave irradiation conditions thus promoting reduction of solvents at the source and excess chemicals in manufacturing. This pollution preventive strategy has been targeted to industrially significant cleavage, condensation, oxidation, and cyclization reactions that currently employ toxic, corrosive, and irritant chemicals and generate hazardous waste. The technology uses material science, molecular modeling, and synthetic organic chemistry expertise and addresses the needs of broad chemical community (polymers, pharmaceuticals, and fine chemicals) by efficient production of valuable intermediates (enones, imines, enamines, nitroalkenes, oxidized sulfur species and heterocycles). Further, the technology teaches pollution prevention to a younger generation of scientists and is extendible to in situ destruction of pollutants and hazardous waste.

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

**Dr. Rajender S. Varma,
Texas Regional
Institute for
Environmental Studies,
Sam Houston State
University**

Professor John C. Warner, Department of Chemistry, University of Massachusetts, Boston

Polaroid Corporation

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

Environmentally Benign Supramolecular Assemblies of Hydroquinones in Polaroid Instant Photography

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

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

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

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

ter goal will significantly improve the economic competitiveness of existing pheromone products, and could provide the basis for the expansion of this promising insect control technology into other markets.

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

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

The elimination or reduction of the use of organic solvents, and the purer products formed, lead to reduced chemical waste (such as, organic solvents for reactions and recrystallization, chromatographic material for purification, etc.). To demonstrate 'atom economy' (more products for all the chemicals used) and the versatility of MORE chemistry techniques, Dr. Bose's group has conducted multistep synthesis (including one-pot reactions for two or more steps) of advanced intermediates for lactam antibiotics, amino sugars, alkaloids, and other biologically active compounds such as Taxol. They have also found that an efficient and eco-friendly nitration method can be accomplished by irradiating with microwaves, have observed mild acceleration of chemoenzymatic reactions under low intensity microwave irradiation, and have devised a very eco-friendly oligopeptide synthesis that needs no conventional peptide bond forming agents. In brief, MORE chemistry techniques can make very significant reduction of pollution at the source for small scale as well as large scale synthesis and thus make the development and production of life-saving drugs more eco-friendly.

National Microscale Chemistry Center: The Leader in Worldwide Implementation of Microscale Technology

The simplest definition of Green Chemistry is "the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, byproducts, solvents, reagents, etc., that are hazardous to human health or the environment." While more commonly being applied to industrial applications, the concepts of Green Chemistry also have been incorporated into education pedagogy, using microscale laboratory methods. The microscale chemistry technique is a laboratory based educational program, resulting in waste reduction at the source; elimination of toxic emissions, fire, and accident hazards; enhancement of a healthful laboratory environment; and significant cost savings. Microscale methodology uses minute amounts of chemicals (50 mg of solids, 500 μ L of liquids on average), new methods for determining physical properties; milder and safer alternative reaction conditions; alternative benign solvents; and differ-

**Dr. Ajay K. Bose,
Stevens Institute of
Technology**

**Dr. Mono M. Singh,
National Microscale
Chemistry Center,
Merrimack College**

**Craig L. Hill,
Department of
Chemistry, Emory
University**

**Ira A. Weinstock, USDA
Forest Service, Forest
Products Laboratory**

ent synthetic pathways, often employing catalytic and other environmentally safe techniques. The National Microscale Chemistry Center was established at Merrimack College in 1993. The center offers workshops, training and other related support to teachers and industrial chemists in microscale chemistry techniques. Currently, more than 2000 institutions in the United States have, either fully or partly, adopted this approach. NMC² is also the lead site of an international consortium promoting the microscale/Green Chemistry revolution.

A New Catalytic Biomimetic Technology to Convert Wood to Paper Without Pollution

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

Nature carries out this chemically and technically challenging multistep process by using a complex ensemble of selective metalloenzymes (glyoxal oxidase, ligninase, and Mn peroxidase). The pulp and paper industry, since its inception many decades ago, has yet to achieve what nature has. Chlorine compounds, and not O₂, have been the dominant oxidants. While decades of optimization have led to highly selective delignification (minimally damaged cellulose), these man-made technologies produce waste streams that contain environmentally deleterious phenolic compounds as well as nonbiodegradable chloroaromatics. In consequence, societal and legislative pressure in all developed countries is compelling pulp manufacturers to phase out chlorine. The most attractive alternative oxidants, hydrogen peroxide (H₂O₂) or ozone (O₃) are encumbered by inherent limitations. Hydrogen peroxide is simply not effective. Ozone processes, while potentially effective, fall far short of the selectivity required for general commercial use or of the selectivity seen in nature.

The new catalytic biometric approach uses versatile, nontoxic, and inexpensive inorganic clusters known as polyoxometalates (POMs) in two steps. The first step involves delignification of wood pulp (bleaching) by reaction with the oxidized POM providing high quality cellulose fibers. As the POM is reversibly reduced, the lignin is oxidized and solubilized. In the second step, O₂ is added to the bleaching liquor and the same POM catalyzes the complete conversion (mineralization) of the dissolved lignin fragments to CO₂ and H₂O. The two steps sum to the selective removal of lignin from wood, using only air and water, an ideal process that only nature has achieved to date. This biomimetic and catalytic technology eliminates the environmental problems associated with conventional chlorine-based processes, while overcoming the limitations inherent in other chlorine-free pulp bleaching strategies. It is green in at least six ways including the complete elimination of waste streams (a “closed process” is achieved). The high selectivity entails less consumption of the natural renewable resource, wood. It is energy efficient and as current analyses indicate, cost effective.

A Non-Toxic Liquid Metal Composition for Use as a Mercury Substitute

Mercury is used extensively in switches and sensors; yet, mercury is toxic to humans and animals. In addition to being an excellent conductor of electricity, mercury, unlike any other metal known, remains fluid throughout a wide temperature range which encompasses 0°C. Another important physical attribute of mercury is that it has significant surface tension which means that it does not wet glass, metal, or polymer surfaces. Because of these properties, mercury is found in numerous commercial products such as automobiles, thermostats, steam irons, pumps, computers, and even tennis shoes. In each of these cases, mercury functions as a liquid electrical switch. Discarded consumer items which contain mercury have become an environmental hazard. Several states have banned new products that contain mercury. Since billions of mercury switches are made each year worldwide, a nontoxic replacement for mercury appears highly desirable.

At Virginia Tech, a gallium-based alloy containing indium, zinc, and copper has been identified. The alloy conducts electricity, freezes below 0°C, and exhibits high surface tension. In other words, this material which looks and acts like mercury does not contain a single toxic element. The alloy can conduct both AC and DC current, exhibits a solidification temperature near -10°C, possesses a very high boiling point and very low vapor pressure, and has similar flow characteristics to mercury. Both glass- and metal-housing switches have been found to be highly acceptable with the nonmercury material after extensive testing. In addition to the environmental advantages, nonmercury switches and sensors can replace mercury switches and sensors without modifying existing technology. In fact, the methodology for fabrication of nonmercury switches and sensors would be identical to that currently being used with toxic mercury. Mercury also is used in temperature sensors, pressure activated switches, pumps and filters, slip rings, liquid mirror telescopes, fluid unions, dental amalgam, and in medical devices such as sphygmomanometers and bougies. The nonmercury described herein also can serve as a substitute for elemental mercury in many of these applications.

Novel Applications of Polymer Composite from Renewable Materials

Metal corrosion costs the United States about 4.2 percent of its gross national product, or more than \$250 billion in 1996. To improve the longevity of the engineered material, the surface coatings must be refurbished to meet design requirements. Recoating of the surface involves paint stripping and application of a fresh paint coating. Traditional stripping methods employ organic solvent methylene chloride. Methylene chloride is carcinogenic and poses a health risk to the maintenance crew. Consequently, the aircraft maintenance industry has begun to utilize alternative approaches for repainting aircraft. One method that has proved reliable is dry-blasting to remove the paint coating mechanically. The repainting process using blast media, however, is reported to be the largest single source of solid waste on military bases where aircraft repainting is performed.

The work of Dr. Dharmaraj Raghavan at Howard University addresses the development of an organic coating removal technique based upon renewable plastic media. As such, the degradable dry-blast process is developed so as to eliminate 90 to 97 percent of the waste by biological or chemical degradation of the spent media. The degradation of solid media waste (based on renewable polymer) results in the production of speciality solvents which are environmentally safe and are value added chemicals. Another application, where degradability of renewable polymer composite can be exploited is in membrane design. Membranes represent

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

Virginia Tech Intellectual Properties

Dr. Dharmaraj Raghavan, Department of Chemistry, Howard University

a worldwide market approaching \$1 billion, annually. Membranes have found wide application in the industries, the separation industry remains the most important segment. In the design of these membranes, solvents used include acetone, dimethyl sulfoxide, dimethyl formamide and dimethyl acetamide. There is a general concern of the exposure of the working crew to carcinogenic solvents during the preparation of membranes. To address these concerns, Dr. Raghavan has designed a compatibilizer based polymer composite, where the major component is renewable polymeric material and the minor component is nondegradable synthetic polymer. The technology is based on the degradability of the renewable polymer in protic solvent/enzymic system, and the ability to formulate a porous microstructure of synthetic polymer. The degradation of the renewable polymer results in the production of chemicals which are environmentally safe and can be used in the synthesis of renewable polymer.

**Dr. Jimmy E. Antia
and Dr. Rakesh Govind,
Department of Chemical
Engineering, University
of Cincinnati**

Novel In-Situ Zeolite Coatings in Monoliths

A novel in-situ method of depositing binderless zeolite catalysts in monolith reactor systems has been developed at the University of Cincinnati. It has been shown that *in-situ* coatings of zeolites on monolith substrates, maximizes the effectiveness of the "shape-selective" aspects of zeolite catalysis. This technology can be used for a wide variety of zeolites, currently used extensively in the petrochemical industry. It has been shown that binderless zeolites used in monoliths exhibit enhanced performance minimizing the formation of high molecular weight hydrocarbons with minimal diffusional limitations. Two specific studies were conducted to demonstrate the effectiveness of these binderless zeolites in monoliths: conversion of methanol to gasoline hydrocarbons; and catalytic cracking of n-Hexane. Main technical advantages of monolith reactors is low pressure drop, improved performance due to less plugging and channeling, and high surface area per unit volume of reactor. The technology also offers many benefits for human health and the environment. For instance, alcohol obtained from fermented agricultural wastes can be converted to gasoline-range hydrocarbons on monolith reactors. Besides producing useful fuel, this reaction produces no hydrocarbons larger than C₁₂, which are difficult to burn and exhibit low biodegradation rates if released to soil and ground water. Also, this alternative fuel source conserves nonrenewable resources like petroleum and natural gas, while simultaneously reducing dependence on imported crude oil. As a result of lower heavy hydrocarbon content, these fuels are cleaner burning and do not add further carbon dioxide to the environment.

**Dr. Bala Subramaniam,
Department of
Chemical and
Petroleum Engineering,
University of Kansas**

A Novel Solid-Acid Catalyzed 1-Butene/Isobutane Alkylation Process

Alkylation reactions are employed to convert light refinery gases (C₃-C₅) into gasoline compounds (C₇-C₉). Alkylates constitute roughly 15 percent of the U.S. gasoline pool. At present, industrial alkylation employs either hydrofluoric acid or sulfuric acid as a catalyst. For more than three decades, numerous solid acid catalysts have been explored as environmentally-safer alternatives to liquid acids. However, solid-acid catalysts deactivate rapidly due to coke retention in the pores. In gas-phase media, the heavy coke precursors (such as olefinic oligomers) are poorly soluble. In liquid phase reaction media, the transport of coke precursors out of the catalyst pores is severely restricted resulting in their readsorption and transformation to consolidated coke. The work of Dr. Bala Subramaniam at the University of Kansas employs supercritical reaction media, which offer a unique combination of liquid-like density and gas-like transport properties, for the effective removal of the coke precursors. Employing carbon dioxide (P_c = 71.8 bar; T_c = 31.1°C) as an environmentally-benign sol-

vent, 1-butene/isobutane alkylation was performed at supercritical conditions resulting in virtually steady alkylate (trimethylpentanes and dimethylhexanes) production in a fixed-bed reactor on solid acid catalysts (HY zeolite, sulfated zirconia and Nafion) for several days. The carbon dioxide-based supercritical process thus offers an environmentally safer alternative to conventional alkylation by eliminating a major technological barrier impeding the application of solid acid catalysts in alkylation practice.

Novel Waste Minimization Approach: Production of Carbon-Based Catalyst or Sorbent from Biosolids

Biosolids, a byproduct of wastewater treatment facilities, are currently a major environmental concern. Identified problems associated with the management of biosolids are the hazardous content, the large mass produced, the difficulties associated with its treatment, and the few available disposal methods. Furthermore, the production of biosolids has also been increasing due to a greater percent of the global population being served by sewer lines and an increasing population. In 1995, the United States produced 9 million tons of biosolids, and is expected to produce 11 million tons/year by the year 2000. Transformation of biosolids is a novel and innovative idea for waste minimalization and recycling at wastewater treatment facilities.

An innovative process was developed by the Department of Chemical and Environmental Engineering at the Illinois Institute of Technology to convert biosolids produced at wastewater treatment facilities primarily to carbons with a wide range of applications as adsorbents or catalysts. The feedstock for the process was biosolids produced at the Spring Brook Water Reclamation Center, in Naperville, Illinois. The results of the laboratory study showed that biosolids can be effectively and economically converted to a carbon-based catalyst or sorbent with relatively high surface area and small pores with a rather wide pore size distribution. The total surface area, surface structure, and pore size distribution were effectively controlled by varying chemical activation processes and heat treatment methods. The characteristics of the produced carbons were evaluated using N₂-BET (Brunauer, Emmett, and Teller) gas adsorber and X-ray diffraction. This study demonstrates the effective conversion of waste from wastewater treatment processes to a useful carbon-based catalyst or sorbent, and at the same time, replaces fossil fuels in the production of activated carbon.

Orphan Chemical Recycling Program

In April of 1993, the Department of Environmental Health and Safety at Bowling Green State University initiated a program to transfer orphan laboratory chemicals to nonuniversity academic institutions primarily within Wood County, Ohio (note: an orphan chemical is one that is still useful but unwanted by those having them). In 1994, the program gained the participation of an area hazardous waste management company. This joint effort has allowed the program not only to move beyond the boundaries of Wood County, but also to include small business and industry in the recycling effort. The program, which is free of charge, has now seen participation from 30 academic institutions and 52 small business, industry, and governmental facilities throughout Ohio as well as from other states. Since April of 1993, the program has transferred over 3,500 pounds of solids and 1,100 gallons of liquids to “needy” institutions and facilities. These transactions have resulted in cost savings between \$330,000 and \$405,000.

**Dr. Nasrin R. Khalili,
Hamid Arastoopour,
and Laura Walhof,
Department of
Chemical and
Environmental
Engineering, Illinois
Institute of Technology**

**Bowling Green
State University**

**James P. Rybarczyk,
Department of
Chemistry, Ball State
University**

Premature Degradation of Coolant Oil in the Machining of Magnesium in the Automobile Industry

The research of James P. Rybarczyk at Ball State University is concentrated on a fundamental chemical study to increase the longevity of a water-based coolant, cutting oil emulsion used in the machining and manufacture of magnesium cases for the automotive industry. Water-based emulsions have virtually replaced the more toxic organic solvent-based ones, but the difficulty of water-based ones in magnesium applications involves the dissolution/reaction of the machined magnesium fines with water, producing hydrogen gas and dissolved magnesium ions. These Mg^{+2} ions then interact with the emulsion, breaking the oil/water emulsion and splitting out the oil, creating scale deposits of magnesium carbonate, magnesium greases, and the virtual disintegration of both the coolant and cutting properties. This necessitates a changing of the coolant systems at a frequency of 1.5 to 2 months, as opposed to a theoretical 24 months. This high frequency of replacement/disposal results in a significant workload cost, monetary cost, and above all, environmental cost. Rybarczyk's research established the causes of the premature breakdown of the emulsion and provided seven recommendations for chemical and/or physical process modifications. The study focused on the fragility of the emulsion and on the control of pH at basic levels to minimize the water dissolution of magnesium. The study showed an increase of better than 16 times in the lifetime of the emulsion from these recommendations. The industry has currently implemented three of the recommendations, with hopefully more to follow, resulting in a 2 times to 3 times increase in emulsion lifetime.

**Dr. Michael F. Doherty,
Dr. Michael F. Malone,
Department of
Chemical Engineering,
University of
Massachusetts,
Amherst**

Reactive Distillation Technology to Reduce Waste at the Source

Mixtures are azeotropic if they can be distilled (or condensed) without a change of composition. The existence of azeotropes in multicomponent mixtures in the absence of chemical reactions is well understood phenomenologically and theoretically. Azeotropes place a fundamental limit on the compositions attainable in mixtures by fractional distillation, but they can in some cases be 'broken' by carrying out chemical reaction and separation simultaneously rather than sequentially. Here, Dr. Michael F. Doherty and Dr. Michael F. Malone at the University of Massachusetts, Amherst report the discovery of a boiling state of constant composition and temperature in a mixture of acetic acid, isopropanol, isopropyl acetate, and water that is simultaneously in both reaction and phase equilibrium. This project confirmed earlier theoretical predictions by the senior author and others of the existence of reactive azeotropes that would allow combined reaction and distillation without a change in composition. This hybrid combination is also known as "catalytic" or "reactive" distillation. The technology is broadly applicable as the basis for innovative process designs to improve yields and productivity and eliminate or reduce by-product formation. The researchers built a working apparatus to prove the value of reactive distillation at higher pressures and assessed the feasibility of making dimethyl ether by reactive distillation from methanol.

**Dr. Stephen Thompson,
The Center for Science,
Mathematics and
Technology Education,
Colorado State
University**

Small Scale Chemistry: Pollution Prevention in Inorganic Chemistry Instruction Program

Small-Scale Chemistry (SSC) techniques developed by Dr. Stephen Thompson at Colorado State University build pollution prevention, waste minimization, and student safety at the design stage rather than controlling it at the disposal stage. SSC inherently manifests

characteristics of “green chemistry” by incorporating the principles and methodologies of source reduction. The SSC techniques and experiments result in significant waste reduction and reduced risk of chemical exposure to both students and faculty. This is achieved through innovative experiments and methodologies that use alternate reaction conditions and alternate synthesis pathways. The concepts of SSC evolved as a solution to many of the serious problems (e.g., cost, safety, waste disposal, pedagogy) associated with chemistry laboratory instruction. Drops of chemicals used as their own containers replace liters of chemical hazardous waste in breakable glassware. The innovative use of high tech plasticware designed for genetics research reduces cost while maintaining safety and sophistication. SSC techniques and methodologies provides a realistic approach to green chemistry and allows academic institutions to institutionalize lasting behavioral changes. SSC provides an easy to implement, affordable, and wide application remedy to a real environmental management problem face by most college and university chemistry programs.

Source Reduction Through Mass Integration: Mass Exchange Network Synthesis

Mass Integration, and in particular Mass Exchange Network (MEN) synthesis, represents a set of systematic and general methods for the design of networks that increase the mass efficiency of manufacturing processes. Dr. Vasilios Manousiouthakis at the University of California Los Angeles has conceived of these design methods in an effort to provide novel, powerful and versatile tools, for engineers that wish to pursue source reduction and waste minimization. The goal of this project has been the development of the Mass Integration methodology and its industrial application. The general formulation of the design problem, allows the incorporation of any possible network and any mass exchange operation, including that of distillation. It also permits use of the method in both a grassroots and a retrofit design setting. Mass Integration's power and flexibility, have led to its wide applicability. Several academic and industrial mass integration application are being reported and a multi-million dollar mass integration industry is coming into its own. In collaboration with M.W. Kellogg, Dr. Manusiouthakis has recently applied his design method on a phenol manufacturing facility. The resulting process design demonstrated a 17 percent reduction in freshwater use and a 50 percent reduction in waste phenol.

Successful Development of Recombinant Xylose-Fermenting Saccharomyces Yeasts Capable of Effectively Co-Fermenting Glucose and Xylose from Renewable Cellulosic Biomass to Ethanol as Clean Transportation Biofuel

Ethanol is an effective, environmentally friendly, nonfossil, transportation biofuel that produces far less pollution than gasoline, contributes essentially no net carbon dioxide to the atmosphere, and eases the threat of global warming. Furthermore, ethanol can be produced from plentiful, domestic, renewable, cellulosic biomass feedstocks. This reduces our nation's dependency on imported oil, protects its energy security, and reduces our trade deficit. However, a major obstacle in this process is that cellulosic biomass contains two major sugar molecules, glucose and xylose. *Saccharomomyces* yeasts, traditionally used and still the only microorganisms currently used for large scale industrial production of ethanol from glucose, are unable to ferment xylose to ethanol, making the use of the safest, most effective

**Dr. Vasilios
Manousiouthakis,
Department of
Chemical Engineering,
University of California
Los Angeles**

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

Saccharomyces yeasts for conversion of biomass to ethanol economically infeasible. Furthermore, there are no other natural microorganisms that can ferment both glucose and xylose with reasonable efficiency.

After many years of dedicated research efforts, Dr. Nancy W. Y. Ho at Purdue University achieved a historic breakthrough in the development of genetically engineered *Saccharomyces* yeasts that can effectively ferment both major sugars (glucose and xylose) present in cellulosic biomass to ethanol. Her work has made it possible to use the most safe, effective, user friendly *Saccharomyces* to ferment sugars from cellulosic biomass to ethanol to be used as the environmentally friendly transportation fuel. This was accomplished by cloning multiple copies of genes encoding three key enzymes for metabolizing xylose in yeasts. These genes were modified so that they were able to produce the desired enzymes in yeasts in the presence of glucose and/or xylose. This allows yeasts to effectively co-ferment glucose and xylose simultaneously to ethanol. The current best xylose-fermenting *Saccharomyces* yeasts can ferment glucose and xylose efficiently and cost-effectively for industry to produce ethanol from cellulosic biomass. More effective yeasts that will ferment xylose faster and will also be able to produce other high-valued byproducts can still be developed.

The SYNGEN Program for Generation of Alternative Syntheses

Thousands of organic chemicals are synthesized annually on an industrial scale, and their manufacture can often lead to environmental problems. If alternative syntheses that create fewer hazardous wastes and less pollution could be found, a number of these problems could be solved. No one would claim that the synthesis routes currently in use are the only ones possible, or even that they know them to be the best routes. Indeed it is easy to show that the number of possible synthesis routes to target molecules of even modest complexity is usually enormous. However, organic chemistry has traditionally not provided any logical protocol for the systematic design of synthesis routes to any target molecule. If there were such a protocol, other routes to any industrial synthesis target could be systematically explored, and their relative impacts on the environment examined. Although a number of computer programs have been written, few have come out of their academic sources into the world of chemical industry for practical use, and essentially none have been viewed there as successful.

The SYNGEN program developed by Professor James B. Hendrickson at Brandeis University is different from the others in conception and practice. It aims at surveying all possibilities and reduces the vast number of these possibilities quickly and stringently to focus on only the shortest and cheapest routes following a criterion of economy. It is self-consistent and not interactive, and so avoids skewing the results to favor operator's preconceptions. On this base it now adds evaluation of environmental hazards to the best routes selected. Earlier version of SYNGEN were also not successful in the practical world, partly because chemists did not fully understand its logic and also because the program too often generated reactions which the chemists regarded as chemically unworkable. To clarify the logic for chemists, the program first focuses on the criteria of the target skeleton from available starting skeletons. then it 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 compactly 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 both of their cost and their environmental impact. This makes possible for the first time an unbiased collection of real benign synthesis routes for the production of commercial chemicals. With this tool we can truly explore alternatives for green chemistry.

Synthetic Methodology 'Without Reagents'. Commercial Manufacture of Inositols and Other Pharmaceuticals by Tandem Enzymatic and Electrochemical Oxidations and Reductions

The prevention of pollution at its source is addressed by the replacement of currently used methods of oxidation and reduction (i.e., all based on metal reagents) with enzymatic and electrochemical techniques (i.e., all performed in water, alcohols, or other environmentally acceptable solvents). The combination of enzymatic transformations with electrochemistry, along with efficient design, yields unprecedented brevity in the attainment of important pharmaceuticals from metabolites of the arene cis-diol type. Halogenated aromatic compounds, viewed in many cases as harmful to the environment, are enzymatically converted to useful synthons and effectively removed from the hazardous waste pool, with added economic benefits of strategic conversion that would not be available through outright incineration of such compounds. It must be emphasized that the enzymatic conversion of the toxic aromatic materials takes place in the very first step of the synthetic pathway and that all subsequent intermediates are harmless. The residual mass from enzymatic or electrochemical processes is judged suitable for disposal to municipal sewers, thus further reducing the amount of actual waste. The synthesis of a homochiral cyclitol from halobenzene by several steps involving essentially no reagents serves as the illustration of the technology. Given that the length of a synthesis plays a direct role in the attendant accumulated waste mass for the process, it follows that short and efficient syntheses lead to lesser accumulation of waste and thus reduce pollution at the source.

Vibrating Fluidized Bed Combustion Nitridation Processing Using Concentrated Solar Energy

The best way of managing pollution from industrial processes is to devise ways to minimize its production. This is especially true in the synthesis of chemical compounds. New concepts developed at the University of Colorado attack the problem on four levels: maximizing yields, avoidance of post processing, use of non-toxic precursors, and minimizing energy consumption. Professor Weimer and his students have demonstrated model ceramic synthesis systems which have high yield, avoid needle-like particle growth induced by thermophoresis, use metal powders and nitrogen as precursor material, and use sunlight as the source of energy for synthesis reactions. High quality powders of silicon nitride and of aluminum nitride, both technologically important materials, have been produced as proof of concept. The use of a directed energy source for the synthesis produces higher quality materials and reduces the energy budget, thus reducing the pollution associated with conventional heating. The use of concentrated sunlight, instead of a laser beam or arc lamp, further reduces the consumption of fossil fuels to provide the energy for the beam.

Waste Biomass Utilization in the Production of a Biodegradable Road Deicer

The effective utilization of biomass and the residuals from agricultural and food processing operations in the production of fuels and chemicals, is one of the cornerstones of policies aimed at energy conservation and sound environmental management. Biomass wastes such as liquid whey effluents from the Dairy industry are an undue burden on the environment

**Dr. Tomas Hudlicky,
Department of
Chemistry, University
of Florida**

**Professor Alan W.
Weimer, Department of
Chemical Engineering,
University of Colorado**

**Alexander P. Mathews,
Department of Civil
Engineering, Kansas
State University**

due to the high biochemical oxygen demand (BOD) of such wastes. Whey is a byproduct from cheese and casein production operations, and contains about 5 percent lactose and 0.1 percent to 0.8 percent lactic acid. About 50 percent of the total U.S. milk production is used in the production of cheese, resulting in the generation of approximately 57 billion pounds of liquid whey per year. Acid whey containing lactose and lactic acid has a very high BOD of about 40,000 mg/L. As such, this waste can be a tremendous burden to the environment if it is discharged without controls. Treatment of the high BOD waste is both capital and energy intensive. Thus any viable reuse option is likely to offer large savings in cost and energy utilization.

The work of Alexander P. Mathews at Kansas State University is aimed at examining the use of whey permeate in the production of a road deicer substitute for sodium chloride. Each year, about \$2 billion are spent on U.S. highways alone to maintain driveable conditions during winter. Bulk of this expenditure is on the application of chemical deicers, principally sodium chloride. The annual use of NaCl has increased rapidly from 0.5 million tons in 1947 to about 30 million tons in 1996. Many roads and highways in the snowbelt may receive up to 60 tons of salt per km during the winter season. Currently used deicers, such as NaCl cause extensive corrosion related damage to the highway infrastructure and environmental damage by contaminating water supplies and soils.

The main objectives of the work of Mathews were to examine the use of biomass wastes in the production of deicers, calcium magnesium acetate (CMA), and calcium magnesium propionate (CMP). A novel two-stage fermentation process was developed to utilize and convert inexpensive substrates such as whey permeate to acetic and propionic acids for use in the production of the deicer. The two-stage process has a substrate conversion efficiency of about 90 percent compared to 53 percent for a single-stage process. Acid concentrations up to 60 gm/l were obtained in batch and fed-batch fermentations. In addition, the source of calcium and magnesium in the CMA/CMP deicer was obtained from water plant treatment sludges (water treatment operations such as coagulation, flocculation, and chemical softening result in the production of large quantities of solid byproducts containing calcium and magnesium which can be used in the production of CMA/CMP deicer).

Waste Reduction and Recycling of Magnesite-Chrome Refractory into the Steelmaking Process

The primary objectives of the work of Dr. Claudia Lage Nassaralla at Michigan Technology University is to develop the technological basis to minimize the formation of hexavalent chromium (Cr^{6+}), a well-known carcinogen, within magnesite-chrome refractory during its production and use in industrial processes. Magnesite-chrome is a high temperature refractory used in the steel, copper, cement, and glass industries because of its excellent resistance to thermal shock and chemical attack. The spent magnesite-chrome refractory is classified as a hazardous material by EPA when it contains high levels of Cr^{6+} . Of all the chromium ions, Cr^{6+} is the only one soluble in water, and as such, can give rise to detrimental effects on the environment and food chain because it is strongly oxidizing and easily penetrates human tissue. The origin of Cr^{6+} in the refractory is due to the reaction between CaO and Cr_2O_3 . No other oxide present in the refractory is known to form Cr^{6+} . Until recently, spent magnesite-chrome refractory was normally disposed of in authorized landfills. Currently, spent magnesite-chrome refractories with a Cr^{6+} content above 5 ppm must be treated before disposal.

The technology that is currently being developed by Dr. Nassaralla has the potential to minimize the formation of Cr^{6+} by carefully controlling the brickmaking and steelmaking

**Dr. Claudia Lage
Nassaralla, Department
of Metallurgical and
Materials Engineering,
Michigan Technological
University**

practices. It will also allow for the reduction of hexavalent to trivalent, and to chromium metal, di- and trivalent chromium by recycling the brick into the steelmaking converter and the electric arc furnace, respectively. No type of preprocessing of the solid waste or installation of additional equipment will be necessary. The waste material can be treated onsite, and the contaminated bricks can also be recycled as part of the flux that has to be added in the steelmaking converter to absorb the oxides generated in the production of steel or in the electric arc furnace as a source of chromium in the production of ferro-chromium. The information generated from this project can also be used by the copper, cement and glass industries to design their practices to minimize the formation of Cr^{6+} . Besides the savings associated with the costs of disposing spent chrome-magnesite brick, the recycling of Cr^{6+} in the production process and its conversion to chromium metal, di- and trivalent chromium will avoid contamination of the environment by possible leaching of Cr^{6+} after dumping.

Water as Solvent for Chemical and Material Syntheses

Rather than sacrificing one or the other, to synchronize the advancement of science and technology and the advancement of green chemistry is the key feature of the research carried out by Tulane. A range of technologies has been developed that uses water as solvent for chemical, pharmaceutical, and material syntheses. The technologies developed not only offer many benefits for human health and the environment, but also the use of water as solvent plays an essential role in the success of this research. The use of large quantities of organic solvent for industrial scale operations eventually adds to environmental problems. In fact, volatile organic compounds are the principal pollutants of all organic compounds. On the other hand, water is non-toxic, non-explosive, non-flammable, as well as the basis and bearer of life in nature. Numerous biochemical reactions affecting the living system have inevitably occurred in aqueous medium. On the other hand, most organic reactions and syntheses have been carried out in organic solvents. At Tulane, Professor Chao-Jun Li has developed various synthetic methodologies by using water as solvent. By using these methodologies he has synthesized biologically important natural products, novel electronic and optical materials, and nano-carbon materials. In most cases, the studies have the dual advantages of being aqueous and being "atom economical." Also in most cases, the use of water as the reaction solvent does not only make them environmentally friendly, but also essential to the success of this research.

Waterborne Coating Formulations for Video Tape Manufacture

Magnetic tape technology is an important component of the information age and maintaining a domestic tape manufacturing capability is important to the U.S. economy. Magnetic tape is manufactured by a continuous web coating process that uses organic solvents, including tetrahydrofuran, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), toluene and cyclohexanone. MEK, MIBK, and toluene are on the list of 189 hazardous air pollutants and on the list of 18 chemicals for the EPA's 33/50 voluntary pollution reduction program.

Waterborne magnetic tape coating formulations were designed at the University of Alabama and used to prepare experimental magnetic tape samples in a pilot coating trial. The formulations contained a blend of a water-dispersed polyester and an ethylene/vinyl chloride copolymer emulsion. The coatings were thermally cured with a melamine-formaldehyde cross-linker to give tensile properties that were comparable to a standard solvent-based binder composition. The pilot tape trial used existing processing equipment, including calendaring

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

**Dr. David E. Nikles,
Department of
Chemistry, University
of Alabama**

and slitting. The tape had good magnetic properties and excellent adhesion between the pigmented magnetic layer and the base film; easily exceeding the 8 mm helical scan tape standard of 0.96 N peel force. An economic impact analysis for the case of using the waterborne video tape coating process in a conventional tape manufacturing plant showed an 11 percent decrease in hourly operating costs. The solvent-based process generated almost 650 kg of organic solvent per hour operation, while the waterborne process generated less than 5 kg methanol (from the melamine-formaldehyde cross-linker) per hour. In addition to pollution prevention, there was a clear economic incentive to adopt the waterborne video tape manufacturing process.

Entries from Small Businesses

Biodegradable Thermoplastic Material

Mater-Bi™ is a completely biodegradable and compostable resin, which has the physical and mechanical properties of conventional plastics. Mater-Bi™ is designed to be used in the manufacture of a wide-range of disposable products such as trash bags, shopping bags, food service ware, and packagings. Mater-Bi™ is a product technology which offers enormous advantages for dealing with the problems of solid waste disposal. Disposal of conventional plastic products, which constitute the largest share of disposable products, have a significant negative impact on the environment. Typically, disposable products are landfilled and rapidly diminish landfill capacity. Being compostable, disposable products made of Mater-Bi™ are fully recyclable. Biodegradable food serviceware, for example, presents a significant opportunity for reducing the volume of the solid waste stream. In 1994, nearly 39 billion pieces of disposable cutlery (knives, forks, and spoons) were used in the United States. More than 113 billion disposable cups and nearly 29 billion disposable plates were used. Other new and significant applications for biodegradables are being developed for medical products, textiles, etc. Such products can be transformed into much needed composts and soil amendments for agricultural and horticultural use. Mater-Bi™ resin used for films and sheets is made of starch and a polymer, polycaprolactone. Biodegradation time is between 20 and 45 days in composting conditions. Mater-Bi™ resin used for dimensionally stable injection molded items is made from completely natural products, including cotton seeds and cornstarch. Biodegradation time is between 75 and 120 days in normal composting conditions.

Burch Apparatus and Method for Selectively Treating Vegetation to Reduce Pesticide and Fertilizer Use, Eliminate the Release of Certain Toxins to the Environment, Reduce Pesticide Runoff, and Reduce the Potential of Worker Exposure to Toxic Substances.

The Burch Wet Blade® is a new discovery and a revolutionary apparatus and method for controlling vegetation. The Burch Wet Blade® allows for the selective application of various fluids, such as pesticides, growth regulators, biologicals, fertilizers, etc. (hereinafter “pesticides”), to vegetation by causing a minute amount of pesticide to be immediately absorbed into the vascular system of a plant at the moment the plant is cut by a blade. This method of treatment is made possible by bringing a pesticide into contact with a mowing blade designed not to cause a haphazard chemical spray, but rather a precise transfer of pesticide from only the bottom surface of the blade into the vascular system of a plant. The Burch Wet Blade® is a nonspray, enclosed system that provides precise pesticide application thereby reducing the quantity of pesticide needed and eliminating worker exposure and unwanted releases of pesticide.

BIOCORP, Inc.

Burch Company

CerOx Process Technology for Non-Thermal Destruction of Organic Hazardous Wastes

EOSystems, Inc. has commercialized the CerOx (Cerium Oxidation) process for destroying hazardous organic waste streams. The process converts toxic wastes into CO₂ and water. The unique process is an economical alternative to incineration and landfill. The process also can be operated on site, eliminating the need for transportation at reduced cost to the generator. Seven sizes of systems have been designed to meet the needs of various customers ranging from 300 pounds of destruction per day to over three tons per day. The CerOx process is an electrochemical process that allows for the destruction of organic hazardous wastes at near ambient conditions. At the heart of the system is a proprietary reactor cell. The cell is designed to be manufactured in volume from high-density plastics, using advanced injection techniques. The result is a system that is inexpensive to manufacture, service, and replace. In addition, the necessary data for EPA-required reports is recorded and stored. The flexible scalability of the CerOx Process allows it to be placed onsite for destruction of hazardous waste materials at their point of origin thereby eliminating the transportation of these wastes. The relatively mild reaction conditions of the CerOx Process eliminates any of the explosion potential associated with current high temperature and/or pressure thermal methods such as incineration and molten metal pyrolysis.

Conversion of Low-Cost Biomass Wastes to Levulinic Acid and Derivatives

Biofine, Incorporated of Waltham, Massachusetts, has patented a process to convert cellulosic biomass into levulinic acid (LA) using high-temperature, dilute-acid hydrolysis, and is manufacturing LA at a demonstration plant in New York State. The process is economical even without tipping fees for the feedstock. The product, a promising chemical building block, is made with low-cost and abundant waste feedstocks such as papermill sludge. Wet feedstocks can be used without drying, thereby saving energy. LA's niche markets provide excellent small-scale opportunities, and large-scale opportunities will open up as the price of this highly versatile chemical intermediate lowers. LA's worldwide market is about one million pounds per year at a price of \$4 to 6/lb. Large-scale commercial plants are feasible at 50 dry ton/day of feedstock. At this scale, LA could be produced at \$0.32/lb, and converted into commodity chemicals such as diphenolic acid that sell for \$2.00/lb or less. Eventually, Biofine hopes to build larger plants to convert 1,000 dry ton/day of feedstock into \$0.04 to 0.05/lb LA for conversion into economical fuel additives. The worldwide commercial market for LA and its derivatives could someday reach one trillion lbs/yr. Large-scale plant opportunities are being assessed for several locations in the United States and worldwide.

Development and Commercialization of High-Value Chemical Intermediates From Starch and Lactose

Synthon has developed a method for the utilization of high volume carbohydrate feedstock for the production of fine chemicals. One of the major tasks facing the chemical industry today is the identification and development of high volume, renewable, commercially viable raw materials that can assume a large part (if not all) of the central role that oil-based materials play in that industry. Starch is one of the most abundant materials obtainable in pure form from biomass. As a raw material for the practice of chemistry from environmentally benign and renewable resources, it holds much promise and seemingly as many challenges. Three of the most important aspects of starch structure and chemistry that are in step with requirements for a green chemistry feedstock are its solubility in water, the richness of functional groups, and its optical purity. The same is true of lactose, a material that is underutilized and available in thousands of metric tons per year from cheese making. These three promising features represent the three most difficult technical challenges in attempts to use starch and lactose as raw materials. They are practically insoluble in other environmentally friendly solvents such as alcohols and esters thus limiting the range of relevant chemistries. The high density of functional groups (polyhydroxylation) has made it (until now) near impossible to do anything useful with these on a grand scale in a selective fashion. The optical purity is embodied in functionalities that make conserving it a challenge.

Over the past 3 years, Synthon Corporation has been working to overcome these technical barriers by developing, demonstrating, and commercializing a new chemistry that will fundamentally revise the position of these two important and critical raw materials on the list of renewable resources for manufacture of chemical commodities. In the process, these materials are oxidized in dilute aqueous sodium hydroxide under controlled conditions with peroxide anion to form (S)-3,4-dihydroxybutyric acid and 2-hydroxyacetic acid (glycolic acid) with very high conversion. (S)-3,4-dihydroxybutyric acid can be converted to the lactone by acidification and concentration. Glycolic acid and the lactone can be utilized in the production of a variety of fine chemicals for particular use in the pharmaceutical, agrichemical, and polymer industries. Glycolic acid, for example, is used in the manufacture of specialty polyesters and in the preparation of paints. It is normally made by the environmentally unfriendly method of chlorinating acetic acid and hydrolyzing the chloro derivative with sodium hydroxide. The Synthon product brochure now lists over 30 such products available from gram to ton quantities. The process has allowed Synthon to take a substantial lead in the area of high valued chiral intermediates through the green chemistry approach where the pool of natural raw resources is tapped.

Heavy Metals Free, Non-Formaldehyde Fixing Agent for Direct and Fiber Reactive Dyes

Generally, a textile fixing agent is a cationic polymer, which forms a resin film covering the surface of the fiber and adheres to it. This action causes the many cationic groups in the molecule of the polymer to bond with the dye anions in the fabric to block the hydrophilic groups of the dye, thereby forming insoluble salts. Once completed, this process allows the dye to be retained in the fabric, preserving the intended color shade through the normal washing processes. The cationic charges in these types of polymers is often supplied by the positive charge of heavy metal ions such as zinc. It was NICCA's strong commitment to the environment and recognition of the value of such green chemistry that led to the development of NEOFIX® E-117. NEOFIX® E-117 is a heavy metals free, nonformaldehyde based fixing agent for direct and fiber reactive dyes. It significantly improves wash fastness of cellulosic fabrics and their blends. Unlike many fixing agents of this nature, NEOFIX® E-117 adds the extra benefit of helping its users comply with environmental and safety regulations by removing occupational and environmentally hazardous compounds.

High Energy Efficiency, Environmentally Friendly Refrigerants

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

Dr. Jonathan Nimitz, President of ETEC, and his co-inventor Lance Lankford, have discovered an improved family of refrigerants based on blends containing trifluoromethyl iodide (CF3I). The refrigerants are nonflammable, have zero ozone-depletion potential (ODP), low global warming potentials (GWPs) and total equivalent warming impacts (TEWIs), relatively low toxicity, and are more energy efficient than R-134a and R-22. Dr. Nimitz and Mr. Lankford have formed a joint venture with the Dole Food Company, called Ikon, Inc., to support testing and commercialization of the refrigerants. The first blend, Ikon A, has been demonstrated for over two years in Dole Food Company refrigerated transport containers, with excellent results. Ikon A has been approved for use under EPA's Significant New Alternatives Policy (SNAP) program for automotive use. In a project for NASA Kennedy Space Center (KSC), a formulation capable of higher capacity at lower operating temperatures, Ikon B, was developed. Demonstration in a 1.5 ton commercial water chiller unit gave approximately 17 percent higher energy efficiency for Ikon B versus R-134a. Testing in the vapor compression loop at Oak Ridge National Laboratory showed approximately 25 percent higher energy efficiency for Ikon B versus R-22. Demonstration of Ikon B will continue in KSC chiller units.

MRA-D, A New Wastewater Treatment Process

A breakthrough has been made in the technology of treating metal bearing wastes. Great Western Chemical Company's MRA-D (Metal Removal Additive) Series of chemistries allows for an improvement in the methods of printed circuit waste treatment. The most unique feature of the MRA-D process is that it achieves very low effluent metal levels while producing a compact, nearly dry metallic sludge high in metal content. Since the MRA-D process produces sludge of such unusually high metals, it may be suitable for sale as a product, rather than disposed of as a waste like other conventional industry methods. The MRA-D process allows for true recycling of concentrated sludge from the waste of printed circuit board facilities to finally be achieved. Printed circuit board facilities will manufacture printed circuit boards as well as copper concentrates.

N-Methylmorpholine-N-Oxide (NMMO): a Novel, Non-toxic, Reusable Solvent for Cellulose as Source Reduction in the Production of Textile Fibers

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

Natural Recycling of Plastics Through Chemical and Biological Degradation

Modern synthetic polymer manufacturing has reached a high level of efficient resource utilization. An energy efficient system of producing additives based on natural polymers and other chemicals provides an effective means of achieving an alternative to plastics recycling by allowing timed degradation followed by systemic incorporation back into natural organic cycles. The system is based on the continued use of conventional plastics processing machinery and results in a product that has the advantages of existing plastics materials, but with the added benefit of timed degradation in appropriate environments. After disintegration, the elements are available to be incorporated into humus and other soil constituents. The additives work by providing degradation catalysts based on natural organic unsaturated fatty acids and other unsaturates and benign metal cations with multiple oxidation states (such as iron). By combining these with conventional thermoplastic polymers, oxidative degradation of typical plastics can be achieved. In addition, a naturally biodegradable polymer, such as starch or

**Great Western
Chemical Company**

**TechMatch,
Incorporated**

Novon International

**International
Metalizing Corporation**

cellulose, is combined initiating biological attack and microbial colonization of the plastic. In natural environments this starts a slow oxidative biodegradation, similar to that for lignin, which allows incorporation of the carbon directly into humus and growing plants.

Non Toxic Antifouling

IMC has developed a process to apply pure copper to a variety of substrates including aluminum, wood, fiberglass, and steel as a near permanent non toxic antifouling that will not leach poisons into the environment and does not use solvents in the application process. The process is achieved through an electric arc used to melt the metal propelled by clean compressed air. The coating is permanently welded to the substrate and repels all types of marine nuisances, including the "zebra" mussels which are now a very expensive problem throughout the United States. The process is being used currently to protect power plants, cooling water intakes, ships, buoys, and other structures.

Solvent Kleene Inc.

*Non-Hazardous Degreaser that Degreases as Efficiently
as Trichloroethane and Outperforms Aqueous Products*

Degreasing techniques have relied heavily on chlorinated solvents. While these solvents are highly effective in removing grease and oils from metals, at the same time they raise serious environmental and health concerns. Ozone depleting products like 1,1,1 Trichloroethane (1,1,1 TCA) and Trichlorotrifluoroethane (CFC 113) have been phased out under the 1990 Clean Air Act Amendment, leaving users of these products little choice other than to replace them. A number of new non-hazardous cleaners have been introduced as alternatives, but few provide the effectiveness of a chlorinated solvent and most require users to accept a longer cleaning process and add costly new equipment. Solvent Kleene, Inc. developed D-Greeze 500-LO as a safe replacement degreaser/cleaner that does not force companies to compromise cleaning performance for safety. In independent testing, D-Greeze 500-LO was identified as a safe alternative that could also outperform Trichloroethane. While safe products such as aqueous-based cleaners are slow to perform, require heating, and involve an investment in costly new equipment and processes such as wastewater treatment, D-Greeze 500-LO can be easily integrated into an existing cleaning environment without a significant investment in new equipment or processes. Additionally, D-Greeze 500-LO is recyclable. A spent solution can be easily recovered and reused, minimizing both the hazardous waste stream generated and purchases of new cleaner.

Hauser, Inc.

Paclitaxel Process Improvements

Paclitaxel is a chemotherapeutic agent used to treat ovarian, breast, and other cancers. Hauser has developed a green technology centered around a self patented process improvement by which cephalomannine and related ozone oxidizable compounds are separated from paclitaxel and other non-oxidizable compounds in biomass extract (ozonolysis technology). Hauser develops, manufactures, and markets special products from natural sources. Hauser's proprietary extraction and purification processes enable the company to produce natural extracts at a higher quality, yield, and concentration than conventional procedures. Hauser employs proprietary technologies in combination with conventional techniques to process natural raw materials and to produce specialized natural products. Hauser utilizes this technology to produce bulk quantities of the anti-cancer compound paclitaxel from Yew trees.

The implementation of Hauser's ozonolysis technology in the isolation of paclitaxel

spurred many environmental and human health benefits. Several processing solvents (including methylene chloride), their subsequent air emissions (43,000 pounds annually), and significant wastes (254,000 pounds annually) have been eliminated. In addition, the use of natural resources was improved by incorporating renewable feedstocks (422,000 pounds recycled annually). A filter media that required disposal as a hazardous waste was also replaced with an indefinitely reusable alternative (eliminating 100,000 pounds of waste annually). Most importantly, these improvements have made the most effective anti-cancer drug in history more cost effective to produce and more affordable to those in need. The financial impact of all of the process changes has resulted in a 50 percent decrease in the cost of manufacturing paclitaxel.

The PIX Module Software: Combining Life Cycle Assessment with Activity Based Costing to Preserve the Global Environment

The project undertaken by KM Limited was successful in developing the first commercially available software package tool—the LCAPIX module—to simultaneously allow the user to perform both Activity Based Costing (ABC) and Life Cycle Assessment (LCA). By using an industrial engineering approach employing drivers and driver values, the model and relational database provides for a unique combination of two strategies which complement and enhance the implementation of an Environmental Management Strategy (EMS). This approach has strong appeal to those involved in any manufacturing sector—the point source for more than 50 percent of “undesirable effluents” affecting our global climate.

This software tool has been used to compare different products, processes, and service for not only their environmental burden potential (using different valuation techniques—i.e., selected weighted emphasis on global warming, ozone depletion, acid rain, deforestation, biodiversity), but also to understand how different techniques can be used to diminish these burdens while improving internal, external, unseen, or unknown “hidden” costs. The software tool, therefore, is multifunctional, in that it provides for inexpensive, rapid, simple, LCA strategic or environmental comparisons of any product, process, or service; allows for addition and access of general “valuation” databases to perform environmental burden analysis based on various methodologies; performs LCA and ABC simultaneously, not only for implementing and effective EMS, but also to ensure future efficiency and profitability by detailed cost analysis; converts LCA impact analysis information into a suitable form; allows each LCA stage (inventory, analysis-valuation, improvement) to be performed independently; builds a process hierarchy inventory of industrial systems, calculates process substance amounts, and determines the process substance Environmental Load Units; and reduces conventional time approaches (weeks or months) once a single process inventory is completed (several independent calculations or “cases” can be determined in the analysis stage within hours).

KM Limited Inc.

The Radiance Process: A Quantum Leap in Green Chemistry

The Radiance Process is a novel dry non-toxic enabling technology for surface cleaning. It employs the quantum mechanical effects of laser light in combination with an inert gas, ordinarily nitrogen, to clean surfaces. In industries such as semiconductors, photomasks, hard disks, flat panel displays, optics, automotive, and aerospace, current cleaning technology presents a real environmental management problem because of the lavish use of fresh water and toxic chemicals. In semiconductor manufacturing the primary cleaning technique is the RCA wet process. This is washing wafers in solutions of hydrochloric acid, hydrogen peroxide, and ammonium hydroxide, rinsing in deionized water, and drying with isopropyl alcohol. The wet cleaning process accounts for most of the 3 to 6 million gallons of water a typical semiconductor manufacturing facility uses each day.

The Radiance Process provides a cost-effective remedy to real environmental management problems by replacing chemicals and water with light and an inert gas. The Process is inexpensive and adaptable to many manufacturing products, such as computer chips, hard disks, flat panel displays, night vision goggles, and tire molds. Radiance is working with Motorola, the Defense Department's Microelectronics Research Laboratory, and EPA's National Risk Management Laboratory to demonstrate the Process, and expects to enter into up to six joint development projects in 1998. Semiconductor International called Radiance a "breakthrough." Advancing Microelectronics called it "radical." Futuretech called it "indispensable." In December 1995, the Radiance Process was selected by *IndustryWeek* magazine as a Technology of the Year, one of only five, calling it "revolutionary." In 1997, the National Pollution Prevention Roundtable awarded Radiance its Most Valuable Pollution Prevention Award, the only private sector organization to receive this distinction. Radiance provides the ultimate Green Chemistry by eliminating toxic chemicals in cleaning while achieving equal or superior results at a competitive or lower cost. The Radiance Process exemplifies a new innovative pollution prevention technology with broad based applications.

Rynex Biodegradable Dry Cleaning Solvent

In response to the recent problems associated with perchloroethylene, the primary solvent used in the dry cleaning industry in the United States, Rynex Holdings, Ltd. has developed an exciting new and environmentally safe and effective dry cleaning solvent that is economical to use and recycle. Rynex is the trade name for a novel dry-cleaning solvent and a method for effective dry-cleaning. The Rynex dry-cleaning solvent is non-flammable, non-combustible, biodegradable, non-carcinogenic, non-toxic, non-polluting to the water supply and the ozone layer, recyclable, effective detergency, compatible with existing dry-cleaning equipment, and economical to use. The Rynex dry-cleaning solvent is superior to perchloroethylene in its attributes and benefits. The Rynex dry-cleaning solvent has superior cleaning abilities and does not cause shrinkage to the 160 types of fabrics and is dye-fast or non-bleeding with respect to the 900 types of dyes. Most important is that it does not have the problems associated with perchloroethylene and can therefore be used without serious environmental, health, and occupational risks and problems associated with the use of perchloroethylene. The Rynex solvent has been identified as having the advantage of behaving like a single substance. This unique technological breakthrough brings forth new properties that allow for the effective removal of water and oil soluble stains without shrinkage of wool fibers that occurs with wet cleaning methods. Rynex does not suffer from serious environmental, health, and occupational hazards and problems associated with the use of perchloroethylene.

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

Arkenol, Inc., has developed an environmentally sound and cost competitive technology for a carbohydrate industry. While completely analogous to the petrochemical industry, Arkenol's technology is based on innocuous and renewable feedstocks. Arkenol's proprietary acid hydrolysis technology produces mixed sugars from locally available lignocellulosic materials such as agricultural residues, forest residues, and municipal solid wastes. The mixed sugar solution derived from these indigenous and low-value feedstocks is a cost effective raw material for the production of a myriad of chemicals from fermentation or other synthesis. Patented improvements make the acid hydrolysis commercially viable by making it possible to economically and competitively convert feedstocks such as rice straw, sugar cane bagasse, and municipal solid wastes into ethanol and other chemicals (ethanol, for example, is produced from the Arkenol process at a cost of \$0.60 per gallon compared to \$1.29 per gallon from the industry standard process).

An advanced project in Sacramento County, California will use Arkenol's technology to divert approximately 132,000 tons per year of rice straw from open-field burning to produce 12 million gallons per year of ethanol and co-products including precipitated silica, gypsum, and lignin. Eliminating the burning of some 60,000 acres of rice fields, will also result in significant improvements to the region's air quality due to annual net emissions reductions of 280 tons of NO_x, 173 tons of PM₁₀, 130 tons of VOCs, 138 tons of SO₂, and 4988 tons of CO. In addition, significant greenhouse gas benefits from the use of renewable feedstocks will be realized. Since the products are derived from biomass, the carbon dioxide produced in making the products is equal to the amount taken up from the atmosphere by the growth of the crop. As an example, the reduction of greenhouse gas emissions from the use of ethanol produced by the biorefinery to displace fossil fuels provides a significant contribution to reduction of "greenhouse" atmospheric pollution. Arkenol's Sacramento project reduces greenhouse gas emissions by approximately 141,000 tons per year when the ethanol is used in place of gasoline. Arkenol's ability to use a wide variety of feedstocks will enable placement of near zero discharge production facilities (or biorefineries) near the market for the products. Large scale conversion of waste materials into fuels and chemicals is a novel solution to waste management, pollution prevention, and economic development. Widespread implementation of Arkenol's technology will lead to environmentally responsible and sustainable economies relying on local resources.

Ultraviolet (UV) Curing of Small Wood Products: An Industrial Demonstration Project

The "Ultraviolet (UV) Curing of Small Wood Products: An Industrial Demonstration Project" relied on judicious cofunding from the New York State Energy Research and Development Authority to finance the procurement of a compact, fully integrated spray coating/UV curing unit. Two major challenges have been met thus far: (a) the ability to down scale a spray coating/UV curing process so that it could process the small wood products made by E&J Industries, such as brush blocks as small as 6.3cm by 17.8cm, and (b) to do so within the context of a small business environment, wherein personnel have limited, if any, technical background. The sprayable UV curable coating supplied by Strathmore Products has exhibited industry accepted performance while completely eliminating the use of solvent coating systems in E&J Industries' production operation. Production rates as high as 80 meters/minute have been attained in the spray coating/UV curing process with complete

**E&J Industries,
Incorporated**

recycling of overspray. Dialogue has begun with another small wood products manufacturer, a producer of the walnut backing used for plaques and trophies, in order to initiate technology transfer to similar small businesses. Additional interest has been shown by a major manufacturer to use this process to apply an insulating coating to the torroidal ferrite-ceramic cores used in motors and bushings that have dimensions as small as 1.3cm in height and 1.9cm in circumference.

AMSOIL Incorporated

Waste Oil Source Reduction Through Extended Oil Service Life

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

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

IonEdge Corporation

Zero-Waste Dry Plating of Cadmium

Electroplated cadmium is widely used in the defense and aerospace industries for the corrosion protection of steels. However, cadmium is a known toxic material and in addition, the electroplating process generates large quantities of toxic sludge and effluents. A typical medium-sized electroplating shop, for example, discharges well over 100,000 gallons of effluents daily and disposes 15 to 20 tons of hazardous sludge per week. As an alternative to this conventional process, IonEdge Corporation has developed and commercialized a novel "zero-waste" dry plating technology. The dry plating does not use liquid chemicals, and recycles solid materials in situ resulting in elimination of waste. In this dry plating technique, a

vapor-bath concept has been used in vacuum as opposed to the liquid bath of electroplating. This vapor-bath allows for multidirectional and economical plating of cadmium only on the intended parts resulting in a green technology. In addition, the amount of water used, filtered, and deionized on the line is reduced by at least an order of magnitude, and the energy consumption in the dry plating operation is only 35 percent of that in electroplating. Estimated waste treatment and disposal cost savings on the dry plating line are greater than \$1,000 per day, and the capital costs in setting up the line are substantially lower. At IonEdge Corporation's facility in Fort Collins, Colorado, a complete dry plating line has been set up for production. The plating line consists only of four processes and a quality inspection as opposed to more than a dozen baths and related operations in the electroplating. This plating line has been certified by a major aerospace parts supplier, and two dry plating machines are in service for plating cadmium on aerospace components.

The Zyvax "Watershield" Mold Release

Zyvax Watershield is a unique material for its intended purpose, as a mold release for aerospace adhesively bonded parts or fiberglass and other composite aircraft/spacecraft structures. It contains no volatile organic content, ozone depleting chemicals, or other solvents and materials considered hazardous by EPA or state or local regulatory agencies. Furthermore, as a wiping agent, the Watershield could be used as a precleaner for molds for both initial and subsequent applications. And its residues could be easily removed with water or water soluble cleaners, therefore, significantly reducing the need for solvents to remove Watershield residues prior to painting or sealing. It therefore avoids environmental sensitive materials not only in its formulation, but also by its proper use. Watershield was so effective a release agent that its use was enthusiastically adopted by a number of aerospace companies who found they could not only eliminate significant solvent use for environmental, health, and safety concerns. It is particularly satisfying that it eliminated hazardous materials in this area of aerospace manufacturing that EPA had exempted from its regulation because of the absence of available replacement technology and the critical nature of the application. Therefore it allowed the elimination of hazardous material without an absolute regulatory requirement.

Zyvax Incorporated

Entries from Industry and Government

IMC-Agrico Company

AGROTAIN® N-(n-butyl) Thiophosphoric Triamide

Urea is now the favored form of solid nitrogen-containing fertilizer and is rapidly displacing anhydrous ammonia in the nitrogen fertilizer market. The market share of world nitrogen consumption has risen from 5 percent in 1962 to 37 percent in 1986 for urea. There are many reasons for this increase. Urea is a source of nitrogen for crop fertilization that is easily handled and transported, higher in nitrogen content than other common solid nitrogen fertilizers, and can be readily bulk blended with other fertilizer components such as potassium chloride, diammonium phosphate, and other materials to prepare multi-nutrient fertilizers. While urea has many advantages over other nitrogen sources and has already captured a greatly increasing market share, a major drawback to the use of urea is its tendency to lose a substantial portion of the nitrogen values by ammonia volatilization. These losses can easily exceed 30 percent of the available nitrogen in urea under certain climatic and soil conditions.

AGROTAIN® is a formulation containing N-(n-butyl) thiophosphoric triamide (NBPT) the precursor to the active ingredient, N-(n-butyl) phosphoric triamide (the oxygen analog of NBPT). BNPO is far too unstable to be an article of commerce. NBPT serves as an effective precursor to BNPO, a urease enzyme inhibitor that inhibits the hydrolysis of urea by inhibiting the activity of the urease enzyme that catalyzes its hydrolysis. This activity is the result of an interaction between the urease enzyme and the urease inhibitor. There is no interaction with soil microbes that generate the urease enzyme. Moreover, the recommended NBPT treatment rate is only 0.4 lbs/acre, and NBPT is relatively unstable and presents no problems with long-term buildup in the soil. The use of NBPT with urea is also ideally suited for no-till agriculture applications. No-till agriculture is an environmentally friendly approach that involves little or no disturbance of the topsoil, resulting in less soil erosion and less energy intensive operation. Urea, however has not been well suited for use with surface-applied no-till applications until the advent of NBPT because of the possibility of substantial ammonia volatilization losses.

American Air Liquid

Air Liquid PFC Recycle Process

Perfluorocompounds (PFCs), including C_2F_6 , CF_4 , NF_3 , CHF_3 , SF_6 , and C_3F_8 are essential to many manufacturing processes in the semiconductor industry. However, these gases are also classified as greenhouse gases; they are much more potent than carbon dioxide, due to their extremely long life time and strong absorption in radiation. Environmental scientists believe these gases may last as long as 50,000 years in the atmosphere. Over 1.6 million pounds of PFCs were used in 1995 in the U.S. semiconductor industry, at an estimated cost of over 45 million dollars. This amount could be double by the year 2000. The U.S. government has responded to its international commitment (Rio Earth Summit '92) by promoting reduction in PFC emissions in various industries. The semiconductor industry has currently two choices for addressing the immediate emission reduction: (1) abating these gases at considerable financial and environmental cost and (2) recycling of PFCs developed by Air Liquid. Air Liquid has developed a system to capture these gases from process exhaust, to further concentrate, purify, and recycle. This process went through a rigorous qualification test under the umbrella of SEMATECH, demonstrating both capturing and concentrating the PFCs above 95 percent. In summary, this technology improves the environment by

reducing PFC emissions that are part of the global warming reduction objective. It does this by allowing the semiconductor manufacturers to maintain their current process chemistries and operate at a lower cost than any other emissions control alternatives.

Analysis of Liquid Hazardous Waste for Heavy Metals by Energy-Dispersive X-ray Fluorescence (EDXRF) Spectrometry

The laboratory-based elemental analysis of non-aqueous liquid hazardous waste has traditionally been performed using inductively-coupled argon plasma (ICP) and atomic absorption spectrometry (AAS). The preparation of samples and analyses using these techniques, however, generates a large amount of acidic, heavy metal-bearing hazardous lab waste. Laboratory-based energy-dispersive X-ray fluorescence spectrometry (EDXRF) is a mainstay analytical technique in many industries, but has received very limited attention in the environmental field. Within the last 5 years, ASTM Committee D34 on Waste Management has formally approved two Standard Test Methods for the elemental analysis of liquid waste by EDXRF spectrometry. In many cases, data quality objectives can be easily met using EDXRF spectrometry instead of ICP or AAS. The main environmental benefit of using EDXRF spectrometry is the significant decrease in the generation of laboratory waste in comparison to traditional methods. The primary reasons for this reduction in waste generation are that samples do not require dissolution in concentrated acids and calibration standards are not dissolved in acidic solutions and diluted to large volumes. Samples and standards are simply mixed with a nonhazardous substrate such as carbon or alumina prior to analysis or calibration. Also, the frequency of preparing and running standards is much less than traditional techniques because of the inherent stability of EDXRF systems. It is an environmentally-friendly technique because it virtually eliminates the generation of hazardous lab waste.

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.

**American Society for
Testing & Materials
(ASTM)**

**Los Alamos
National Laboratory**

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 byproduct 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.

C-FREE™ Pulp Ozone Bleaching Project

For decades, ozone has been acknowledged as the most promising alternative to chlorine in the bleaching of wood pulp in the forest products industry for the protection of our environment. Despite this recognition, no satisfactory technology was commercially available that met both cost and quality criteria of pulp producers until the early 1980's. Union Camp Corporation, a world leader in pulp and paper production, embarked on a research and development program to solve the problems identified with ozone delignification, including the erection and operation of a \$6 million, 25 TPD pilot plant. Based on the results of its R&D and pilot plant studies, Union Camp became convinced that an environmentally friendly bleaching process could be developed on a commercial scale. The result was the full scale implementation of the world's first high consistency ozone OZ(EO)D bleach line for kraft pine pulp in Union Camp's Franklin, Virginia, fine paper mill during the fall of 1992. The ozone pulp bleaching process is patented under the trade mark C-Free™. While the C-Free™ pulp bleaching technology has significantly lower bleaching costs at equivalent product quality compared to conventional chlorine based bleaching, the most important benefit is the significant reduction in effluent properties, volume and fresh water requirements. The effluent Biological oxygen demand (BOD), chemical oxygen demand (COD), color, absorbable organic halides (AOX) and chloroform have been reduced by 73 percent, 83 percent, 98 percent, 99 percent, and 99 percent respectively compared to conventional chlorine CEDED bleaching. In addition, dioxin and the 28 chlorophenols identified by the EPA are nondetectable.

The Chemical Kinetics Simulator Program

Computer simulators offer a powerful means of minimizing waste generated through physical experimentation during process development and optimization, a waste stream not usually addressed in green chemistry programs. The potential impact of simulations will not be realized, however, unless they are widely accessible in an organization. The Chemical Kinetics Simulator (CKS) Program, developed at the IBM Almaden Research Center to meet this need, is a general purpose, easy-to-use package that allows outcomes of reactions to be predicted for a broad variety of gas, solution, and solid phase systems in static and flowing reactors. Its basic computational method is well founded in theory and has been significantly enhanced through new algorithms that have been awarded U.S. patents. CKS has been in use in IBM for 3 years for process research and development. Since May 1996, the package has been available globally for a no-cost license through the World Wide Web and is used in many other industries for process research and development because of its exceptional ease-of-use and functionality. It also has been frequently licensed by environmental researchers in universities, corporate and government laboratories, and environmental regulatory agencies to develop models and evaluate hazards.

**IBM Research Division,
Almaden Research
Center**

Chloride-Free Processing of Aluminum Scrap

According to the U.S. Geological Survey, U.S. year to date aluminum scrap consumption totaled 724 million pounds. Other than can scrap which is processed separately, the bulk of the aluminum is consumed by the secondary aluminum industry. In spite of the fact that scrap is carefully selected so that a specific charge will meet product specifications, the molten charge typically contains up to 1.0 percent magnesium (Mg). Because the specifications for most diecast aluminum alloys call for a Mg level of less than 0.1 pct Mg, the charge must be demagged. The excess Mg is removed through the addition of chlorine (Cl₂) gas, or occasionally through the addition of AlF₃. Most of the demagging reaction schemes use Cl₂ and in practice require 6 lbs. of Cl₂ gas to remove 1 lb. of Mg as MgCl₂ (approximately 4500 lbs. Cl₂ per batch). Both techniques require both careful handling of the materials to insure operator safety and air pollution controls to insure the protection of the environment. If wet scrubbers are used in the air pollution control systems, then the fugitive chlorides which are captured in the water require additional treatment to meet clean water standards.

A more ideal approach is to remove and recover the Mg from the melt using a technology that is inherently safer and cleaner because it does not require additions of Cl₂ gas or AlF₃ and requires a minimum of processing steps. The Albany Research Center (ALRC) has conducted very successful research to investigate the synthesis and scavenging properties of ionically conducting ceramic oxides such as lithium titanate (Li₂Ti₃O₇) for demagging the aluminum scrap melts. The process known as engineered scavenger compound (ESC) technology offers an alternative to the conventional demagging technology that has distinct safety and/or environmental advantages over previously employed methods. The ESC technology neither generates fugitive chloride emissions nor hard to dispose of drosses or slags. The ESC reaction is easily reversible so that the recovered species is available for recovery and reprocessing as a metal product rather than as a salt in the older process.

**Albany Research
Center, U.S. Department
of Energy**

Designing a Safer, Less Toxic, Less Pollutant and Environmentally Friendly Solvent-ISOMET

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

BetzDearborn, Inc.

Designing an Environmentally Friendly Copper Corrosion Inhibitor for Cooling Water Systems

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

BetzDearborn has developed a new Halogen-Resistant Azole (HRA) which does not react with chlorine and protects copper when chlorine is present. The substitution of this new material for TTA provides substantial environmental benefits. These were demonstrated in a field test at a nuclear power plant which was utilizing chlorine for MB control. HRA was compared to TTA with respect to copper corrosion rates and discharge toxicities. Upon examination of the discharge, it was clear that copper-containing compounds, formed as a result of copper corrosion, were the most significant causes of toxicity to aquatic species. The use of HRA resulted in a fivefold decrease in the amount of copper released to the environment, compared to TTA. In addition, substantially lower concentrations of HRA are required for copper alloy protection compared to TTA. Furthermore a mass balance showed that only 9 percent of the TTA was recovered compared to 90 percent of the HRA. The TTA loss was due to the reaction with chlorine and the formation of a chlorinated azole. Since HRA does not react with oxidizing biocides, considerably less chlorine or bromine is required for prevention of MB activity, resulting in lower amounts of chlorine- or bromine-contain-

ing compounds being released in discharge waters. A reduction in chlorine usage of 10 to 20 percent was observed at the above nuclear power plant, and a reduction of 36 percent was observed at another industrial site. Thus, the use of HRA resulted in a net reduction in the amounts and types of azole and halogenated azole compounds that were released into the environment. Finally, direct measurement of LC50 acute toxicities for fathead minnows, done on site in the plant effluent at the nuclear facility, showed a reduction in toxicity when TTA was replaced by HRA.

Designing Safer Chemicals: Spitfire Ink

As the information age enters significant period, a new paradigm is being introduced to the printing industry. With the advancement of computer technology the demand for peripheral printing devices has accelerated. For the past ten years, this growth industry has been truly in its infancy. Various chemical systems have been employed with a multitude of electronic and/or mechanical printing devices, primarily addressing office applications. The computer based printing devices, which consume large volumes of chemicals (inks, resins, colorants, solvent, etc.) are rapidly progressing to the extent that traditional printing technologies are being challenged. One of these chemical systems is phase change ink. The many attributes of phase change ink make it a viable contender for a leading position in the printing industry to replace less environmentally friendly alternatives. Phase change ink, also known as hot melt or solid ink, addresses many of the limitations of the ink and printing processes associated with the well defined, centuries old printing methods, (e.g. offset, flexography, gravure, letterpress).

To demonstrate the enormity of the opportunity, chemical development of phase change inks has favorably addressed source reduction, pollution prevention, emission standards, ground water contamination, airborne particulates, waste abatement, worker and consumer exposure, hazardous chemical reduction and non-reusable consumables. The traditional printing techniques that often have significant worker and environmental liabilities can now be replaced with modern technology sensitive to, and having an understanding of, complex “green chemistry” issues. Tektronix is commercializing a four color set of process shade, phase change inks (Spitfire Ink) for use in color printers also manufactured by Tektronix. The chemical design of Spitfire Inks started with consumer and manufacturing operator safety, environmental concerns and the expected application performance. A retro-synthetic analysis accounting for these primary, “must haves”, translated to the synthesis of new resins that were water insoluble, required *no* volatile organic solvents (VOCs) to manufacture or use, allowed for safe manufacturing, complied in “spirit and intent” with environmental regulations and provided a flexible technology to a growing and expanding industry. These goals were satisfied by foresighted design aimed at safer chemicals ultimately embodied in Tektronix’ Spitfire Ink.

Development and Implementation of Low Vapor Pressure Cleaning Solvent Blends

Lockheed Martin Tactical Aircraft Systems (LMTAS) (formerly General Dynamics Fort Worth Division) has developed low vapor pressure organic solvents. LMTAS patented these solvent blends and the technology is being used by the aerospace industry, the military, and various industries. Additionally LMTAS substituted one of the new solvent blends (DS-104) for a CFC-113 based general purpose cleaning solvent used in the surface wiping of aircraft parts, components, and assemblies in all aspects of aircraft manufacturing. The substitution resulted in major reductions in solvent use and air emissions, the elimination of ozone deplet-

Tektronix, Inc.

**Lockheed Martin
Tactical Aircraft
Systems**

ing compounds from cleaning during aircraft assembly, cost reductions, and improved chemical handling and usage practices.

From 1986 to 1992, LMTAS produced mainly F-16 fighter aircraft at a rate of 220 to 350 aircraft per year. Throughout the 6 years, LMTAS used a general purpose wipe solvent containing 85 percent CFC-113 by weight throughout the manufacturing process. The use of the CFC-113 solvent blend resulted in the emission of approximately 255 tons per year of CFC-113 and 45 tons per year of volatile organic compounds (VOC) The implementation of DS-104 at LMTAS has reduced wipe solvent VOC emissions to 7 tons per year in 1993, 3 tons per year in 1994, and 2 tons per year in 1995, with no CFC emissions. Cost savings plus cost avoidance have been documented at \$0.95 million for 1993 and \$1.3 million for 1994. LMTAS management recently estimated the cost savings from the wipe solvent implementation to be \$8.2 million for the five year period of 1993 to 1997.

After the LMTAS implementation, other companies and military operations throughout the United States have implemented this technology. Additionally, this technology has been implemented in several countries, such as Australia, Canada, Greece, Israel, Mexico, the Netherlands, South Korea, Taiwan, and Turkey. Several other European countries will implement this technology in 1997. These cleaners were developed primarily for aerospace; however, they have found cleaning applications in many industries such as: automotive, bubble gum removal in movie theaters and universities, various ink removal industries, postal operations, electronics, building maintenance, steel industry, and nondestructive testing methods. EPA has recognized this technology in the Aerospace National Emission Standard Hazardous Air Pollutants and the proposed Aerospace Control Technology Guideline

Development of a New 'Core' Line of Cleaners

Cleaning is an important practice and necessity of modern civilization. An effective cleaner must be able to penetrate through soil to disrupt and destroy the complicated types of bonding that cause it to adhere to the surface being cleaned. Most modern cleaners are comprised of surface active agents derived from petrochemical resources. While these components are effective, they tend to be environmentally harsh and depend upon a natural resource whose supply is finite and limited. The market for these products is estimated to be in the range of \$5 billion, which equates to approximately 5 billion pounds of product annually. The impact of developing chemistries that are less polluting during the extraction, manufacturing, use, and disposal of these products is, therefore, quite significant, as are the human health and safety impacts.

During the past few years a new family of cleaners was developed that are less toxic and have reduced impacts to both people and the environment when compared to traditional products used for the same purpose. The chemistries incorporated into these products resulted in products that are readily biodegradable, comprised of zero to very low volatile organic components and ozone depleting substances, effective in their intended purpose (i.e., cleaning), and economically competitive. In addition, these products have low human and aquatic toxicity and low corrosivity. Main molecular components of these products are derived from renewable, bio-based resources that are lower polluting and typically less toxic than their petrochemical alternatives. This new 'core' line of cleaners is an innovative approach to the formulation of an important series of products and is the safest yet developed in its field.

DuPont Petretec Polyester Regeneration Technology—Making Polyester Evergreen

Thirty-five billion pounds of polyethylene terephthalate polyester (PET) are produced globally each year. PET goes into thousands of end uses and it is also the “greenest” of the polymers. Due to this polymer's inherent thermal stability, PET-type thermoplastics lend themselves to direct recycling and serve as a raw material for the production of numerous products. The success of PET bottle recycling, for example, annually diverts more than 600 million pounds of PET bottles per year from landfills. This recycling technology, however, requires high-purity waste and the recycled material generally may only be used for carpeting or pillow fibers. There are a large number of uses for virgin PET where the material has been dyed, coated, or mixed with a co-polymer and therefore is not suitable for direct recycling. This material is landfilled.

The patented DuPont PetretecSM polyester regeneration technology provides an environmental and economical alternative to landfills and offers many advantages over recycling. PetretecSM, DuPont's proprietary form of methanolysis, makes polyester evergreen. The process provides a safer and more economical way to reuse materials, especially those with much higher contaminant levels than other recycling methods. It takes PET fibers, films, and resins currently going to landfills, unzips the PET molecule, and breaks it down into its raw materials, dimethyl terephthalate (DMT) and ethylene glycol (EG). The PetretecSM process allows these raw materials to retain their original properties so they can be reused over and over again in any first-quality application. The process accepts polyester with a broader variety of contaminants and at higher levels than any other process. PetretecSM reduces dependence on oil-derived feedstocks and diverts polyester from the solid-waste stream into useful new products.

DuPont invested \$12 million to convert part of its Cape Fear facility, near Wilmington, North Carolina, to a methanolysis plant. The new plant can handle more than 100 million pounds of scrap PET and capacity is easily expandable. By actually unzipping the molecules, we can begin the cycle of using these materials in an endless series of new applications.

Elimination of Ozone-Depleting Chemicals (ODCs) Through the Use of a Water Soluble Adhesive “Green Wax”

The process operations involved in manufacturing polished silicon wafers include silicon crystal growth and wafering. Crystal growth refers to process steps to convert polycrystalline silicon into single crystal ingots (also called silicon rods). The crystal growth process is carefully controlled to produce silicon rods meeting different electrochemical properties specified by customers. Wafering refers to process steps to slice silicon rods into wafers and to prepare the wafer surface for microchip manufacturing by customers. The final polished silicon wafer must meet exacting standards for flatness, chemical purity, and surface cleanliness. An epitaxial layer of silicon is added to the surface of some polished wafers to produce premium product required for microprocessors and logic devices.

In 1992, MEMC Electronic Materials, Inc., a silicon wafer manufacturer, began investigating ways to eliminate all Class I Ozone Depleting Chemicals (ODCs) from manufacturing operations. Over 80 percent of the target ODCs used by MEMC were in direct silicon processing steps like slice mounting, polishing, slice demounting, and slice dewaxing. The mounting of silicon slices prior to polishing was performed with a material known as “wax” which was capable of controlled viscosity and thickness application. The old

MEMC Electronic Materials, Inc.

wax formulation contained trichloroethylene (TCE), while the old block cleaning method utilized 1,1,1-trichloroethane (TCA), and the old slice dewaxing process utilized Freon 113. The wax formulation was changed to a water soluble one (“green wax”), that utilized a commercially available water soluble resin (a modified maleic resin in solution with ammonium hydroxide and water). Slice mounting (block cleaning) and dewaxing were modified to use a dilute basic solution (such as ammonium hydroxide) instead of TCA and Freon 113. The flatness, particle count, and metal concentration of slices produced with green wax are equal to or better than the old wax. It is estimated that, since 1993, MEMC has avoided the production of almost 5 million pounds of ODC emissions worldwide through the use of green wax.

Pharmacia & Upjohn

Environmental Improvements from Redesigning the Commercial Manufacture of Progesterone

For more than 40 years, the steroid bisnoraldhyde (BNA) has been produced at Pharmacia & Upjohn because it is a key intermediate for the commercial synthesis of progesterone and corticosteroid classes of pharmaceuticals. Recently, a redesigned route to BNA was implemented. This new synthetic route to progesterone is founded on both the development of a new fermentation process which improves the utilization of a renewable, naturally derived feedstock from 15 to 100 percent, and the development of a chemical oxidation process that offers high selectivity and reduced waste streams. The fermentation employs a genetically modified bacterium to convert soya sterols directly to a new synthetic intermediate, bisnoralcohol. The new chemical process oxidizes bisnoralcohol (BA) to bisnoraldhyde, a key intermediate for the registered, commercial manufacture of progesterone.

Contrary to standard chemical methods for oxidizing alcohols to aldehydes, the new oxidation process does not use hazardous or noxious materials and does not generate toxic waste streams. The reaction conditions developed to oxidize BA to BNA are environmentally superior to the standard methods used to convert primary alcohols to aldehydes. During the development of the process, considerable focus was placed on waste minimization, not just for that step but also for the production of the substrate and the catalyst. The process minimizes solvent use and maximizes solvent recovery as well. The new bisnoralcohol route eliminated a process with a running, recycled inventory of 60,000 gallons of ethylene dichloride (EDC), a known carcinogen, which needed up to 5,000 gallons of EDC input annually. The new route produces the same amount of product as the previous route with 89 percent less nonrecoverable organic solvent waste and 79 percent less aqueous waste. The new route also has the chemical selectivity required for high quality bulk pharmaceutical manufacture and can be applied to the oxidation of other primary alcohols.

The development and implementation of the new chemical oxidation process allowed for the utilization of the new bioconversion, thereby creating a new synthetic route from soya sterols to therapeutic steroids. The new bisnoralcohol route exemplifies the synergism possible between biochemical and chemical process development. By implementing this redesigned, commercial synthesis of BNA, Pharmacia & Upjohn has substantially reduced the chemical waste associated with manufacturing progesterone, while simultaneously improving process economics through a dramatic increase in feedstock utilization.

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

Supercritical fluid extraction (SFE, or fractionation, SFF), or more recently synthesis under supercritical conditions, have attracted considerable attention as possible alternatives to existing processes which employ organic solvents or catalysts requiring post reaction disposal. Those methods utilizing carbon dioxide (CO₂) have received the preponderance of attention due to CO₂'s compatibility with the environment (i.e., toxicity, flammability). To date, however, no one has demonstrated how CO₂ can be utilized in a series of processes embodying synthesis, extraction and/or fractionation, thereby creating an entire process or plant that practices "green" chemistry from start to finish.

Studies conducted at the National Center for Agricultural Utilization Research have produced two alternative synthesis for producing monoglyceride-containing mixtures via glycerolysis, that employ CO₂, either as a catalyst or extraction/reaction medium coupled with enzymatic-based catalysis. The first synthesis uses carbon dioxide as a catalyst or transport medium coupled with a lipase biocatalyst, to produce mixtures of varying monoglyceride content. Further, the same carbon dioxide medium can then be used in a sequential fashion to affect an enrichment of the synthesized glyceride mixtures to yield products having a monoglyceride content in excess of 90 weight percent that have high value as emulsifiers, lubrication aids, and food additives. Using carbon dioxide under pressure, we have shown that metal-based catalysts can be eliminated from the traditional batch, stirred reactor glycerolysis to yield a product that is lighter in color, less odoriferous, and a monoglyceride content between 35 to 45 weight percent, depending on botanical oil source.

Alternatively, the National Center for Agricultural Utilization Research has demonstrated and patented a synthesis which uses CO₂ in the supercritical state to dissolve vegetable-based oils prior to transport over a supported enzyme catalyst which also affects glycerolysis, but depending on variables such as CO₂ flow rate and the water content content of the starting reactants, can yield designer glyceride mixtures having a variable monoglyceride content between 50 to 90 weight percent. Finally, by coupling one of the two CO₂-based synthesis processes with a thermal gradient fractionation column, it is possible to utilize a totally environmentally benign process for the production and enrichment of high value oleochemicals from natural sources.

Environmentally-Responsible Liquid Polymers

High molecular weight polymers based on acrylamide, produced either as a dry powder or as water-in-oil emulsions, are commonly used as process aids and as water treatment agents in various industries. In fact, about 200 million pounds of high molecular weight polymers based on acrylamide, with an approximate market value of one billion dollars, are sold annually worldwide for such treatment. The powder form presents significant exposure hazards and requires expending substantial energy during its manufacture as well as the end-use. The emulsion form overcomes some of the limitations of the dry form. To produce these emulsions, however, large quantities of a "carrier" consisting of hydrocarbon solvents and surfactants (30 to 40 weight percent of the finished product) are required. This "carrier" plays no active role other than to permit the polymers to be manufactured in liquid form and discharging at the rate of about 90 million pounds per year, into the environment as a necessary evil. To overcome these environmental and health hazards, Nalco introduced a new liquid form of these polymers, manufactured through a unique dispersion polymerization process

**Lawrence Livermore
National Laboratory**

**U.S. Department of
Defense, Office of
Munitions**

**U.S. Department of
Energy, Weapons
Supported Research**

**U.S. Army Edgewood
Research, Development,
and Engineering Center**

using an aqueous salt solution as a reaction medium instead of oil and surfactants. These dispersions are completely water soluble and are very easily dissolved in water. They contain almost zero volatile organic contents and eliminate the environmental and health hazards associated with the respective emulsion and dry polymer forms.

Environmentally-Driven Preparation of Insensitive Energetic Materials

The Vicarious Nucleophilic Substitution (VNS) of hydrogen is a well-established procedure for the introduction of carbon nucleophiles onto electrophilic aromatic rings. An innovative approach was developed at Lawrence Livermore National Laboratory to synthesize 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and other insensitive energetic materials through the use of 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 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 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) as starting materials in lieu of the chlorinated species, TCB. Several million pounds of Explosive D are targeted for disposal in the United States; 30,000 metric tons of UDMH also await disposal in a safe and environmentally responsible manner. The use of these surplus energetic materials as feedstocks in the new VNS method of synthesizing TATB allows an improved method of demilitarization of conventional munitions that also should offer significant savings in production, thereby making this IHE more accessible for civilian applications.

Filter Leak Test Using Ozone-Benign Substances

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

With the advent of the Montreal Protocol eliminating production of ozone-depleting substances, the search for substitute materials for common items including air-conditioning and fire extinguisher fluids has been intensive. Work at the U.S. Army Edgewood Research, Development, and Engineering Center was directed at finding filter leak test materials that were not destructive to earth's stratospheric ozone layer and capable of rapidly identifying fil-

ter assembly problems. Materials investigated included several hydrogenated fluorocarbons (HFCs) of differing volatility. HFCs do not contain chlorine or bromine which have been implicated as potent stratospheric ozone destroyers. Two HFCs were identified as substitute filter leak test vapors, 1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC-4310mee) for in-service filters and 1,1,1,2-tetrafluoroethane (HFC-134a) for new filters. These materials have been adopted by the U.S. Army to test the integrity of filters used to provide respiratory protection against chemical warfare agents.

Greenhouse Gases: From Waste to Product

About 5 billion pounds of adipic acid are manufactured worldwide each year. In the United States alone, approximately 3 billion pounds of adipic acid are produced every year. Adipic acid is used in the manufacture of a large number of consumer products, including nylon for carpets, apparel, industrial fabrics, and also for urethanes, plasticizers, and food additives. Essentially all adipic acid is manufactured today by a three-step process starting with benzene: the benzene is hydrogenated to cyclohexane, the cyclohexane is oxidized with air to a mixture of cyclohexanol and cyclohexanone (KA oil) and the KA oil is oxidized to adipic acid using nitric acid as the oxidant. Waste generation is a serious environmental issue with the traditional processes used to make adipic acid: the oxidation processes produce large amounts of nitrous oxide and organic wastes which must be disposed of or destroyed. For example, with the current technology, the production of 5 billion pounds of adipic acid also results in the production of 2 billion pounds of nitrous oxide. Nitrous oxide is a known greenhouse gas with a global warming potential 300 times greater than carbon dioxide and is also a suspected ozone depleter. It has been estimated that release of nitrous oxide from adipic acid manufacture accounts for 10 percent of the annual releases of manmade nitrous oxide into the atmosphere worldwide.

As part of Solutia's program to search worldwide for new technologies to reduce or eliminate waste from its operations, the company initiated a partnership with Borekov Institute of Catalysis in Novosibirsk, Siberia, to develop an alternative method for manufacturing adipic acid. This new process recycles the nitrous oxide waste gas and uses it as a raw material in the production of phenol. This eliminates either the direct release of this greenhouse gas into the atmosphere or the use of expensive, energy intensive CO₂ greenhouse gas producing abatement processes. At the same time, the yield of phenol from Solutia's new technology is very high. Furthermore, since the cost of this alternative method of producing adipic acid is lower than the commercial method traditionally used by the chemical industry, the process is both environmentally and economically sustainable.

A pilot plant demonstrating the process on a continuous basis was started at Solutia's Pensacola Technology Center in May 1996. The unit has operated successfully since startup and provided the data currently being used in design of the full-scale commercial plant. The new plant will utilize all of Solutia's nitrous oxide (250 million pounds per year) to produce more than 300 million pounds per year of phenol. This revolutionary process represents the first major breakthrough in the production of phenol in more than 50 years. The new efficient process saves energy, eliminates the emission of massive amounts of greenhouse gases, while greatly reducing the production of organic wastes.

Solutia Inc.

Heavy Metal Free Alternative to Standard Anti-Corrosive Pigments

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

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

Hydrogen Sulfide Elimination From the Substances Not Precipitated by H₂S Test

Mallinckrodt Baker has developed a method that eliminates hydrogen sulfide from the substances not precipitated by H₂S test. The existing method uses hazardous hydrogen sulfide, takes about 5 hours to perform, and is precise only for combined alkali results. The new method is safer (does not use hazardous reagents), takes only 30 minutes to perform, and is accurate for individual element determinations

Imation™ No Process Plates

Although the principles of lithography were first applied to printing in 1796, aluminum plated pre-coated with photoactive polymers did not enter volume production until the 1950s. Availability of these presensitized plates fueled rapid growth in the lithographic printing industry due to superior print performance and economy. When a conventional presensitized plate is exposed to ultraviolet radiation through a contact masking film, formation of ink receptive image areas is initiated. These plates then require wet development to activate the printing surface, most often using a mechanical processor that also rinses the plates. Many developers contain hazardous solvents. Developer solutions saturate with dissolved coating compounds, including toxins and heavy metals. Total U.S. printing plate consumption in the year 2000 is expected to reach 68 million square yards. Wet processing

of this total volume will consume over one million gallons of aqueous developer, based upon typical depletion rates. Depleted solutions containing coating solids require disposal at hazardous waste sites in many regions of the United States. In addition, more than 1.2 billion gallons of rinse water would become part of the waste stream.

Recognizing the environmental costs of the total waste stream, Imation launched an intensive Research and Development effort to commercialize plates requiring no wet chemical processing of any kind. Today, their no process technology provides a superior printing plate, without wet processing, under the trademark name "Imation No Process Plates." Demand for the technology is growing rapidly across the printing industry. Imation No Process Plates employ photoactive polymers that form printing surfaces without wet chemical processing. When the plate is exposed to ultraviolet radiation through a masking film, formation of ink receptive areas is initiated, but activation takes place on press under action of the ink/water emulsion during the normal plate rollup process. This technology is applicable across the printing industry, from general commercial lithographic printing, to forms, packaging, and newsprint operations. Environmental benefits available to the industry are truly significant and valuable because pollution is prevented through source reduction. When Imation™ No Process Plates are used along with Imation's DryView™ imagesetting films, even greater waste reductions are possible. If 68 million square yards of DryView™ film were used to image plates, an additional 2.4 million gallons of film developer, 4.1 million gallons of fixer, and 675 million gallons of rinse waste could be eliminated from the waste stream.

Implementation and Verification of Aqueous Alkaline Cleaners

Lockheed Martin Tactical Aircraft Systems (LMTAS) was the first aerospace company to implement innovative aqueous cleaning technology for cleaning tubing and honeycomb core. Tubing is used in the aerospace industry for transferring pressurized oxygen within an aerospace vehicle. Honeycomb core is used in the aerospace industry for producing bonded structural parts. Both applications require that the parts meet stringent cleanliness requirements. These requirements were previously met by using cold cleaning or vapor degreasing with chlorinated solvents. These solvents included 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE). These chlorinated solvents are toxic, and TCA is an ozone depleting compound. The use of chlorinated solvents posed a threat to the environment because the solvents were commonly released into the air during cleaning operations and because the likelihood of a spill during their use was significant.

These solvents were successfully replaced with aqueous cleaning technology at LMTAS. As of November 1993, 100 percent of tubing manufactured at LMTAS (including oxygen tubing) is being cleaned in an aqueous cleaning system. As of May 1994, 100 percent of all honeycomb core used at LMTAS is also being cleaned in an aqueous cleaning system. Implementation of aqueous cleaning technology at LMTAS has eliminated approximately 360 tons of air emissions per year and has resulted in a cost savings of \$490,000 per year. In addition to replacing chlorinated solvents with the innovative aqueous cleaning technology, LMTAS has also explored the use of environmentally safe methods for quantifying surface contaminants on parts cleaned by various cleaning technologies. Traditionally, extraction with CFC-113 followed by gravimetric or FTIR analysis has been used for quantifying surface contaminants. The use of CFC-113 is undesirable due to its ozone depleting potential. LMTAS has demonstrated the usefulness of carbon dioxide coulometry for determining the amount of residue remaining on a surface after cleaning and has used this technique for comparing the cleaning effectiveness of various cleaning technologies.

**Lockheed Martin
Tactical Aircraft
Systems**

The INFINITY Process

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

Liquid Oxidation Reactor (LOR)

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

Magnetic Separation for Treatment of Radioactive Liquid Waste

High gradient Magnetic Separation (HGMS) is the application of intense magnetic fields to selectively separate solids from other solids, liquids, or gases. The HGMS process has demonstrated promise for the treatment of waste streams containing actinide at Los Alamos National Laboratory (LANL). The caustic liquid waste generated by operations in the LANL Plutonium Processing Facility (TA-55) can produce up to 30,000 L of liquid effluent annually, with an average alpha activity of 10^{10} dpm/L. Treatment and disposal of the liquid effluents at the LANL Waste Water Treatment Facility (TA-50) can ultimately produce up to 15 tons of TRU solid waste per year. In order to avoid the TA-50 treatment, the goal at TA-55 is to reduce the radioactivity in the waste streams to less than 5.8×10^5 dpm/L.

Physical separation processes, such as HGMS, are particularly attractive because no additional waste is generated during processing. HGMS is capable of concentrating the actinides in process waste streams to form a low volume, actinide-rich stream for recycling, and a high volume, actinide-lean stream for direct discard. The proposed technology has been demonstrated successfully on a laboratory scale at TA-55 where results from screening experiments on radioactive caustic liquid waste water indicate that over 99.9 percent extraction of Pu activity can be achieved using HGMS (represents decontamination levels of three orders of magnitude to about 4.4×10^5 dpm/L). The application of this technology to radioactive liquid waste effluents would eliminate radioactivity from the source, in addition to reducing the volume of transuranic solid waste that is produced with the current treatment technologies. The hazard of pumping radioactive liquid waste to offsite facilities would also be eliminated because treatment of TA-55 effluent would occur prior to transportation.

Molyphos: A Chromate-Free Alternative for Corrosion Protection of Metal Parts

For over forty years, metal fabricators have used a yellow chromate coating for the corrosion protection of metal parts and for electromagnetic shielding protection. While this coating has been a very successful corrosion preventative, it has a serious drawback—it uses hexavalent chromium, a known human carcinogen. Metal finishing for corrosion resistance is a significant source of chromium waste generation and emissions to the environment and a danger to worker and public health. The Toxic Release Inventory reported over 2 million pounds (1000 tons) of chromium and chromium compounds generated or released from metal finishing facilities with an average of approximately 15,000 pounds (7.5 tons) reported per facility in 1993. Additionally, the electromagnetic interference (EMI) protection provided by yellow chromate is proving inadequate for today's higher speed electronic applications.

Nortel (Northern Telecom) developed an alternative to the use of hexavalent chromium for the corrosion protection of metal parts. The new technology—a molybdenum-phosphate (Molyphos) based conversion coating—replaces the chromate conversion technology (yellow chromate). In 1997, Nortel successfully applied the Molyphos technology in tests and commercial production of several of its telecommunications products. Molyphos technology achieves multiple environmental benefits. First, and most importantly, hexavalent chromium is eliminated as a raw material in the metal coating process, resulting in a safer work environment and the reduction in hazardous emissions and wastes. Second, Molyphos

Nortel Technology

alleviates the internal stresses of zinc plating, which allow Nortel to replace cyanide-based zinc electroplating with an alkaline process. Third, the superior electrical conductivity of Molyphos coatings, compared to chromate conversion coatings, allows Nortel to eliminate the beryllium copper gaskets and the tin-lead precoat required to achieve continuous conductivity in some applications further reducing toxicity. For one product, the Spectrum/I Link, Nortel will reduce the lead content of the system by 770 pounds annually. In addition, removal of this processing step and associated costs is expected to result in a 70 percent cost savings. Fourth, for end-use applications that require painting, Molyphos allows the use of powder paints, rather than liquid volatile organic content-based paints required by chromate-coated products.

Dupont Company

NAFION Membrane Technology

Membrane technology is now recognized as state-of-the-art for chloralkali chemical production, which constitutes the second largest commodity chemical volume produced globally. NAFION membranes are acknowledged as the world leader in bringing about a technology 'revolution,' which has made the membrane electrolyzer system the technology of choice over the incumbent mercury amalgam cells and asbestos diaphragm electrolyzers. While significantly reducing the environmental impact of the old technologies, membrane systems confer the advantages of a new electrolysis process with lower investment and lower operating costs. Before NAFION and membrane technology, the production of chloralkali chemicals was dependent on either mercury amalgam cells or asbestos diaphragm systems. While these systems might 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 Chemical Company

Nalco Fuel Tech NO_xOUT Process

Nalco Fuel Tech develops and markets air pollution control technologies worldwide. Their flagship technology, NO_xOUT[®], reduces harmful nitric oxide emissions of stationary combustion sources to yield nitrogen gas and water, leaving no disposal solids. Nitrogen Oxide (NO_x), the pollutant targeted in NO_xOUT[®] technologies, is a major "primary" pollutant, and reducing it directly reduces acid rain, particulate matter less than 2.5 microns in diameter, "greenhouse" gases and mitigates nitrogen eutrophication sensitive watersheds. NO_x also is a precursor in the formation of ground level ozone which, along with NO_x, is one of EPA's six criteria pollutants. More than 100 million of our nation's citizens and many more global inhabitants live in areas that are classified "nonattainment for ozone," i.e., ambient air ozone levels exceed 120 parts-per-billion (ppb). High ozone levels are linked to many forms of respiratory problems, leading EPA to promulgate the new National Ambient Air Quality Standard of 0.080 ppm for an 8 hour period to adequately protect human health and welfare. The NO_xOUT[®] process meets today's environmental challenges by using less toxic chemistry, reducing or eliminating toxic releases to the environment, converting wastes to more environmentally acceptable discharges, and reducing energy consumption. The NO_xOUT[®] process provides an economical solution for complying with the stringent regulatory

requirements for NO_x reduction from fuel combustion sources. NO_xOUT[®] can reduce NO_x emissions by 75 percent compared to the 20-50 percent reduction from existing treatment.

The NO_xOUT[®] process is being used commercially. It can be used on new combustion units for small industrial units to large utility installations, or it can be retrofitted to existing units. The environmental benefits are significant NO_x reduction, elimination of byproduct disposal, toxic use elimination of SARA (Superfund Amendment and Reauthorization Act) Title III chemicals, and increased energy efficiency.

Nalco LAZON Technology

The U.S. paper industry suffers more than \$1,000,000,000 per year in lost production alone due to biological contamination problems. Nalco LAZON Technology gives paper-makers a new integrated approach that allows them to improve control of microorganisms with significantly lower environmental impact. This technology is a unique bundling of innovations that includes a synergistic biocide combination, two new monitoring technologies and specialized feed equipment. The primary component of LAZON Technology is the chemistry, a combination of the non-halogen oxidant peracetic acid and a standard organic biocontrol agent, which together provide antimicrobial activity that is far greater than expected from the individual components. Improved microbiological control is demonstrated with the Nalco BIOWATCH[™] Optical Fouling Monitor. Minimal or no environmental impact is assured by Nalco's BIOWATCH TRA-CIDE[®] system, which rapidly measures biocide toxicity and microbial ATP on-site. Finally, a specially designed chemical feed system and Nalco's PORTA-FEED[®] returnable container complete the program. This interlocking network of novel technology decreases biocide use, measures product performance and residual toxicity, and minimizes the chances of accidental biocide release during transportation or product feed. This Nalco technology is a complete program that improves safety, increases energy conservation, reduces operating costs, and minimizes point source release.

Nalco NALMET[®] Heavy Metal Removal Technology

Stricter NPDES discharge limits for effluent metals impact both metal and non-metal industries. The parts-per-billion (ppb) limits for heavy metals removal cannot be met by traditional metal precipitation processes. Membrane processes such as ion exchange, ultrafiltration and reverse osmosis are historically recommended for metal removal. They require significant capital investment and still require pre-treatment of these waste streams. A chemical removal process that can reduce metals to acceptable NPDES levels represents an important new technology for industrial waste treatment. Nalco has developed NALMET[®], a patented program for metal removal. This low toxicity technology includes a liquid polymer containing a metal chelating functional group that simultaneously precipitates metals and clarifies the waste stream, all in one product. It also includes an automated chemical feed system with patented sensor technology to guarantee standard treatment. The program allows customers to have their NALMET[®]-generated sludge reclaimed by our partner company. The benefits of the NALMET[®] program are that sludge volumes are reduced 25 to 90 percent, product overfeed is reduced, environmental releases of treatment chemical are reduced, a less toxic treatment chemical is used, customers consistently meet ppb metals discharge limits. Through Nalco's integrated, innovative approach, our customers achieve pollution prevention. Cradle-to-grave environmental management is achieved with environmental toxicity reduction.

**Nalco Chemical
Company**

**Nalco Chemical
Company**

Nalco PORTA-FEED®

During the 1980s, disposal of chemical residue and its containers was a potential human health and environmental risk for chemical users and the public. In 1985, Nalco developed the PORTA-FEED® Advanced Chemical Handling System for chemical applications worldwide. It is the largest private fleet of returnable containers in the world at a capital cost of \$240 million. These 105,000 units are owned, monitored, maintained, and cleaned by Nalco as a cradle-to-grave risk management process. The program consists of the units, a computerized tracking system, a zero defect delivery system, and a systematic maintenance and cleaning program. This pollution prevention program has prevented the disposal of over 3 million drums and 30 million pounds of chemical waste. In 1985, 33 percent of our annual sales \$659 million were shipped in 500,000 nonreturnable drums. Fifteen percent of 1996 annual sales of \$1.3 billion were shipped in nonreturnable drums. By the year 2000, we expect to have eliminated the disposal concerns from 10 million drums and 100 million pounds of chemical waste worldwide. The system benefits are reduction of human and environmental risk from transportation to disposal, reduced chemical inventory, and renewable resource implementation.

Nalco TRASAR Technology

From tracing to tagging to product performance monitoring, Nalco impacts the way the world manages water. Using monitoring approaches, customers are provided with a window into their water systems, helping them detect and control chemical feed, reduce pollution at its source, conserve energy, and prevent unintended environmental releases. The first approach adds low levels of inert fluorescent "trace" to water treatment products. The tracer allows controlled chemical application instantaneously and automatically. Chemical treatment reductions of 20 to 30 percent have resulted from this process. The second approach involves direct, automatic detection of a fluorescence tagged treatment chemical. The chemical's presence can be detected in systems where low level detection was not possible, correlating variations in treatment consumption with variations in the water system's operation. The final approach tracks the resulting product performance, such as corrosion protection or foam elimination in the process system, allowing further refinement of chemical dosing. These technologies provide wide-ranging benefits: less consumption and more effective use of industrial water, reduced chemical use, energy conservation, measurement of the fate of chemical additives, detection of industrial and biocide treatment for enhanced risk management and minimization of environmental release. These applications provide a complete cradle-to-grave approach to water management.

A New, Environmentally Friendly Corrosion Inhibitor for Industrial Cooling Systems

The U.S. industrial water treatment market for corrosion inhibitors is 50 million pounds per year, growing at 5 to 7 percent annually. There are more than 500,000 individual use sites in this industry category. Exposure to corrosion inhibitors is thus a major concern. Conventional corrosion inhibitors used for the control of corrosion in industrial cooling systems are either hazardous to the environment or have other drawbacks, such as instability in the presence of oxidizing biocides, limiting their applicability. A new, all-organic corrosion inhibitor, Bricorr® 288, a phosphonocarboxylate mixture, has been discovered and patented. Bricorr® 288 is a highly effective corrosion inhibitor with wide applicability to industrial cooling systems. Bricorr® 288 has an environmental profile permitting, in many instances,

discharge of treated water directly into rivers without any adverse effects. In many cases, the recommended treatment level is at least an order of magnitude below that which would be toxic to fish. Bricorr® 288 is also extremely water soluble and, therefore, will not bioaccumulate; this represents a much reduced risk to higher life forms. Additionally, the manufacture of Bricorr® 288 is via a new, patented aqueous route that does not use toxic solvents. The process is inherently 'clean', in that it does not produce any discharges to water or air, nor any by-products. Bricorr® 288 also has excellent handling characteristics due to its low mammalian toxicity helping to improve safety, particularly when used by those with minimal experience handling industrial chemicals.

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. Through CTS Corporation's commitment to a responsible environmental policy, many of its manufacturing methods have been modified with the goal of reducing or eliminating hazardous waste byproducts. One such method to reduce waste was the implementation of a No-Clean soldering process. This No-Clean soldering process, which began in March 1993, has eliminated the use of wave oil, soldering fluxes, and solvent cleaning. Changing to the No-Clean soldering process involved installing hoods over the solder pots. Using the hoods, an inert atmosphere is maintained over the molten solder. By using the inert atmosphere, oil and flux are no longer required. The parts are clean after solder and thus no solvent cleaning is needed.

Previously, TCA (1-1-1 Trichloroethane) and TCE (1,1,2 Trichloroethylene) were used as part of a post-solder cleaning operation to remove flux and wave oil residues. Due to the elimination of flux and wave oil, these cleaning operations became unnecessary. Therefore, the amounts of waste TCA and TCE from soldering operations were reduced from 9,900 pounds and 226,000 pounds in 1992, respectively, to zero in 1995. As an added benefit of eliminating solvent-based cleaning operations, air emissions due to the use of these chemicals have dramatically decreased. From 1992 through 1996, TCA and TCE related air emissions from soldering operations have been reduced from 99,000 pounds and 250,000 pounds, respectively, to zero. A cleaning operation, not related to soldering, generated a small amount of TCE air emissions in 1995. This operation was eliminated in June of 1995. The No-Clean soldering process has eliminated the generation of waste oil, flux, and cleaning solvents at the solder operation. Workers are no longer exposed to fumes from fluxes, oils, and cleaning solvents, which are typical of soldering operations. The product quality has also been improved.

Polyacrylamide Technology Reduces Soil Erosion

Irrigated agriculture produces one-third of earth's total harvested crop and comprises one-half of the total value of all harvested crop yet it comprises only one-sixth of the world's cropland. Erodible irrigated soils typically lose over 20 tons of soil per acre per year under furrow irrigation. Scientists at the Northwest Irrigation and Soils Research Laboratory developed and verified the use of a polyacrylamide (PAM) to reduce sediment loss by an average of 94 percent. In 1997 farmers used PAM to control erosion on an estimated 600,000 acres of furrow irrigated land, saving an estimated 12 million tons of soil in the third year of use. The key to developing an economical PAM technology for use in agriculture is in the conditions under which the primary reactive components polymer and soil were allowed to react. The conventional method applied polymers directly to the soil surface and mixed them with the soil to a maximum depth of six inches. This method was effective, but required the use of up

**CTS Corporation
Resistor Networks**

**Northwest Irrigation
and Soils Research
Laboratory, U.S.
Department of
Agriculture**

to 500 pounds per acre of polymer and sometimes required the application of a second agent used to activate the PAM. Associated costs made this method impractical for agricultural applications.

The scientists at Northwest Irrigation and Soils Research Laboratory altered the traditional approach by first dissolving very small quantities of water soluble PAM (10 mg per liter) in the irrigation source water and supplying furrows with the amended water only during the irrigation advance phase, i.e., during that time when irrigation water initially advances along the furrow and first wets the soil. This procedure greatly simplified the use of the polymer, minimized the amount of reactants required, and selectively limited PAM-soil stabilization reactions to those soil surfaces that were exposed to furrow-stream shear flow. This efficient methodology required only 1 to 2 pounds per acre of PAM and was equal or more effective than previous soil conservation approaches. PAM technology sustains agriculture/soil productivity because millions of tons of soil and associated fertilizers/pesticides remain in the field. Its use substantially reduces maintenance expenses (more than \$100,000 per year for some irrigated tracts) required to remove and dispose of sediment from regional irrigation systems and reservoirs, and can save farmers \$25 to \$50 per acre by eliminating on-farm pond/ditch cleaning and soil redistribution costs. This nontoxic, environmentally safe, and affordable chemical will provide irrigated agriculture a tool to greatly reduce sediment and associated pollutant contributions to streams and other water sources. Its use will help preserve irrigated agriculture production which is twice as productive as rainfed agriculture.

**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 1990s by the Polymer Products Unit of the Eastman Kodak Company in Rochester, New York. The original process to produce the polycarbonate of bisphenol A, diethylene glycol, and bisaminopropyl polydimethylsiloxane 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 1996.

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

About 7 billion pounds of cumene are produced each year in the United States (15 billion pounds worldwide). Most of it is converted to acetone and phenol, an intermediate in the production of epoxy resins, nylon 6, and polycarbonate plastics. Conventional cumene processes, based on Friedel-Crafts alkylation of benzene with propylene, use either solid phosphoric acid (SPA) or aluminum chloride (AlCl_3) catalysts. Both catalysts are corrosive, hazardous when spent, and difficult to dispose of safely. And SPA, the most widely used cumene catalyst, generates heavy aromatic by-products, once used to enhance gasoline octane, but now increasingly restricted by the U.S. Clean Air Act. A new environmentally friendly catalytic process for producing cumene is rapidly sweeping the industry, due to its substantial environmental and economic performance advantages. In 1998, about 70 percent of U.S. produced cumene will be made by this new technology, a Mobil/Badger joint development introduced in 1996. The Mobil/Badger technology employs a new zeolite catalyst that is environmentally benign and significantly more stable, more active, and more selective to cumene. Manufactured by Mobil, this zeolite requires no special handling and is returned environmentally inert to Mobil after use. The Mobil/Badger technology, proven in Badger pilot units, will remove 4.4 million pounds of SPA from use, while reducing heavy aromatic by-products by 250 million pounds/year. Its use will boost cumene yield by 5 percent and energy efficiency by more than 15 percent, enabling U.S. industry to meet growing cumene demand with substantially reduced costs.

PVC Replacement Technology

Phthalates and chlorine, two components of PVC products, are among the synthetic chemicals that environmental activists claim are interfering with the hormone system in animals and humans. In addition, when PVC is manufactured or combusted, dioxins are formed as byproducts. Many countries including Germany, Australia, Denmark and Sweden are taking actions to restrict the use of and manufacture of PVC. Today, there is a new breed of polymer catalysts that allow, during the course of polymerization, the production of polymers with unique product characteristics. These characteristics make it possible for polyolefins to enter and compete in new markets hitherto not seen. These catalysts are called metallocenes and essentially allow polymer properties to be tailor made during reactor polymerization.

The basic challenge of the product replacement (vinyl flooring) program was to develop a system that could combine the excellent physical properties of metallocene polyolefins with the unique processing characteristics of PVC. For instance, a patented chlorine free floor covering was developed showing that a metallocene based polyolefin utilizing selected non-volatile monomers goes beyond the conventional melt processing procedure and allows processing on conventional PVC manufacturing equipment. Unlike plastisol, where the "cure" is due to the solubilization of the plasticizers, the final polyolefin product contains no dissolved liquid and results in a multi-phase polymer system. This same system can be utilized in a wide array of applications and manufacturing processes, and offers environmental and product performance improvements.

The use of metallocene polyolefins is important for two distinct reasons. The most obvious is the inherently superior physical properties relative to conventional polyolefins. The second is directly associated to their chemical structure. Their unique polymerization process results in each polymer chain having a terminal double bond. This double bond can participate in the free radical polymerization of the liquid monomers (methacrylate and acrylate).

The copolymers that result will contain both olefinic and acrylic segments. Such combined polymers will act as compatibilizers for the two polymeric phases. This compatibilization will play a major role in several characteristic functions of various applications.

Recycling of Hydraulic Fluid

The U.S. Army, in cooperation with industry, recently developed a methodology for returning used hydraulic fluid to vehicle service. The effort was conducted in three phases. First, a laboratory investigation was conducted to determine the viability of restoring used fluid to specification performance (the test fluid was obtained through the military supply system and consisted of new and used fluid qualified to specification MIL-H-46170 (FRH), hydraulic fluid, rust inhibited, fire resistant, synthetic hydrocarbon). Second, a field investigation designed to identify commercially available equipment that could successfully process the used fluid as well as demonstrate the performance of the restored fluid in military vehicles was conducted. Third, the Army pursued an automated diagnostic effort aimed at optimizing the process. The developed technologies were successfully demonstrated with innovative technologies and processes in place to implement throughout both military and commercial industry

Reduced Volatility Alkylation Process

Alkylate is considered to be a critical component of reformulated gasolines. It is a clean burning, high octane mixture of paraffins and isoparaffins and contains no sulphur, olefins, or benzene. Reduced volatility Alkylation Process (ReVAP) provides refiners with a low-cost option for risk management and olefin conversion to such a high octane, clean-burning gasoline component. The process employs an additive in the acid phase of a hydrogen fluoride (HF) alkylation which suppresses the vapor pressure of HF and reduces its tendency to form aerosols when released to the atmosphere. It is a drop-in replacement acid system for existing HF alkylation units, which minimizes capital investments. The technology differs from existing sulphuric acid processes in that recovery and re-use of the additive is required. Separation from byproducts and recovery of the additive was deceptively complex initially. To remove all traces of acid required large capital investments and would lead to more waste generation. With ReVAP, a simple but elegant separation vessel was designed, allowing the recovery and reuse of the additive with minimal capital costs. The additive is a commercially available product, with extremely low toxicity, high chemical and thermal stability, and is soluble with HF in all proportions. HF aerosol reductions of 60 to 90 percent can be achieved. These results have been combined with extensive process development chemistry and engineering to design a commercial process which is as safe as, if not safer than, existing sulfuric acid processes.

Reducing VOC Emissions by Eliminating Painting and Labeling Operations with a New Color Laser Marking System for Plastic Parts

Decorating, marking, or coding plastic parts can be a challenge. Many plastics require surface treatments before paint will adhere. In certain environments, printed marks lack durability and may require a protective topcoat. Self-adhesive labels, another option, pose similar durability problems coupled with high scrap rates. A new technology to mark plastic parts in color with a laser has been developed by M.A. Hanna Color. This technology offers dramatic improvements in the ability of processors and end users to permanently mark a wide

range of plastic parts using a broad color palette. The technology is expected to replace a significant portion of plastic printing and adhesive label decorating/coding operations in most major market segments. The results will be significant reduction in VOC emissions (via elimination of solvents in ink production, usage, and clean up), enhanced recyclability of scrap plastic parts (unlike labels, there is no effect on melt reprocessability), and reduced liability on critical components, where safety warning labels often scrape or fall off the part.

Compared to earlier first-generation laser marking of plastics, the new technology offers greater contrast between mark and background, applicability to most major classes of thermoplastics and some thermosets (since custom-additive packages and manipulation of laser energy rather than base resin reformulation is used), the ability to move beyond what was essentially a monochrome palette, and reduction in potential thermal damage to the wallstock of the part, since the new technology does not work by pyrolyzation. Speed, flexibility, and economics are further benefits. Based on figures supplied by the Commerce Department and Rauche Guide to the U.S. Ink Industry, total solvent usage associated with inks for the plastics industry amounts to 22,400,000 pounds (11,200 tons) annually, conservatively assuming an average solvent content of 30 percent. M.A. Hanna Color estimates that within the first 2 years of use, the new color laser marking technology could effectively replace approximately 10 percent of the plastics decorating processes that involve inks. Within 10 years, this figure could rise to 50 percent. Meeting the 10 percent projection would eliminate approximately 1,120 tons (2,240,000 pounds) of VOC emissions from the production of plastic parts in the U.S. annually.

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

Phosgene is an important intermediate in the synthesis of polycarbonate plastics, high performance polymers, agricultural intermediates, and urethane foams. Current global production is about 10 billion pounds per year. Although the process chemistry is selective, the byproduct carbon tetrachloride, CCl_4 , is generated at a rate of 300 to 500 parts per million, amounting to 5 million pounds per year globally. Since carbon tetrachloride is a carcinogen, an ozone depleting chemical, and a greenhouse gas, it was necessary to reduce or eliminate this undesirable byproduct.

A DuPont team discovered a new catalyst that was produced in Siberia, Russia. After much laboratory work, it was decided to try a plant test, a scaleup of greater than 250,000 times. The catalyst was purchased, shipped from Siberia, and implemented in less than 1 year after the start of the program. After 1.5 years of commercial production, the new catalyst has consistently demonstrated high phosgene production rates and achieved a 90 percent reduction in the level of carbon tetrachloride generation (to less than 50 ppm, apparently a new global record). By conceptualizing, identifying, testing, securing from Russia, and implementing a novel phosgene production catalyst (well within the proposed 18 month deadline), the team saved the business a cost of \$2 million associated with the installation of a new abatement furnace, which would have been the only other alternative. Furthermore, the resulting need for fewer catalyst changes in the reactor as well as the prevention of maintenance costs that would have been associated with the abatement furnace will save approximately an additional \$400,000 per year. The catalyst technology is being offered for license globally, which could reduce emissions of CCl_4 by up to 5 million pounds per year.

DuPont Company

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

The removal of oxides of nitrogen (NO_x) by in-situ addition of hydrogen peroxide to a dissolving process was developed by Mallinckrodt Inc. Salts are produced by dissolving metals in nitric acid. 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 dissolving process. The literature states 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, thus completely eliminating NO_x emissions. This proposal was demonstrated in the laboratory. Next, two trial runs using this technology was completed. In both cases the formation of NO_x was completely eliminated. Based on the information from the trial runs, manufacturing with help from research and development designed a hydrogen peroxide addition process. The hydrogen peroxide addition process was successfully started. The new process has eliminated the generation of 30 tons per year of NO_x while at the same time reducing nitric acid usage by approximately 109 tons per year. Also, 13,000,000 gallons per year of scrubber waste water were eliminated since the scrubber is no longer needed.

Replacement of Methanol Solutions with Aqueous Dispersions in Photographic Coatings

Photographic films and papers are based on coatings of small silver halide crystals. A few photons of light absorbed by a crystal are converted to a small cluster of silver atoms and this cluster serves as the catalyst for the reduction of the entire grain when the coating is immersed in a solution of a reducing agent. The contrast between exposed and subsequently reduced areas of the coating and the unexposed areas forms the basis of black and white photography. In color photography, reducing agent byproducts react with very small oil droplets of color-forming precursors in the same layer as the silver halide to produce a dye. Differently sensitized silver halide crystals made sensitive to specific wavelengths of light are paired with oil droplets of appropriate color-forming precursors in a multiple layer sandwich to make photographic film and paper capable of giving full color images.

Along with the silver halide crystals and color-forming precursors, small amounts of other organic chemicals are essential for photographic performance. Antifoggants are needed to control the stability and catalytic activity of the silver atom clusters generated by exposure. Sensitizing dyes are used to make the silver halide sensitive to different wavelengths of light. These chemicals are substantially water insoluble and their introduction into the aqueous coating melt can be accomplished by making methanol solutions of these chemicals. Mixed with the coating melt, these chemicals in these solutions rapidly adsorb onto the silver halide grains. In some cases, the low solubility of the chemical requires very dilute methanol solutions. This, and the need to add several different dyes and antifoggants to a given photographic product results in coating melts with significant percentages of methanol. There are workplace concerns associated with such melts as well as the undesirable emission of methanol to the atmosphere during the coating and drying of the photographic product.

To reduce or eliminate methanol use, Eastman Kodak Company has prepared aqueous dispersions of sensitizing dyes and antifoggants using milling techniques. Such dispersions consist of small particles (less than 1 micrometer in diameter) of the chemical of interest stabilized by surfactant and/or polymer. Methods such as ball, sand, or media milling can

be used with the processing details such as milling time and composition optimized for the chemical of interest. These dispersions are miscible with the aqueous coating melt and give chemical activity comparable, and in some cases superior, to that of methanol solutions. Using this technology, methanol emission to the atmosphere during coating and drying has been greatly reduced even in time of increasing production. In addition, environmental concerns regarding the storage, and handling of methanol in manufacturing operations have been avoided.

Selective Hydrodechlorination of Carbon Tetrachloride

In 1987, the Montreal protocol was signed which called for a freeze on the production and use of chlorofluorocarbons at 1986 levels with subsequent reductions and complete elimination by January 1, 1996. A similar ban applies to carbon tetrachloride also due to environmental concerns associated with ozone depletion, global warming, and ground level smog. However, in the production of methylene chloride and chloroform, carbon tetrachloride is produced as a byproduct. It is estimated that in the United States and Europe, there is about 60,000 tons excess CCl_4 produced per year. The disposal of this byproduct, CCl_4 , typically by incineration, has become an environmental challenge and major economic burden to manufacturers of methylene chloride/chloroform.

Hydrodechlorination of carbon tetrachloride to chloroform is an attractive alternative to the disposal of by-product carbon tetrachloride by incineration. Until now, the catalytic conversion of CCl_4 to CHCl_3 has been problematic due to lack of catalyst, selectivity, poor conversion efficiency, and catalyst deactivation. Akzo Nobel made the elegant discovery of treating an aluminum oxide supported egg shell type platinum catalyst with an ammonium chloride solution. This provides a remarkably durable catalyst, with high conversion of CCl_4 to CHCl_3 that resists deactivation for over 2,000 hours. In contrast, untreated catalysts were rapidly deactivated with conversions dropping from 90 percent to 2 percent within one hour. The treated catalyst provides a cost effective, efficient method for the conversion of carbon tetrachloride to chloroform. Akzo Nobel BU Base Chemicals is in the process of implementing this technology internally and might offer it for commercial licensing in the future.

Splittable Surfactants

Union Carbide has developed a new class of surfactants, splittable surfactants, which provide a substantial reduction in emulsified organics discharged in waste water streams from industry. Splittable surfactants exhibit superior end-use performance, compared to current waste-treatable surfactants and other proposed treatments, which have not gained widespread use due to performance limitations. Waste streams containing splittable surfactants are quickly, easily, thoroughly, and irreversibly “split” and deactivated, via a chemical trigger, into non-surface active components, allowing rapid separation of oily waste from the water stream. A more concentrated oily waste is generated, facilitating either incineration for fuel value (industrial laundry applications), isolation for recycling (metal working fluids), or direct use (isolating lanolin from wool scouring). Before splitting and deactivation, Splittable Surfactants have an environmental profile comparable to conventional nonionic surfactants. Upon deactivation, both the hydrophilic and hydrophobic components biodegrade rapidly, and the hydrophilic component remaining in the waste water is essentially non-toxic to aquatic life. Splittable Surfactant technology represents the first industry partnership under the EPA's Environmental Technology Initiative for Chemicals, and EPA has recognized these products as “a significant innovation in surfactant chemistry, one that greatly reduces risk to the aquatic environment,” with its Recognition of Achievement in Pollution Prevention.

**Akzo Nobel Business
Unit Base Chemicals**

**Union Carbide
Corporation**

STABREX Microorganism Control Chemical

Water treatment is mostly about managing surface-fouling processes. There are three surface-fouling processes to manage (microbial, scaling, corrosion) and they occur simultaneously. Of these three, the microbial fouling process requires application of the most potentially hazardous products in water treatment, by far. Effective control of microbial fouling is the key to water treatment because modern scale and corrosion inhibition chemicals simply do not work unless microbial fouling is properly controlled. Predominately, chlorine, bromine, and/or other oxidants are used as the principal microbial control agent with more toxic nonoxidizing biocides used to supplement the program when necessary. Natural processes to control microbial fouling have been optimized by the test of environmental competition and natural selection. STABREX microorganism control chemical is a new stabilized liquid hypobromite product that is modeled after antimicrobials used in natural microbial fouling control processes. Response in the industry to this new technology has been positive because the product is safer, simpler, and less expensive to use compared to current alternatives. Marketplace acceptance of this new technology has been dramatically rapid. There are already over 400 commercial applications of the product in the United States and several million pounds of product were produced and sold in its first year of commercial introduction.

Starch Graft Polymers as Phenolic Resin Extenders

Starch graft polymers are derived from modified starch and conventional vinyl and acrylic monomers. While starch graft polymers have been known previously, a technology developed by Sequa Chemicals overcame rheological problems associated with prior products and afforded a convenient, fluid latex-like form. Drawing on glyoxal-based paper coating technology, these new starch graft polymers also utilized a novel non-formaldehyde cross-linking system. This new technology was initially used as a replacement for conventional latex polymers made with N-methylol acrylamide (which is a source of formaldehyde emissions) as the cross-linking system. Applications were as binders for fiberglass and polyester non-woven mat. This provided a binder system which eliminated formaldehyde emissions and maintained good performance and reasonable economics.

These starch graft emulsion polymers are water-based, non-toxic and non-irritating. Recent work has examined the use of these starch graft polymers as extenders for phenol-formaldehyde (PF) resins. An aqueous PF resin typically contains approximately 2 percent free formaldehyde. Approximately a billion pounds of aqueous PF resins are sold in the United States each year. That adds up to approximately 20 million pounds of free formaldehyde emitted to the environment and work place each year. It has been found that starch graft polymer products not only decrease formaldehyde emissions greatly, but also work synergistically with PF resins. Optimum performance is near the mid-point of composition. Such synergistic performance has not previously been observed with conventional latex emulsion polymers. Performance properties such as tensile strength, burst, and stiffness are improved over either the PF resin or the starch graft alone. Extending PF resins proportionally lowers the residual unreacted phenol in the final products. Proportional reductions of formaldehyde emissions have been measured, and a scavenging effect has been noted in testing designed to evaluate exposure to workers handling treated substrate. This technology is now sold commercially in tank truck quantities and its benefits are being promoted in various industries.

Stepan Company PA Lites Polyester Polyol

Stepan Company's Polyester Polyol product, manufactured using the Phthalic Anhydride Process Light Ends (PA Lites), uses a previously categorized waste as a raw material in its manufacture, thereby eliminating the material's disposal via incineration. This Polyester Polyol is the basic raw material for the manufacture of various types of insulating wallboard used in the home construction and commercial building industry. By substituting traditional raw materials with PA Lites, Stepan Company is providing the construction industry and consumer with a cost effective alternative to traditional building construction products.

Benefits from this product substitution go beyond the elimination of a waste requiring disposal. With its substitution as a raw material, it has reduced the requirement for phthalic anhydride, the traditional raw material for the polyol product, and the air emissions associated with its manufacture. As part of the development of this process, the distillation operation in the phthalic anhydride facility was also improved. An estimated 350 tons per year of organic waste material has been eliminated with the development and implementation of this technology. This not only represents a significant reduction in waste requiring disposal by incineration, but also the air emissions associated with these processes. Since this previously categorized waste material is now used on site to produce Polyester Polyol, potential exposure to the general public during offsite transportation to disposal facilities has been eliminated.

This project resulted in two economic benefits. The first is the savings associated with the transportation and disposal via fuel blending for energy recovery. On an annual basis the expected saving is \$200,000. The second economic benefit is the raw material savings due to the replacement of the Pure PA with the PA Lites material on a pound for pound basis. This results in additional savings of \$20,000 annually.

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

Stepan Company's STEPANFOAM® Water-blown Polyurethane Foam is a product in which CFCs and HCFCs are replaced with water as the blowing agent in rigid polyurethane foam. Historically, polyurethane foams used in insulating applications incorporated Trichlorofluoroethane (CFC-11), or more recently 1,1-Dichloro-1-fluoroethane (HCFC-141b), as the blowing agent. CFCs and HCFCs have been demonstrated to play a role in the depletion of Earth's stratospheric ozone layer and to contribute to global warming. Traditional rigid polyurethane foam products have the potential to release CFCs and HCFCs into the environment during formulation, manufacture, use, and disposal. The replacement of these compounds with water as an innocuous blowing agent eliminates the requirement for these environmentally unfriendly compounds and the resultant emissions to the environment. Throughout the 1990s Stepan Company has remained committed to the development of a lower cost, technologically advanced polyurethane foam which replaces environmentally unfriendly and potentially hazardous blowing agents with water. Stepan's Research and Development Department and Business Teams have partnered with our customers throughout the development and continued application of this product to promote its use as a viable alternative to CFCs and HCFCs.

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

Halogenated solvents have traditionally been used to remove a broad range of soils and contaminants generated during manufacturing operations. Their use, however, has left a legacy of potential environmental and health problems. *Synergy CCS™* (critical cleaning solvent) was developed to address these problems. *Synergy CCS™*, formulated from agriculturally-derived, naturally renewable products, is a potential replacement for many of these traditional cleaning solvents.

Synergy CCS™ had its beginnings at the Department of Energy's Kansas City Plant (managed and operated by AlliedSignal Inc.) when the plant began an effort focused on the elimination of toxic, restricted, or environmentally damaging solvents. Experience derived from this solvent substitution and elimination effort proved beneficial when, through its Technology Transfer Program, Kansas City Plant personnel were asked for help by a small manufacturer needing a safe, one-step cleaning solvent. *Synergy CCS™* Precision Cleaning Agent was formulated to meet this need. *Synergy CCS™* is a blend of environmentally derived products that forms a safe, powerful, yet distillable precision cleaning solvent capable of being heavily loaded with contaminants. *Synergy CCS™* is comprised of natural components that have been in industrial use for more than 45 years: d-limoene, a solvent derived from citrus byproducts, and tetrahydrofurfuryl alcohol, a solvent produced from the waste products of corn, oats, and sugar production. Individually, these materials are already used for cleaners, paint stripping formulations, and agricultural applications.

The solvent was further developed and adopted by a Hewlett-Packard Co. division, patented, and licensed to Petroferm, Inc., a worldwide leader in sales and technical support for alternative solvents and cleaning technologies. This partnership demonstrates how government and private industry can work together to develop safe chemical alternatives to solve environmental problems while simultaneously improving America's industrial competitiveness.

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

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.

**U.S. Navy, Office of
Naval Research**

**U.S. Navy, Naval
Surface Warfare Center**

Aerojet Propulsion

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

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.

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

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

Waste Reduction During Development of a New Process for Manufacture of Pharmaceutical Products

Evista® is the first of a new class of selective estrogen receptor modulators, or SERMs, that was approved in December 1997 for the prevention of osteoporosis in postmenopausal women. Waste reduction and minimization of overall environmental impact were key elements in development and commercialization of a process for manufacture of Evista®. To identify, address, and track environmental issues and opportunities early in the development and commercialization of manufacturing processes, Eli Lilly and Company has developed a new management system called New Product Environmental Requirements Tracking (NPERT). Development and commercialization of the manufacturing process for Evista® served as a pilot for this program.

The initial process proposed for manufacture of Evista® would have generated over 3.1 pounds of solid hazardous aluminum chloride waste per pound of product. In addition, the manufacture required the use of 114 liters of organic solvents for each pound of product produced. Of the total solvent used, 85 percent was composed of Superfund Amendment and Reauthorization Act (SARA) Title III listed material. While the process was still in develop-

**Alliance for
Environmental
Technology (AET)**

Eli Lilly and Company

ment, Lilly chemists and engineers found a way to eliminate the use of aluminum chloride and the need for disposal of the corresponding hazardous solid waste. This eliminated the generation and disposal of more than 371,000 pounds of hazardous solid waste during the first year of commercial production. During process development, the NPERT process focused attention on reducing total solvent usage and particular attention on the reduction in the use of all SARA Title III solvents. For example, one of the processing steps initially used methylene chloride. Evaluation of 26 alternative solvents resulted in the ability to completely eliminate the use of methylene chloride. Another process step used methyl isobutyl ketone (MIBK) and generated a waste stream that could not be solvent recovered and required incineration. Process development work resulted in a modification of the process that allowed the use of amyl acetate rather than MIBK. The revised process was more efficient and economical, generating an amyl acetate waste stream that could be easily recovered.

By the time the Evista® process was in full scale manufacturing, process modifications and improvements in efficiency during development and scale-up had reduced the total volume of solvent required to produce a pound of product by 61 percent. These improvements also reduce the use of SARA Title III solvents by 67 percent. Currently, on-going efforts are underway to further decrease waste, reduce volatile emissions and increase the recovery and recycle of solvent. The NPERT process and the example of its use on Evista®, show that focused efforts early in development and scale-up can dramatically reduce the environmental impacts of a new chemical manufacturing process. This effort highlights Lilly's commitment to minimizing the worldwide environmental impact of its manufacturing operations.

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

1,3,3-Trinitroazetidine (TNAZ) is a promising new melt-castable explosive that has significant potential for providing environmental benefits and capability improvements in a wide variety of defense and industrial applications. Initial lifecycle pollution burden was associated with the demilitarization of the munitions, and in particular, the use of thermoset polymeric binders that require removal with water jet cutting. TNAZ is the only energetic material other than trinitrotoluene (TNT) that can be melt-cast in existing TNT loading plants. Demilitarization of TNAZ simply requires heating the device above the melting point and pouring the liquid out, rather than the complicated and destructive methods used for RDX- and HMX-based plastic bonded explosives. The stability of TNAZ in the melt allows it to be easily recycled.

TNAZ has performance slightly better than that of HMX, the most powerful military explosive in current use. Thus, TNAZ might offer 30 to 40 percent improvements in performance as a replacement for TNT-based formulations such as Composition-B. The alternative synthesis of TNAZ, developed at the Los Alamos National Laboratory, allows TNAZ to be produced in a waste-free process that also eliminates the use of halogenated solvents. This alternative synthesis produces 5.3 pounds of waste per pound of product compared to the original synthesis of TNAZ, which produces 1,200 pounds of waste per pound of product. The alternate technology has been transferred to industry, where it has been scaled up to production-plant quantities. Further improvements in waste reduction have been demonstrated in the laboratory that might eventually lead to a process giving little more waste than one pound of salt per pound of TNAZ.

**U.S. Navy, Office of
Naval Research**

**U.S. Navy, Naval
Surface Warfare
Center**

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

**Los Alamos National
Laboratory
Aerojet**

Zero Effluent Photographic Processing in the Printing Industry

In its pre-press operations, the printing industry consumes about 1.5 billion square feet of silver halide photographic film annually. Processing the film consumes enormous amounts of water and chemicals and produces an equally large amount of liquid waste which is primarily disposed of in POTWs. The process also produces millions of waste plastic containers. Virtually none of this material is recycled and the environmental burden is very large. Some 400,000,000 gallons of fresh water is consumed each year and, after washing contaminant from the processed film, is sent to local POTWs for treatment. In addition to that, 15,000,000 gallons of photographic developer containing thousands of tons of obnoxious chemicals like hydroquinone is similarly dumped on the POTWs. Further, 15,000,000 gallons of photographic fixer containing high levels of ammonia and silver is also sent to the POTWs for treatment. Although some of the silver is removed by various processes, these are not very efficient and recovery of this precious metal is only on the order of 50 percent. The limited environmental efforts have been directed primarily at silver recovery because of the value of the silver, or, where water prices are high, to reduction in wash water use.

The wastes generated in the pre-press printing industry are complex and require a coordinated effort to eliminate them. The Dupont DuCare™ Photochemical Film Processing System is such a coordinated effort. It attacks the largest volume piece of the problem, the wash water, by developing novel technology that reduces the amount of wash water required by 99 percent and completely eliminates the wash water effluent by sending used wash water into the fixer. The DuCare™ system includes a novel, recyclable developer based on erythorbic acid instead of hydroquinone in a process that allows about 75 percent of returned developer to be used in making fresh recycled developer. The DuCare™ system also includes a recycled fixer. Although the technology used is not new, it is made much more effective and efficient than in the past. The fixer is returned to a central recycling center, much like the developer is, where the silver is recovered with an efficiency of 99 percent. In addition, the analytical capability and control at a recycling center allow about 90 percent of the returned fixer to be used in making fresh recycled fixer. The net effect of this coordinated approach would virtually eliminate the liquid waste generated if it was applied across the industry. Fresh water savings would be over 395,000,000 gallons annually. No liquid waste would be sent to POTWs. All liquids would be returned for recycling. Those that could not be recycled would be disposed of at commercial, licensed TSDFs. Packaging waste would drop significantly. The efficient recycling and reuse of the spent chemical stream would eliminate the need for thousands of tons of raw materials as well.

Index

Award winners are indicated with *.

Akzo Nobel Business Unit Base Chemicals

Selective Hydrodechlorination of Carbon Tetrachloride. 63

Albany Research Center, U.S. Department of Energy

Chloride-Free Processing of Aluminum Scrap 41

Albright & Wilson Americas Inc.

A New, Environmentally Friendly Corrosion Inhibitor for Industrial Cooling Systems 56

Alliance for Environmental Technology (AET)

The Use of Chlorine Dioxide, the Foundation of Elemental Chlorine-Free (ECF) Bleaching for Pulp and Paper, as a Pollution Prevention Process 67

AlliedSignal Federal Manufacturing and Technologies

Synergy CCS™ Precision Cleaning Solvent: A Government/Industry Solution to a Complex Environmental Problem 66

American Air Liquid

Air Liquid PFC Recycle Process. 38

American Society for Testing & Materials (ASTM),

Analysis of Liquid Hazardous Waste for Heavy Metals by Energy-Dispersive X-Ray Fluorescence (EDXRF) Spectrometry 39

AMSOIL Incorporated

Waste Oil Source Reduction Through Extended Oil Service Life 36

Antia, Jimmy E. and Govind, Rakesh, Department of Chemical Engineering, University of Cincinnati

Novel In-Situ Zeolite Coatings in Monoliths 18

***Argonne National Laboratory**

Novel Membrane-Based Process for Producing Lactate Esters--Nontoxic Replacements for Halogenated and Toxic Solvents 6

Arkenol, Holdings, L.L.C.

Sugars From Lignocellulosic Materials for the Production of Bio-Based Fuels and Chemicals 35

Asarco Incorporated

Asarco—West Fork Biotreatment Project 40

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

Design of CO₂-Soluble Ligands for Affinity Extraction Using CO₂ 10

BetzDearborn, Inc.

Designing an Environmentally Friendly Copper Corrosion Inhibitor for Cooling Water Systems 42

BIOCORP, Inc.

Biodegradable Thermoplastic Material. 27

Biofine, Incorporated

Conversion of Low-Cost Biomass Wastes to Levulinic Acid and Derivatives 28

Bose, Ajay K., Stevens Institute of Technology <i>Microwave-Induced Organic Reaction Enhancement (More) Chemistry for Eco-Friendly Synthesis.</i>	15
Bowling Green State University <i>Orphan Chemical Recycling Program</i>	19
Burch Company <i>Burch Apparatus and Method for Selectively Treating Vegetation to Reduce Pesticide and Fertilizer Use, Eliminate the Release of Certain Toxins to the Environment, Reduce Pesticide Runoff, and Reduce the Potential of Worker Exposure to Toxic Substances.</i>	27
Ciba Specialty Chemicals Corporation <i>Heavy Metal Free Alternative to Standard Anti-Corrosive Pigments</i>	50
Collins, Terrence J., Department of Chemistry, Carnegie Mellon University <i>Efficient, Selective, Totally Chlorine Free (TCF) Wood Pulp Bleaching Technology</i>	12
CTS Corporation Resistor Networks <i>No-Clean Soldering.</i>	57
Doherty, Michael F. and Malone, Michael F., Department of Chemical Engineering, University of Massachusetts, Amherst <i>Reactive Distillation Technology to Reduce Waste at the Source</i>	20
*Draths, Karen M. and Frost, John W., Department of Chemistry, Michigan State University <i>Use of Microbes as Environmentally-Benign Synthetic Catalysis</i>	3
DuPont Company <i>INFINITY Process</i>	52
<i>NAFION Membrane Technology</i>	54
<i>Reduction of Carbon Tetrachloride Emissions at the Source, by Development of a New Catalyst</i>	61
DuPont Polyester <i>DuPont Petretec Polyester Regeneration Technology—Making Polyester Evergreen .</i>	45
E&J Industries, Incorporated <i>Ultraviolet (UV) Curing of Small Wood Products: An Industrial Demonstration Project</i>	35
E.I. duPont de Nemours & Co., Inc. <i>Zero Effluent Photographic Processing in the Printing Industry.</i>	69
Eastman Kodak Company <i>Polycarbonate/Polydimethylsiloxane Copolymers for Thermal Print Media</i>	58
<i>Replacement of Methanol Solutions With Aqueous Dispersions in Photographic Coatings</i>	62
Eli Lilly and Company <i>Waste Reduction During Development of a New Process for Manufacture of Pharmaceutical Products</i>	67

Environmental Technology and Education Center, Inc. (ETEC) <i>High Energy Efficiency, Environmentally Friendly Refrigerants</i>	30
EOSystems, Inc. <i>CerOx Process Technology for Non-Thermal Destruction of Organic Hazardous Wastes</i>	28
*Flexsys America L.P. <i>Elimination of Chlorine in the Synthesis of 4-Aminodiphenylamine: A New Process Which Utilizes Nucleophilic Aromatic Substitution for Hydrogen</i>	5
Govind, Rakesh and Singh, Rajit, Department of Chemical Engineering, University of Cincinnati <i>Bioconversion of Carbon Dioxide into Organic Feedstocks</i>	8
Great Western Chemical Company <i>MRA-D, A New Wastewater Treatment Process</i>	31
Gross, Richard A., Department of Chemistry, University of Massachusetts, Lowell <i>Biotechnological Routes to 'Tailored' Polymeric Products of Environmental and Industrial Importance</i>	9
Hauser, Inc. <i>Paclitaxel Process Improvements</i>	32
Hendrickson, James B., Department of Chemistry, Brandeis University <i>The SYNGEN Program for Generation of Alternative Syntheses</i>	22
Hill, Craig L., Department of Chemistry, Emory University; Weinstock, Ira A., USDA Forest Service, Forest Products Laboratory <i>A New Catalytic Biomimetic Technology to Convert Wood to Paper Without Pollution</i>	16
Ho, Nancy W.Y., Laboratory of Renewable Resources Engineering, Purdue University <i>Successful Development of Recombinant Xylose-Fermenting Saccharomyces Yeasts Capable of Effectively Co-Fermenting Glucose and Xylose from Renewable Cellulosic Biomass to Ethanol as Clean Transportation Biofuel</i>	21
Hudlicky, Tomas, Department of Chemistry, University of Florida <i>Synthetic Methodology "Without Reagents." Commercial Manufacture of Inositols and Other Pharmaceuticals by Tandem Enzymatic and Electrochemical Oxidations and Reductions</i>	23
IBM Research Division, Almaden Research Center <i>The Chemical Kinetics Simulator Program</i>	41
Imation™ Corporation <i>Imation No Process Plates</i>	50
IMC-Agrico Company <i>AGROTAIN® N-(n-butyl) Thiophosphoric Triamide</i>	38
International Metalizing Corporation <i>Non Toxic Antifouling</i>	32

IonEdge Corporation <i>Zero-Waste Dry Plating of Cadmium</i>	36
Khalili, Nasrin R., Arastoopour, Hamid, and Walhof, Laura, Department of Chemical and Environmental Engineering, Illinois Institute of Technology <i>Novel Waste Minimization Approach: Production of Carbon-Based Catalyst or Sorbent from Biosolids</i>	19
KM Limited Inc. <i>The PIX Module Software: Combining Life Cycle Assessment With Activity Based Costing to Preserve the Global Environment</i>	33
Knipple, Douglas C., Department of Entomology, Cornell University <i>In Vivo Synthesis of Lepidopteran Pheromone Precursors in Saccharomyces Cerevisiae: An Economical Process for the Production of Effective, Nontoxic, Environmentally Safe Insect Control Products</i>	14
Ladisch, Michael R., Laboratory of Renewable Resources Engineering and Department of Agricultural and Biological Engineering, Purdue University <i>Biobased Adsorbents for Desiccant Coolers</i>	8
Lawrence Livermore National Laboratory; U.S. Department of Defense, Office of Munitions; U.S. Department of Energy, Weapons Supported Research <i>Environmentally-Driven Preparation of Insensitive Energetic Materials</i>	48
LeBlanc, Carole, The Massachusetts Toxics Use Reduction Institute, University of Massachusetts, Lowell <i>The Determination of Alternative Solvents Quantifying and Qualifying Green Chemistries in Industrial Surface Cleaning</i>	11
Li, Chao-Jun, Department of Chemistry, Tulane University <i>Water as Solvent for Chemical and Material Syntheses</i>	25
Lin, Chhiu-Tsu, Department of Chemistry and Biochemistry, Northern Illinois University <i>Chrome-Free Single-Step In-Situ Phosphatizing Coatings</i>	10
Lockheed Martin Tactical Aircraft Systems <i>Development and Implementation of Low Vapor Pressure Cleaning Solvent Blends</i> 43 <i>Implementation and Verification of Aqueous Alkaline Cleaners</i>	51
Los Alamos National Laboratory <i>Application of Freeze Drying Technology to the Separation of Complex Nuclear Waste</i>	39
<i>Magnetic Separation for Treatment of Radioactive Liquid Waste</i>	53
M.A. Hanna Color—Technical Center <i>Reducing VOC Emissions by Eliminating Painting and Labeling Operations with a New Color Laser Marking System for Plastic Parts</i>	60
Mallinckrodt Baker Inc. <i>Hydrogen Sulfide Elimination from the Substances Not Precipitated by H₂S Test</i> . 50	
Mallinckrodt Inc. <i>The Removal of Oxides of Nitrogen (NO_x) by In-Situ Addition of Hydrogen Peroxide to a Metal Dissolving Process</i>	62

Manousiouthakis, Vasilios, Department of Chemical Engineering, University of California Los Angeles	
<i>Source Reduction Through Mass Integration: Mass Exchange Network Synthesis . . .</i>	<i>21</i>
Mathews, Alexander P., Department of Civil Engineering, Kansas State University	
<i>Waste Biomass Utilization in the Production of a Biodegradable Road Deicer . . .</i>	<i>23</i>
McDonough Braungart Design Chemistry, LLC	
<i>PVC Replacement Technology</i>	<i>59</i>
MEMC Electronic Materials, Inc.	
<i>Elimination of Ozone-Depleting Chemicals (ODCs) Through the Use of a Water Soluble Adhesive “Green Wax”</i>	<i>45</i>
Mobil Technology Company	
<i>Production of Cumene with Zeolite Catalyst—The Mobil/Badger Cumene Process</i>	<i>59</i>
Nalco Chemical Company	
<i>STABREX® Microorganism Control Chemical</i>	<i>64</i>
<i>Nalco NALMET® Heavy Metal Removal Technology</i>	<i>55</i>
<i>Nalco Fuel Tech NO_xOUT® Process</i>	<i>54</i>
<i>Nalco TRASAR® Technology</i>	<i>56</i>
<i>Nalco LAZONSM Technology</i>	<i>55</i>
<i>Environmentally-Responsible Liquid Polymers</i>	<i>47</i>
<i>Nalco PORTA-FEED®</i>	<i>56</i>
Nassaralla, Claudia Lage, Department of Metallurgical and Materials Engineering, Michigan Technological University	
<i>Waste Reduction and Recycling of Magnesite-Chrome Refractory into the Steelmaking Process</i>	<i>24</i>
National Center for Agricultural Utilization Research	
<i>Environmentally Benign Synthesis of Monoglyceride Mixtures Coupled With Enrichment by Supercritical Fluid Fractionation</i>	<i>47</i>
NICCA U.S.A., Inc.	
<i>Heavy Metals Free, Non-Formaldehyde Fixing Agent for Direct and Fiber Reactive Dyes</i>	<i>30</i>
Nikles, David E., Department of Chemistry, University of Alabama	
<i>Waterborne Coating Formulations for Video Tape Manufacture</i>	<i>25</i>
Nortel Technology	
<i>Molyphos: A Chromate-Free Alternative for Corrosion Protection of Metal Parts .</i>	<i>53</i>
Northwest Irrigation and Soils Research Laboratory, U.S. Department of Agriculture	
<i>Polyacrylamide Technology Reduces Soil Erosion</i>	<i>57</i>

Novon International	
<i>Natural Recycling of Plastics Through Chemical and Biological Degradation</i>	<i>31</i>
Paquette, Leo A., Department of Chemistry, The Ohio State University	
<i>Environmental Advantages Offered by Indium-Promoted Carbon-Carbon</i>	
<i>Bond-Forming Reactions in Water.</i>	<i>13</i>
Pharmacia & Upjohn	
<i>Environmental Improvements from Redesigning the Commercial Manufacture</i>	
<i>of Progesterone</i>	<i>46</i>
Phillips Petroleum Company	
<i>Reduced Volatility Alkylation Process</i>	<i>60</i>
Praxair, Inc.	
<i>Liquid Oxidation Reactor (LOR)</i>	<i>52</i>
*PYROCOOL Technologies, Inc.	
<i>Technology for the Third Millennium: The Development and Commercial</i>	
<i>Introduction of an Environmentally Responsible Fire Extinguishment and</i>	
<i>Cooling Agent.</i>	<i>4</i>
Radiance Services Company	
<i>The Radiance Process: A Quantum Leap in Green Chemistry.</i>	<i>34</i>
Raghavan, Dharmaraj, Department of Chemistry, Howard University	
<i>Design of Rubberized Concrete from Recycled Rubber Tires</i>	<i>11</i>
<i>Novel Applications of Polymer Composite from Renewable Materials.</i>	<i>17</i>
Rochester Midland Corporation	
<i>Development of a New 'Core' Line of Cleaners</i>	<i>44</i>
*Rohm and Haas Company	
<i>Invention and Commercialization of a New Chemical Family of Insecticides</i>	
<i>Exemplified by CONFIRM™ Selective Caterpillar Control Agent and the</i>	
<i>Related Selective Insect Control Agents MACH 2™ and INTREPID™</i>	<i>7</i>
Rybarczyk, James P., Department of Chemistry, Ball State University	
<i>Premature Degradation of Coolant Oil in the Machining of Magnesium in the</i>	
<i>Automobile Industry</i>	<i>20</i>
Rynex Holdings, Ltd.	
<i>Rynex Biodegradable Dry Cleaning Solvent</i>	<i>34</i>
Sequa Chemicals, Inc.	
<i>Starch Graft Polymers as Phenolic Resin Extenders</i>	<i>64</i>
Singh, Mono M., National Microscale Chemistry Center, Merrimack College	
<i>National Microscale Chemistry Center: The Leader in Worldwide Implementation</i>	
<i>of Microscale Technology</i>	<i>15</i>
Solutia Inc.	
<i>Greenhouse Gases: From Waste to Product</i>	<i>49</i>

Solvent Kleene, Inc.	
<i>Non-Hazardous Degreaser that Degreases as Efficiently as Trichloroethane and Outperforms Aqueous Products.</i>	<i>32</i>
Stepan Company	
<i>Stepan Company PA Lites Polyester Polyol</i>	<i>65</i>
<i>Stepanfoam® Water-Blown Polyurethane Foam HCFC-Free, Environmentally Friendly, Rigid Polyurethane Foam</i>	<i>65</i>
Stewart, Jon D., Department of Chemistry, University of Florida	
<i>Engineered Baker's Yeast as a Means to Incorporate Biocatalysis Early in Process Design: Application to the Asymmetric Baeyer-Villiger Oxidation</i>	<i>12</i>
Subramaniam, Bala, Department of Chemical and Petroleum Engineering, University of Kansas	
<i>A Novel Solid-Acid Catalyzed 1-Butene/Isobutane Alkylation Process</i>	<i>18</i>
Synthon Corporation	
<i>Development and Commercialization of High-Value Chemical Intermediates from Starch and Lactose.</i>	<i>29</i>
Taylor, Larry T., Department of Chemistry, Virginia Tech and Virginia Tech Intellectual Properties	
<i>A Non-Toxic Liquid Metal Composition for Use as a Mercury Substitute.</i>	<i>17</i>
TechMatch, Incorporated	
<i>N-Methylmorpholine-N-oxide (NMMO): A Novel, Non-Toxic Reusable Solvent for Cellulose as Source Reduction in the Production of Textile Fibers</i>	<i>31</i>
Tektronix, Inc.	
<i>Designing Safer Chemicals: Spitfire Ink</i>	<i>43</i>
Thompson, Stephen, The Center for Science, Mathematics, and Technology Education, Colorado State University	
<i>Small Scale Chemistry: Pollution Prevention in Inorganic Chemistry Instruction Program</i>	<i>20</i>
*Trost, Barry M., Department of Chemistry, Stanford University	
<i>The Development of the Concept of Atom Economy.</i>	<i>2</i>
Union Camp Corporation	
<i>C-FREE™ Pulp Ozone Bleaching Project</i>	<i>40</i>
Union Carbide Corporation	
<i>Splittable Surfactants.</i>	<i>63</i>
U.S. Army Edgewood Research, Development, and Engineering Center	
<i>Filter Leak Test Using Ozone-Benign Substances.</i>	<i>48</i>
U.S. Army Tank & Automotive Armaments Command	
<i>Recycling of Hydraulic Fluid.</i>	<i>60</i>
U.S. Bureau of Engraving & Printing	
<i>Designing a Safer, Less Toxic, Less Pollutant and Environmentally Friendly Solvent--ISOMET</i>	<i>42</i>

U.S. Navy, Office of Naval Research; U.S. Navy, Naval Surface Warfare Center; Aerojet Propulsion; and Professor Joseph M. DeSimone, Department of Chemistry, University of North Carolina at Chapel Hill <i>Use of Carbon Dioxide as an Alternative Green Solvent for the Synthesis of Energetic Thermoplastic Elastomers</i>	66
U.S. Navy, Office of Naval Research; U.S. Navy, Naval Surface Warfare Center; U.S. Army Armament Research, Development and Engineering Center; Los Alamos National Laboratory; Aerojet <i>Waste Reduction in the Production of an Energetic Material by Development of an Alternative Synthesis</i>	68
Varma, Rajender S., Texas Regional Institute for Environmental Studies, Sam Houston State University <i>Environmentally Benign Solvent-Free Chemical Processing</i>	13
Warner, John C., Department of Chemistry, University of Massachusetts, Boston and Polaroid Corporation <i>Environmentally Benign Supramolecular Assemblies of Hydroquinones in Polaroid Instant Photography</i>	14
Weimer, Alan W., Department of Chemical Engineering, University of Colorado <i>Vibrating Fluidized Bed Combustion Nitridation Processing Using Concentrated Solar Energy</i>	23
Zyvax Incorporated <i>The Zyvax “Watershield“ Mold Release</i>	37



United States
Environmental Protection Agency
(7406)
Washington, DC 20460

Official Business
Penalty for Private Use
\$300