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The Presidential Green Chemistry Challenge Awards Program

Summary of 1999 Award Entries and Recipients

GREEN CHEMISTRY CHALLENGE

Printed on paper that contains at least 30 percent postconsumer fiber.

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

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

Entries received for the 1999 Presidential Green Chemistry Challenge Awards were judged by an independent panel of technical experts convened by the American Chemical Society. The criteria for judging included health and environmental benefits, scientific innovation, and industrial applicability. Five projects that best met the scope of the program and the criteria for judging were selected for 1999 awards and nationally recognized on June 28, 1999.

This document provides summaries of the entries received for the 1999 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 1999 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.

Terry Collins
Department of Chemistry, Carnegie Mellon University

TAML™ Oxidant Activators: General Activation of Hydrogen Peroxide for Green Chemistry

Twenty years of research by Professor Terry Collins at Carnegie Mellon University has led to the successful development of a series of environmentally friendly oxidant activators based on iron. These TAML™ (tetraamido-macrocyclic ligand) activators catalyze the reactions of oxidants in general. Their activation properties with hydrogen peroxide in water are of greatest environmental significance. TAML™ activators arise from a design process invented by Professor Collins which is complementary to that employed by Nature to produce powerful oxidizing enzymes. The activators promise extensive environmental benefits coupled with superior technical performance and significant cost savings across a broad-based segment of oxidation technology. Users of TAML™ peroxide activators will range from huge primary extractive-processing industries to household consumers throughout the world. In laboratory tests, the Collins activators have shown this potential in the major industrial application of wood pulp delignification and in the broad-based consumer process of laundry cleaning.

Annually, bleached pulp has a global value of approximately $50 billion. The key to quality papermaking is the selective removal of lignin from the white fibrous polysaccharides, cellulose, and hemicellulose. Wood-pulp delignification has traditionally relied on chlorine-based processes that produce chlorinated pollutants. It has been clearly demonstrated that TAML™ activators can provide the Pulp and Paper Industry (P&PI) with the first low-temperature hydrogen peroxide-based delignification technology for treating pulp. The new process moves the elemental balance of pulp delignification closer to what Nature employs for degrading lignin, a strategy reflected in the industry's recent development of totally chlorine free (TCF) bleaching procedures. TAML™ activated peroxide delignification proceeds rapidly and efficiently at 50 °C indicating that minimal capital will be required to retrofit existing mills for its use. The new technology is more selective than any other TCF process and, except at low lignin content, is as selective as the current dominating delignification technology based on chlorine dioxide. These parameters show that the new technology can significantly reduce persistent pollutants associated with chlorine-containing delignifying agents by enabling the industry to use peroxide to remove the majority of lignin from kraft pulp more selectively and more rapidly.

In the laundry field of use, most household bleaches are based upon peroxide. Here, TAML™ activators enable the most attractive dye transfer inhibition processes ever developed. Almost all the approximate 80 dyes used on commercial textiles are safe from TAML™ activated peroxide while they are bound to a fabric. But in almost every case, should a dye molecule escape a fabric, the same TAML™ activated peroxide will intercept and destroy it before it is able to transfer to other fabrics. This attribute and the improved stain removal properties of TAML™ activated peroxide, offer significant commercial advantages for laundry products producers. In addition, the combined features translate to both direct and indirect environmental benefits by enabling laundering that replaces stoichiometric with catalytic procedures and that requires less water. Numerous other fields of use are anticipated; some are currently being developed including the use of TAML™ peroxide activators for water disinfection.

Small Business Award

Biofine, Incorporated

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

Using biomass rather than petroleum to manufacture chemicals has numerous advantages. Renewable biomass contributes no net CO_2 to the atmosphere, conserves fossil fuels, and leads to a secure domestic supply of feedstocks capable of making a huge array of chemical products. Biofine, Incorporated, has developed a high-temperature, dilute-acid hydrolysis process that converts cellulosic biomass to levulinic acid (LA) and derivatives. Cellulose is initially converted to soluble sugars, which are then transformed to levulinic acid. The process is economical even without receiving waste disposal fees for feedstock, and wet feedstocks can be used without drying, thereby saving energy.

In August 1997, Biofine, the U.S. Department of Energy, the New York State Energy Research and Development Authority (NYSERDA), and Biometics, Inc. began manufacturing LA from paper mill sludge at a one-ton-per-day demonstration plant at Epic Ventures, Inc. in South Glens Falls, New York. Biofine's process had already been demonstrated at a smaller scale with a variety of cellulosic feedstocks, including municipal solid waste, unrecyclable municipal waste paper, waste wood, and agricultural residues. Biofine hopes to serve the growing need for environmentally acceptable waste disposal options.

LA niche markets provide excellent small-scale opportunities; large-scale opportunities will open up as Biofine lowers the price of this highly versatile chemical intermediate. LA's worldwide market is about one million pounds per year at a price of $4-6/lb. Full-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 succinic acid and diphenolic acid, which sell for $2/lb or less, or acrylic acid, which sells for $0.50/lb. Eventually, Biofine hopes to build larger plants to convert 1,000 dry ton/day of feedstock into $0.04-0.05/lb LA. The worldwide commercial market for LA and its derivatives could reach one trillion lbs/yr. Full-scale plant opportunities are being assessed for several locations in the U.S. and worldwide. One full-scale commercial plant using 1,000 dry ton/day of feedstock could manufacture more than 160 million lbs/yr of product. Fortunately, Biofine's technology is economical for a broad range of plant sizes; even the one-ton-per-day demonstration plant is self-sufficient at LA's existing price.

Because LA is a platform chemical, it need not be sold as a commodity chemical. Derivatives are the key to marketability, and markets for such LA derivatives as tetrahydrofuran, butanediol, gamma butyrolactone, succinic acid, and diphenolic acid exist. Fortunately, many economical conversion processes are possible. The National Renewable Energy Laboratory (NREL), Pacific Northwest National Laboratory (PNNL), and Rensselaer Polytechnic Institute (RPI) are developing market applications and production methods for other derivatives, including methyltetrahydrofuran (MTHF), a gasoline fuel additive; δ-amino levulinic acid (DALA), a broad-spectrum, non-toxic, and biodegradable pesticide; and new biodegradable polymers.

Alternative Synthetic Pathways Award

Practical Application of a Biocatalyst in Pharmaceutical Manufacturing

Lilly Research Laboratories

The synthesis of a pharmaceutical agent is frequently accompanied by the use and generation of a large amount of hazardous substances. This should not be surprising, as numerous steps are commonly necessary, each of which may require feedstocks, reagents, solvents, and separation agents. An example of an effort to reduce these hazards, employed by Lilly Research Laboratories, is the use of an alternate synthetic pathway designed for the environmentally responsible production of a LY300164, a central nervous system compound in the early stages of development. The original synthesis which was employed to support early clinical development proved to be an economically viable manufacturing process. The approach, however, involved several problematic steps. The process required the use of large solvent volumes, chromium oxide (a cancer suspect agent) and led to the generation of disproportional quantities of chromium waste compared to drug produced. These points provided compelling incentive to pursue an alternate synthetic approach.

The new synthetic pathway successfully increased worker safety and limited environmental impact by offering a strategy which more appropriately controlled oxidation state adjustments. The new synthesis involved the implementation of several inventive steps on large scale. In particular, keto-reductase activity of a common microorganism, *Zygosaccharomyces rouxii*, was discovered that led to excellent stereocontrol in the asymmetric reduction of a dialkyl ketone. Implementation of the biocatalytic process was enabled on a large scale by employing a novel, yet simple, three-phase reaction system. The protocol overcame long-standing limitations preventing the practical application of yeast-mediated reductions by allowing high concentrations of the substrate to be charged to the aqueous reaction medium and by providing a facile method for product isolation. An unprecedented autoxidation reaction of a C-l aryl isochroman which involved the treatment of the substrate with air and sodium hydroxide was also discovered that eliminated the use of transition metal oxidants.

The new process was developed by combining innovations from chemistry, microbiology, and engineering. The process circumvented the use of non-recycled metal and significantly reduced solvent usage. For example, when conducted on a scale to generate 100 kg of LY300164, the new process avoids the use of approximately 34,000 liters of solvent and eliminates production of approximately 300 kg of chromium waste. In addition, the synthetic scheme proved more efficient as well, with percent yield climbing from 16 to 55%. The inventive steps of the process represent low cost, easily implemented technology which should find broad manufacturing applications.

Alternative Solvents/Reaction Conditions Award

Nalco Chemical Company

Water Based Liquid Dispersion Polymers

Annually, at least 200 million pounds of water soluble, acrylamide-based polymers are used to condition and purify water in various industrial and municipal operations. These water-soluble polymers assist in removing suspended solids and contaminants and effecting separations. Conventionally, in order to prepare such polymers in liquid form for safety and ease of handling, the water soluble monomers, water, and a hydrocarbon (oil) and surfactant "carrier" mixture are combined in approximately a 1:1:1 ratio (to form an emulsion). The monomers are then polymerized. Regrettably, the oil and surfactant components of these inverse emulsions lend no value to the performance of the polymers; they simply allow their manufacture in liquid form. This means that approximately 90 million pounds of oil and surfactant are introduced into the environment (at the current consumption rates) as a consequence of their use. Until now, there has been no alternative technology available to manufacture liquid polymers without the obvious environmental disadvantages associated with the oil and surfactant based carrier systems.

In order to overcome the disadvantages of conventional liquid emulsion polymers, Nalco has developed a series of new polymer products that are produced through a unique polymerization technology that permits the manufacture of these widely used polymers as fine particles dispersed in aqueous solutions of the inorganic salt ammonium sulfate. Thus, while the chemistry of the active polymer component is the same, the technology allows for the production of the polymers as stable colloids in water. Since these dispersion polymers are liquid, they retain the virtues of ease and safety of handling, but employing aqueous salt solutions instead of hydrocarbons and surfactants as the reaction medium and polymer carrier means that no oil or surfactants is released into the environment when the polymers are used in the water treatment application.

By choosing to manufacture water-based dispersions instead of water-in-oil emulsions, over one million pounds of hydrocarbon solvent and surfactants have been conserved by Nalco since 1997 on just two polymers in the product line. There are also benefits over the water-in-oil emulsion polymers for the users of these products as a consequence of their water-based formulations. For example, as the products contain no oil, they are safer to transport and use since they are non-flammable and emit no VOCs.

As mentioned, the water-based dispersion polymers make use of ammonium sulfate salt, a waste by-product from the manufacture of caprolactam, the precursor to nylon. The preparation of water-based dispersion polymers instead of water-in-oil emulsions allows Nalco to recycle and make use of this by-product from another industry for water treatment and purification. Choosing to produce these polymers as water-based dispersions instead of as water-in-oil emulsions allowed Nalco to utilize over 3.2 million pounds of caprolactam-produced ammonium sulfate in 1998 alone.

Finally, because these new polymers are water based, they dissolve readily in water without the complex and relatively expensive mixing and feeding equipment that is required for the use of water-in-oil polymers. This distinct advantage provides new opportunities for medium and smaller sized operations to treat wastewater streams cost effectively.

Designing Safer Chemicals Award

Dow AgroSciences LLC

Spinosad, A New Natural Product for Insect Control

Estimates of monetary losses in crops as a result of uncontrolled insect infestations are staggering, far in excess of the current $12 billion dollar market for insect control products. Man's continuing quest to control damaging insect pests in crops or on property has spawned several eras of agricultural insect control, most recently the advent of synthetic organic chemicals as insecticides. However, the development of resistance has reduced the effectiveness of many of the currently available insecticides, and more stringent environmental and toxicological hurdles have restricted the use of others.

It was against this backdrop that researchers at Eli Lilly and Company introduced high volume testing of fermentation isolates in agricultural screens in the mid-1980s. From this program, the microorganism *Saccaropolyspora spinosa* was isolated from a Caribbean island soil sample, and the insecticidal activity of the spinosyns, a family of unique macrocyclic lactones, was identified and developed by Dow AgroSciences as highly selective, environmentally-friendly insecticide.

In Latin, "saccharopolyspora" means "sugar-loving, with many spores", and "spinosa" refers to the spiny appearance of the spores. The microorganism is an aerobic gram-positive, non-acid fast, nonmotile, nonfilamentous bacterium. Most of the activity is produced by a mixture of spinosyn A and spinosyn D, assigned the common name of spinosad. Spinosad combines highly efficacious control of many chewing insect pests, in cotton, trees, fruits, vegetables, turf, and ornamentals with superior environmental profile, mammalian and non-target safety. Insects exposed to spinosad exhibit classical symptoms of neurotoxicity, including lack of coordination, prostration, tremors, and other involuntary muscle contractions eventually leading to paralysis and death. Detailed investigations of the symptomology and electrophysiology have indicated, however, that spinosad is not acting through any known mechanism. It appears to effect insect nicotinic and gamma-aminobutyric acid receptor function through a novel mechanism.

Spinosad presents a favorable environmental profile. Spinosad does not leach, bioaccumulate, volatilize or persist in the environment. Hundreds of innovative product development trials conducted over several years characterized the activity and determined that spinosad left 70 to 90% of beneficial insects and predatory wasps unharmed. The low levels of mammalian toxicity result in reduced risk to those who handle, mix and apply the product. Similarly, relatively high margins of safety for avian and aquatic species translate into reduced or non-existent buffer zones and fewer regulated non-target compliance measures. These advantages allow growers to control damaging crop pests with fewer concerns about human or environmental safety and costly secondary pest outbreaks.

The first product containing spinosad (Tracer Naturalyte™ Insect Control) received expedited review by the U.S. EPA and was granted registration as a "reduced risk" insect control product for cotton in early 1997. Additional registrations, introduced as SpinTor™, Success™, Precise™, and Conserve™, have recently been granted for insect control in vegetable and tree crops and in the urban environment for control of turf and ornamental plant nests.

Entries from Academia

Professor Richard P. Wool, University of Delaware

Affordable Composites from Renewable Sources (ACRES)

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

Professor Krzysztof Matyjaszewski, Department of Chemistry, Carnegie Mellon University

Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a new technology that allows for the development of novel, high-performance polymeric materials. The process utilizes a transition metal catalyst, which can be recycled, to mediate the control of a radical polymerization. The polymerization process allows for the direct preparation of polymer in bulk monomer, precluding the use of volatile organic compounds (VOCs) to moderate the rate of polymerization. Additionally, ATRP can be conducted in environmentally friendly solvents such as water or carbon dioxide (CO_2). The products prepared by ATRP are advanced materials that can help solve current and future environmental/health concerns. An example is the preparation of self-plasticizing poly (vinyl chloride) (PVC), which can be used to replace harmful phthalates that are currently used to soften PVC used in children's toys.

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

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.

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% 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 (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

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

It has been established that emissions of carbon dioxide gas are responsible for about half of the increase in global warming. Efforts to decrease the consumption of fossil fuels are limited by increasing human population and industrialization and the fact that alternatives to fossil fuels 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 regard, a unique bioprocess has been developed that 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 requires anaerobic conditions, which requires that carbon dioxide gas has to be separated from oxygen and is an expensive 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% 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 electrodialytic fermentation to acetic acid and methane in a batch reactor with yields of over 85% to acetic acid and 89% 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.

Biosynthetic Production of p-Hydroxybenzoate Improves Regiospecificity and Minimizes Byproduct Generation

Steven W. Peretti, Department of Chemical Engineering, North Carolina State University

The work of Steven W. Peretti at North Carolina State University illustrates the utility of biocatalysis in effecting green chemistry by focusing on the development of an innovative, alternative, biosynthetic pathway for the production of p-hydroxybenzoate (HBA). Biocatalytic production of HBA provides improved regiospecificity over the two-step Kolbe-Schmitt carboxylation of phenol, the current state of the art. Due to the specificity of enzyme catalyzed reactions, significant source reductions in the generation of waste byproducts are obtained. Increased levels of safety for both the environment and human health are achieved due to the mild reaction conditions employed. HBA production can now be achieved by a single processing step, a unique feature that cannot be accomplished using traditional chemistry.

HBA production is achieved by contacting an active cell mass with toluene. The toluene passively diffuses into the cells and is transformed through a series of intracellular enzymatic reactions to HBA. Since the pathway for HBA catabolism is blocked through the use of chemical mutagenesis, the HBA generated from toluene conversion is neither incorporated into cellular material nor oxidized for energy, but instead is secreted out of the cell and into the culture media. The HBA can then be recovered by precipitation from an acidified process stream following removal of cell mass.

Albert Robbat, Jr., Chemistry Department, Tufts University

Cheminfomatics: Faster, Better, Cheaper Chemical Analysis Software

Mass spectrometry (MS) data analysis algorithms have been developed that, when combined with large-volume gas chromatography (GC) sample injection, provide quantitative analysis of a wide range of EPA targeted pollutants in <10 min and semiquantitative data in five min by GC/MS. Soil analysis data were produced in the field, verified by EPA, and used to determine risk to ground water and to delineate the extent of contamination within the airfield at Hanscom Air Force Base. The proposed technology significantly reduces sample preparation time, solvent consumption, the need for multiple methods of analysis to analyze the wide range of EPA target compounds, and improves laboratory productivity by a factor of 3 to 6. In addition to MS, the core algorithms are applicable to any detection system that produces narrow band, characteristic signals including atomic emission detection (AED) for metals. For example, the same deconvolution algorithms should untangle overlapping spectral signals, as they do for GC/MS, in techniques such as liquid chromatography/MS (LC/MS), capillary electrophoresis/MS (CE/MS), and inductively coupled plasma/AED and MS applications. Faster run times mean less solvent consumption when operating LC/MS and CE/MS instruments. This is especially important when one considers the explosion in the number of LC/MS assays that will be required in the biopharmaceutical markets now that one chemist can synthesize 1,000 to 10,000 new compounds per year as compared to 10 because of advances in combinatorial chemistry technology.

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 multistep 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 multistep 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 predispersed 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 pretreatment 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 Rubberized Concrete From Recycled Rubber Tires

Dr. Dharmaraj Raghavan, Department of Chemistry, Howard University

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. The technology to reuse rubber tires into cement system yields value-added infrastructural material, while eliminating the imminent threat of health hazard and explosion potential because of the flammable nature of rubber tires.

Gregory Moller, Holm Research Center, University of Idaho

Effects of the Corrosion of Elemental Iron on Heavy Metal Contamination from Pyrite Oxidation

The activity of corroding iron metal is examined in the acid rock drainage (ARD) to determine the effectiveness in neutralizing the ARD and reducing the load of dissolved heavy metals in solution and soils. In acidic solution, iron hydrolyzes water producing hydride and hydroxide ion resulting in a concomitant increase in pH, decrease in Eh, and removal of dissolved heavy metals by a variety of mechanisms. A colloidal iron batch reactor effectively treats ARD from Berkeley Pit, Montana. Iron columns effectively treat soil column water and model ARD solution leachates. A model ARD solution (bisulfate buffer pH = 4) with dissolved zinc was treated with colloidal metallic iron. Kinetic studies demonstrated the first order dependence of the initial rate of reaction on the surface area of metallic iron where the rate of the disappearance of zinc is –rZn = 1.2*AFe. The reaction half-life of dissolved zinc removal from solution was 140 minutes. X-ray diffraction analysis of the oxidized bulk solids from these experiments indicated green rust, magnetite, and goethite structures. Corroding iron also creates a reducing environment supportive for sulfate reducing bacteria (SRB) growth, increasing populations 5,000 fold to provide sulfidogenesis as an additional pathway to further stabilize heavy metal precipitates.

Craig L. Hill, Department of Chemistry, Emory University

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

Effluent-Free Process for Use of Oxygen in Place of Chlorine Compounds in Wood-Pulp Bleaching

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

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

The new catalytic biomimetic approach uses versatile, nontoxic, and inexpensive inorganic clusters known as polyoxometalates (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, O_2 is added to the bleaching liquor and the same POM catalyzes the complete conversion (mineralization) of the dissolved lignin fragments to CO_2 and

H_2O. The two steps sum to the selective removal of lignin from wood, using only air and water, an ideal process that only nature has achieved to date. This biomimetic and catalytic technology eliminates the environmental problems associated with conventional chlorine-based processes while overcoming the limitations inherent in other chlorine-free pulp bleaching strategies. It is green in at least six ways including the complete elimination of waste streams (a "closed process" is achieved). The high selectivity entails less consumption of the natural renewable resource, wood. It is energy efficient and as current analyses indicate, cost-effective.

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

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

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 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 yeasts 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 O_2 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

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

In view of increasing demands to reduce emissions during the production of chemical and pharmaceutical end-products, it is imperative to consider the development of effective carbon-carbon bond forming reactions in aqueous media. The work of Dr. Leo A. Paquette at The Ohio State University demonstrates not only that the counterintuitive 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.

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

Polaroid Corporation

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.

Chi-Huey Wong, Ernest W. Hahn Professor of Chemistry, The Scripps Research Institute

Enzymes in Large-Scale Organic Synthesis

This nominated project is concerned with Wong's original contributions in the development of novel enzymatic and chemo-enzymatic methods for large-scale organic synthesis. Three significant achievements in this field include: a breakthrough technology for oligosaccharide synthesis using genetically engineered glycosyltransferases coupled with in situ regeneration of sugar nucleotides, which has enabled the large-scale synthesis of complex carbohydrates for clinical evaluation; the use of enol esters (e.g., vinyl acetate and isopropenylacetate) in enzyme-catalyzed transesterification reactions, which has been a widely used method for enzymatic synthesis of enantiomerically pure hydroxy compounds; and the use of recombinant aldolases for asymmetric aldol reactions, which has opened a unique and practical route to novel monosaccharides and related structures, including, for example, sialic acids, L- configurated sugars, and iminocyclitols. Other important enzymatic methods developed by Wong include the synthesis of glycopeptides, glycoproteins, chiral amines, prostaglandins, and numerous chiral synthons. All these synthetic transformations are environmentally friendly for use in large-scale processing and are important for the pharmaceutical and fine chemical industries. They are, however, impossible or impractical to achieve by nonenzymatic means.

Dr. Richard H. Fish, Lawrence Berkeley National Laboratory, University of California

Fluorous Biphasic Catalysis: A New Paradigm for the Separation of Homogeneous Catalysts From Their Reaction Substrates and Products, as Demonstrated in Alkane and Alkene Oxidation Chemistry

Fluorous biphasic catalysis (FBC) is a new concept for homogeneous catalysis where the fluorocarbon soluble catalyst and the substrates/products reside in separate phases. The work of Dr. Richard H. Fish, Lawrence Berkeley National Laboratory, presents the synthesis of a novel fluoroponytailed ligand, tris-N-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN), that is soluble in the perfluoroalkanes [$Mn(O_2C(CH_2)_2C_8F_{17})_2$] and [$CO(O_2C(CH_2)_2C_8F_{17})_2$]. The initial results on the functionalization (oxidation) of alkanes/alkenes, using in situ generated fluorous phase soluble R_fMn_2+-R_fTACN and R_fCo_2+-R_fTACN complexes ($R_f = C_8F_{17}$) as the precatalysts, in the presence of t-butyl hydroperoxide (t-BuOOH) and O_2 gas as oxidants, demonstrated that alcohols, aldehydes, and ketones could be produced catalytically and that the oxidation products and fluorous phase soluble precatalysts were indeed in separate phases. The fact that fluorocarbon solvents are relatively nontoxic provides the FBC concept with an entry to the new "Green Chemistry" regime of being environmentally friendly, and therefore, attractive to a wide variety of industrial processes for the ultimate catalytic production of important organic chemicals worldwide.

Generation of Hydrogen Peroxide in Carbon Dioxide

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

Hydrogen peroxide is currently produced via the sequential hydrogenation and oxidation of a 2- alkyl anthraquinone. While H_2O_2 is generally considered to be a green reagent, the anthraquinone process generates several waste streams and also exhibits inefficiencies from both a raw material and energy use standpoint. Functionalized anthraquinones (FAQ's) have been generated that are miscible with carbon dioxide, thus making it possible to generate hydrogen peroxide in liquid CO_2. Use of CO_2 as the sole process solvent ameliorates several environmental and engineering problems inherent to the process, including (a) eliminating the contamination of the product during its recovery by liquid-liquid extraction into water, (b) minimizing degradation of the anthraquinone during hydrogenation by allowing control of residence time distribution in the reactor, and (c) optimizing throughput through each reactor via elimination of mass transport limitations, which also reduces energy input. Not only is the use of CO_2 as a solvent a green route to hydrogen peroxide manufacture, but it is also economically feasible owing to the ability to recover the product without employing a large pressure drop, ready recycling of the functionalized anthraquinone, and operation at relatively low absolute pressure and in concentrated solution owing to the characteristics of the FAQ-CO_2 phase diagram.

Green Chemistry Through the Use of Supercritical Fluids and Free Radicals

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

The research of Professor James M. Tanko at Virginia Polytechnic Institute and State University explores the use of supercritical carbon dioxide (SC-CO_2) as a replacement for many of the toxic and/or environmentally threatening solvents used in chemical synthesis. The project demonstrated that SC-CO_2 is a viable, "environmentally benign" alternative, and there are numerous advantages from a chemical perspective associated with the use of SC-CO_2. This work led to the development of a new, environmentally friendly chemical process for hydrocarbon functionalization and C-C bond formation.

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

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

Green Separation Science and Technology: Using Environmentally Benign Polymers to Replace VOCs in Industrial Scale Liquid/Liquid or Chromatographic Separations

One area of opportunity for new chemical science and engineering technology, which will help meet the goals of Technology Vision 2020, is the development of new separations technologies that eliminate the use of flammable, toxic VOCs as industrial solvents. Used in conjunction with, or instead of, appropriate current manufacturing processes, such technologies would help to prevent pollution and increase safety. The nominated technologies are based on the use of water soluble polyethylene glycol polymers in either liquid/liquid (aqueous biphasic systems—ABS) or chromatographic (aqueous biphasic extraction chromatographic resins—ABEC) separations. Two patented technologies are highlighted: a) applications in radiopharmacy to allow the use of cleaner neutron-irradiated isotopes rather than fission-produced isotopes, and b) applications in remediation where reduction of secondary waste streams or conventional technologies are anticipated. The separations approach followed in developing these technologies suggest a wider industrial application for VOC-free separations. Within a paradigm of pollution prevention and with industry participation, a tool-box approach to Green Separation Science & Technology can be developed based on the use of environmentally benign polymers.

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

In Vivo Synthesis of Lepidopteran Pheromone Precursors in Saccharomyces Cereviseae: 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, including their acute toxicity to nontarget organisms (including human applicators), their persistence in the biosphere, and major point-source pollution associated with their manufacture. Despite these effects, the scale of release of active ingredients in insecticide formulations into the global environment is enormous; in the United States alone it is more than 400 million kg/year.

Pheromones have been used on a worldwide basis for the control of insect pests for more than 15 years. Unlike conventional broad-spectrum insecticides, pheromones are nontoxic and highly specific for the species they are intended to control. Unfortunately, their effectiveness and selectivity depend upon high chemical and 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 latter goal will significantly improve the economic competitiveness of existing pheromone products, and could provide the basis for the expansion of this promising insect control technology into other markets.

Metal Extraction and Recovery Using Carbon Dioxide

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

Recovery of metals from dilute solution, whether the matrix is solid or liquid, remains a considerable technical and financial challenge. Methods currently exist whereby metals can be extracted from either type of matrix, yet these methods consume significant quantities of reagents and can also generate multiple waste streams in the process. Technology developed in the lab of Eric J. Beckman, University of Pittsburgh, over the past three years allows efficient application of environmentally benign CO_2 to a number of separation problems involving metals. For example, biphasic mixtures of CO_2 and water have been employed as a green acid leach medium. Metals have been extracted from a steelmaking process residue and then recovered as metal carbonates through depressurization. In this process, metals are extracted and recovered without the use of reagents other than CO_2 and water, and CO_2 is sequestered as a solid. In addition, through synthesis of CO_2-miscible phase transfer agents, CO_2 can replace the organic solvent currently used in refining of precious metals. The sensitivity to pressure of phase behavior in a CO_2-mixture may allow significant streamlining of the process as well. Finally, CO_2-soluble chelating agents have been used to extract toxic metals from acidic effluent such as that found in plating facilities.

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

Dr. Ajay K. Bose, Stevens Institute of Technology

Microwave assisted organic synthesis is an emerging technology of great potential. Dr. Ajay K. Bose at the Stevens Institute of Technology has contributed to this field through the development of nontraditional methods for using domestic microwave ovens for conducting a wide variety of organic reactions that are fast, safe, and friendly to the environment. Dr. Bose's group has shown that for a wide variety of reactions, microwave irradiation of reaction mixtures in open glass vessels can lead to faster reaction rates, fewer byproducts, and higher steric control. 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 (e.g., organic solvents for reactions and recrystallization and chromatographic material for purification). 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.

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

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 µL of liquids on average); new methods for determining physical properties; milder and safer alternative reaction conditions; alternative benign solvents; and different 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 2,000 institutions in the United States have, either fully or partly, adopted this approach. NMC_2 is also the lead site of an international consortium promoting the microscale/Green Chemistry revolution.

H. Alan Rowe, Department of Chemistry/Center for Materials Research, Norfolk State University

New Reducing Sugar Assay

The chemical measurement of reducing sugars [sugars containing hemiacetal/hemiketal groups] is common in biochemical research and teaching laboratories. The currently available methods depend on the reaction of copper ions in hot alkaline solution with complexing and color-forming reagents. Typically, tartrate is used as the complexing agent and a solution of molybdenum and arsenate ions for the color-forming reagent [the arsenomolybdate reagent]. The arsenomolybdate reagent has a limited shelf-life and is extremely toxic. This presents formidable problems in the use and disposal of the assay solution. This solution must be stored as waste and disposed of commercially. The original assay outlined here is a procedure that uses a more stable complexing agent (EDTA) and replaces arsenate with phosphate in the color-forming complex. The materials produced in this assay are much more benign.

Dr. Dharmaraj Raghavan, Department of Chemistry, Howard University

Novel Applications of Polymer Composite from Renewable Materials

Metal corrosion costs the United States about 4.2% 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 the surface involves paint stripping and application of a fresh paint coating. Traditional stripping methods employ the 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 depainting aircraft. One method that has proved reliable is dry-blasting to remove the paint coating mechanically. The depainting 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% 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 that 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 a worldwide market approaching $1 billion, annually. Membranes have found wide applications in industry, particularly in the separations industry. 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 compatabilizer-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 that are environmentally safe and can be used in the synthesis of renewable polymer.

Novel Chemical Analysis Technologies by Water Liquid Chromatography, Raman Spectroscopy, and High Speed Gas Chromatography

Dr. Robert E. Synovec, Department of Chemistry, University of Washington

Dr. Robert E. Synovec's research addresses the development of novel liquid and gas chromatographic chemical analysis technology and related methodologies that are consistent with the goals of the Green Chemistry Program and pollution prevention. The goal of this research has been to develop unique chromatographic instrumentation and methods for laboratory, field, and process analysis that reduce the toxicity and volume of consumable materials used in separations-based analyses, while enhancing the performance and information gleaned from the analyzer. This goal is a major research initiative at the Center for Process Analytical Chemistry (CPAC). The chemical analyzers and methodologies that have been produced by these research efforts benefit U.S. industry by enhancing the applicability of liquid and gas chromatography in a variety of arenas: routine and automated EPA methods, industrial process chemical analysis, conventional bench-top analysis, and remote chemical monitoring. A reduction in industrial pollution is a key result of these technologies, by minimizing chemical waste through optimum process control.

Novel In Situ Zeolite Coatings in Monoliths

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

A novel, in situ method of depositing binderless zeolite catalysts in monolith reactor systems has been developed at the University of Cincinnati. In situ coatings of zeolites on monolith substrates maximize 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. The main technical advantages of monolith reactors are 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 C_{12}, 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% 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 solvent, 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.

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

A 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 been increasing due to an increase in the world 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 minimization and recycling at wastewater treatment facilities.

An innovative process was developed to convert biosolids to carbon-based sorbents and catalysts. The feedstocks for the process were biosolids produced at a sewage treatment plant (Spring Brook Water Reclamation Center in Naperville, Illinois) and wastewater treatment sludge produced in the paper mill industry (Fort James Corporation in Green Bay, Wisconsin). The research conducted at the Illinois Institute of Technology suggests two new innovative ideas for the production of activated carbon from carbonaceous waste material: 1) exposure of the chemically activated raw material to light and humidity in a controlled environment can enhance the surface pore structure of activated carbons by about 20%, and 2) the time and energy required for the drying of sludge can be reduced by about 98% if microwave drying is used. The surface properties of the produced carbons were effectively controlled by varying different chemical, surface, and physical activation processes. This project demonstrates a tremendous potential for alleviating serious environmental problems associated with the mass production and disposal of untreated sludge by development of a process for converting sludge to activated carbon and catalyst.

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

Dr. Lee R. Lynd, Department of Engineering, Dartmouth College

This project addresses technical and visionary issues associated with utilizing plant biomass, the only foreseeable sustainable source of organic fuels, chemicals, and materials. The project involves multiple topics related to consolidated processing, a widely applicable potential breakthrough in cellulose processing entailing production of cellulose enzymes, hydrolysis of biomass components, and fermentation of resulting soluble carbohydrates in a single process step. Additional project elements aimed at overcoming the recalcitrance of cellulose biomass encompass aspects of applied enzymology and microbiology, kinetics and reactor design for enzymatic hydrolysis of cellulose, pretreatment of biomass using compressed hot water, and conversion of paper sludge. Process design and analysis work support the contention that advanced biomass-based processes have the potential to be cost-competitive with petroleum-based processes even at low oil prices. Accomplishments involving resource and policy analysis include analysis that identifies and explores the potential of biomass-based processes to have near-zero net CO_2 emissions, prioritizes among uses for the large but ultimately limited biomass resource, and seeks to reconcile the vast range of estimates for the magnitude of potential biomass availability for industrial uses.

Pollution Preventing Lithographic Inks

Professor E.L. Cussler, Department of Chemical Engineering and Materials Science, University of Minnesota

Conventional printing techniques use solvents that contribute to pollution through evaporation and cleaning processes. Professor Cussler has developed a new ink that eliminates these emissions. A pollution preventing lithographic ink works conventionally at pH less than 7, but becomes its own emulsifying agent at higher pH. As a result, it can be washed off printing presses with aqueous base. The emulsification kinetics are not predicted by conventional correlations. Instead, they are consistent with an interfacial reaction between hydroxide and ink resin, which produces a soap layer that can be removed by shear. The results imply a strategy for other pollution preventing technologies.

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 provide a realistic approach to green chemistry and allow academic institutions to institutionalize lasting behavioral changes. SSC provides an easy to implement, affordable, and wide application remedy to a real environmental management problem faced by most college and university chemistry programs.

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

Solvent-Free Chemical Synthesis

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 $NaIO_4$-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. Nancy W.Y. Ho, Laboratory of Renewable Resources Engineering, Purdue University

Successful Development of Hazard-Free, User-Friendly Genetically Engineered Microorganisms for Effective Production of Environmentally Friendly Chemicals from Renewable Biomass using Green Chemical Methodologies

Ethanol is an effective, environmentally friendly, nonfossil transportation biofuel that produces far fewer pollutants than gasoline. Furthermore, ethanol can be produced from plentiful, domestically available, renewable cellulosic biomass, thereby reducing our nation's dependence on imported oil. Although ethanol has been produced by the fermentation of glucose-based feedstocks with *Saccharomyces* yeasts since the preindustrial age, the conversion of cellulosic biomass to ethanol has presented a major challenge. This is because cellulosic biomass contains two major sugars, glucose and xylose, and the *Saccharomyces* yeasts cannot ferment xylose to ethanol. Dr. Ho, at Purdue University, has developed genetically engineered *Saccharomyces* yeasts that not only ferment xylose, but effectively coferment glucose and xylose to ethanol. The genetically engineered yeasts produce at least 30% more ethanol from cellulosic biomass than the unengineered parent yeasts.

Lactic acid, an important industrial feedstock in the manufacture of inexpensive, biodegradable plastics from renewable biomass, is traditionally produced by the fermentation of glucose with lactic acid bacteria. Lactic acid bacteria, however, grow very slowly and cannot tolerate 1 to 2% lactic acid. Dr. Ho's group has succeeded in genetically engineering a safe, effective microorganism that can produce lactic acid more than twice as efficiently as lactic acid bacteria. These examples demonstrate that genetic engineering technology, guided by the principle of green chemistry, is a powerful tool in modifying microorganisms for the production of important chemicals from renewable biomass.

Synthetic Dyes Based on Toxicological Considerations

Harold S. Freeman, Ciba-Giegy Professor of Dyestuff Chemistry, North Carolina State University

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

This investigation led to the discovery of nontoxic alternatives to high-volume chromium-based commercial black dyes, without compromising the desirable photostability of the latter. In addition, red and blue 1:2 Fe-complexed dyes (1 iron atom per 2 dye molecules) were discovered, an achievement heretofore unreported and presumed unachievable. An explanation for the dull colors that have traditionally characterized Fe-complexed dyes was also developed, providing a basis for further achievements in this area.

Toward Synthetic Methodology "Without Reagents" Increased "Effective Mass Yield" for Pharmaceuticals by Tandem Enzymatic and Electrochemical Oxidations and Reductions

Professor Tomas Hudlicky, Department of Chemistry, University of Florida

The prevention of pollution at its source is addressed by the replacement of currently used methods of oxidation and reduction (i.e., all based on metal reagents) with enzymatic and electrochemical techniques (i.e., all performed in water, alcohols, or other environmentally 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.

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

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

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

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

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 nontoxic precursors, and minimizing energy consumption. Professor Weimer and his students have demonstrated model ceramic synthesis systems that 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.

Washington State Pollution Prevention, Health, and Safety Initiative in Academic Chemistry Laboratories

Washington State Department of Ecology

In 1997, the Washington State Department of Ecology and the Educational Service District 101 began planning workshops to educate chemistry teachers on green chemistry techniques, health and safety issues, and proper hazardous waste management. The workshops included detailed information on better laboratory practices that reduce the risk of accidents, maintain employee and student health and safety, and reduce the use of hazardous substances and generation of hazardous waste. Green chemistry techniques such as microscale chemistry and conducting experiments that use only nontoxic substances or less toxic chemicals were also taught. The workshops also included environmental, health, and safety regulations that schools must observe in the state of Washington. A Step-by-Step Guide to Better Laboratory Management was produced and used as part of the workshops.

A coordinated multiagency team was formed to plan and implement the workshops. Six workshops were held throughout the state of Washington in the spring of 1998. Ecology, ESDs, OSPI, Washington State Department of Health and Washington State Department of Labor and Industries developed and implemented the workshops. Over 300 chemistry instructors attended throughout the state.

Ecology trained six staff members and King County Hazardous Waste Program (Metro) staff to conduct site visits at middle and high schools throughout the state of Washington. The lab team was trained to: 1) Organize chemicals in compatible storage system; 2) Tag or remove chemicals of concern that are extremely hazardous, unstable, in poor condition or in excess; 3) Sort waste chemicals into Department of Transportation shipping categories; 4) Labpack waste chemicals for shipping and disposal; 5) Explain proper hazardous waste management and disposal; 6) Assist with preparing a chemical hygiene plan for laboratory; 7) Assist with creating a complete and up-to-date chemical inventory. To date, about 100 schools have been visited.

Waste Biomass Utilization in the Production of a Biodegradable Road Deicer

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

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 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% lactose and 0.1 to 0.8% lactic acid. About 50% 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. The bulk of this expenditure is on the application of chemical deicers, principally sodium chloride (NaCl). 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 Mathews' work 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 9% compared to 53% 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 that can be used in the production of CMA/CMP deicer).

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

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

The primary objective of the work of Dr. Claudia Lage Nassaralla at Michigan Technological 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 being developed by Dr. Nassaralla has the potential to minimize the formation of Cr^{6+} by carefully controlling the brickmaking and steelmaking 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 on site, 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

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

Rather than sacrificing one or the other, to synchronize the advancement of science and technology with 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 nontoxic, nonexplosive, nonflammable, 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

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

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

Waterborne magnetic tape coating formulations were designed at the University of Alabama and used to prepare experimental magnetic tape samples in a pilot coating trial. The formulations contained a blend of a water-dispersed polyester and an ethylene/vinyl chloride copolymer emulsion. The coatings were thermally cured with a melamine-formaldehyde cross-linker to give tensile properties that were comparable to a standard solvent-based binder composition. The pilot tape trial used existing processing equipment, including calendering and slitting. The tape had good magnetic properties and excellent adhesion between the pigmented magnetic layer and the base film, easily exceeding the 8 mm helical scan tape standard of 0.96 N peel force. An economic impact analysis for the case of using the waterborne video tape coating process in a conventional tape manufacturing plant showed an 11 percent decrease in hourly operating costs. The solvent-based process generated almost 650 kg of organic solvent per hour operation, while the waterborne process generated less than 5 kg methanol (from the melamine-formaldehyde cross-linker) per hour. In addition to pollution prevention, there was a clear economic incentive to adopt the waterborne video tape manufacturing process.

Entries from Small Businesses

BIOCORP, Inc.

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 serviceware, and packagings. Mater-Bi™ is a product technology that offers enormous advantages for dealing with the problems of solid waste disposal. Disposal of conventional plastic products, which constitute the largest share of disposable products, has a significant negative impact on the environment. Typically, 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. Biodegradables are being developed for medical products, textiles, and other new and significant applications. Such products can be transformed into much needed composts and soil amendments for agricultural and horticultural use. Mater-Bi™ resin used for films and sheets is made of starch and a polymer, polycaprolactone. Biodegradation time is between 20 and 45 days in composting conditions. Mater-Bi™ resin used for dimensionally stable injection molded items is made from completely natural products, including cotton seeds and cornstarch. Biodegradation time is between 75 and 120 days in normal composting conditions.

Burch Company

Burch Apparatus and Method for Selectively Treating Vegetation to Reduce Pesticides 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, and fertilizers (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.

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

CerOx Corporation

CerOx (Cerium Oxidation) Corporation has commercialized its process for destroying hazardous organic waste streams. The unique process, which converts toxic wastes into CO_2 and water, 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 3 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.

Chemically Modified Crumb Rubber Asphalt

SaLUT Inc.

A process was developed for producing Chemically Modified Crumb Rubber Asphalt (CMCRA). The Chemically Modified Crumb Rubber (CMCR) was produced by using H_2O_2 (free radical generator; in this case, carbonium ion generator) to produce carboxylic sites on the surface of crumb rubber by utilizing the oxygenated sites of carbon black [these oxygenated sites will obtain hydrogen from a source and then be converted into carboxylic acid (COOH) groups]. These sites in crumb rubber could possibly be the cause of devulcanization and could interact with functional groups available in asphalt, resulting in a homogenous modified asphalt. Compared to controls, asphalt modified using this process has improved rheological properties at both low and high temperatures, as well as improved separation and homogeneity characteristics. Several asphalts were tested and were found to have improved rheological properties (high and low temperature), homogeneity, and separation characteristics. Since rubber, the main component of CMCR, is known as a poor conductor of heat, it is probable that CMCRA can be used in constructing asphaltic pavements at lower pavement temperatures than other neat or modified asphalts. The first pavement test installation was successfully made at a lower pavement temperature than that recommended by the Connecticut Department of Transportation, suggesting that CMCRA can extend the pavement construction season.

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

Synthon Corporation

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) nearly 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.

Burlington Chemical Company

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

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

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

High Energy Efficiency, Environmentally Friendly Refrigerants

Environmental Technology and Education Center, Inc. (ETEC)

Environmentally safe alternatives to CFC, HCFC, and HFC refrigerants are badly needed. The phaseout of CFCs and HCFCs and increasing concern about greenhouse gases create the urgent need for nontoxic, nonflammable, environmentally safe refrigerants with high capacity and energy efficiency. Dr. Jonathan Nimitz and his co-inventor, Lance Lankford, have discovered and patented a family of improved refrigerants based on blends containing trifluoromethyl iodide (CF_3I). CF_3I has attractive physical properties, is a combustion inhibitor, has zero ozone depletion potential (ODP), low global warming potential (GWP), and relatively low toxicity. CF_3I can be combined with high-capacity, energy-efficient, environmentally friendly, but flammable refrigerant compounds to obtain excellent refrigerant blends that remain nonflammable. The result is an energy-efficient, environmentally friendly, safe refrigerant.

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

The LCAPIX Module Software: Combining Life Cycle Assessment with Activity Based Costing to Assist in Preservation of the Global Environment and Sustained Economic Growth

KM Limited Inc.

Life cycle assessment (LCA) is a technique that was developed in the late 1960s to address the socioeconomic and politically charged issues of use and reuse of all man-made products, processes, or services. The LCAPIX module is a software tool that efficiently enhances facilitation of both the LCA process and entices industrial management (of chemical and other industries) to perform these studies by yielding a simultaneous activity based cost (ABC) analysis .

By using an industrial engineering approach employing drivers and driver values, the model and relational database provides for a unique combination of two strategies that complement and enhance the implementation of an Environmental Management Strategy (EMS). This software tool has been used to compare different products, processes, and services for not only their potential environmental burden potential (i.e., using different valuation techniques such as selected weighted emphasis on global warming, ozone depletion, acid rain, deforestation, or biodiversity), but also to understand and illustrate how different techniques can be used to diminish these burdens while improving internal, external, unseen, or unknown (“hidden”) costs. This software tool is multifunctional, providing inexpensive, simple, rapid LCA strategic or environmental comparisons of any product, process, or service.

TechMatch, Incorporated

N-Methylmorpholine-N-Oxide (NMMO): A Novel, Nontoxic 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 a strong base to produce a xanthate complex. Carbon disulfide is highly flammable and toxic to humans as well as being a greenhouse gas. Further, to produce fibers the xanthate must be regenerated by extrusion into an acid coagulating bath where it decomposes and produces polluting byproducts that are discharged into water.

Novon International

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 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 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.

Solvent Kleene Inc.

Nonhazardous 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 Trichlorotrifloroethane (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 nonhazardous 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.

Nontoxic Antifouling

International Metalizing Corporation

IMC has developed a process to apply pure copper to a variety of substrates including aluminum, wood, fiberglass, and steel as a near permanent nontoxic 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.

Paclitaxel Process Improvements

Hauser, Inc.

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 anticancer 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 anticancer 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% decrease in the cost of manufacturing paclitaxel.

BAT Technologies Inc.

Primer for Anti-Fouling Paint

This technology and material is a primer to be used in conjunction with the bottom paint (anti-fouling paint) that is found on the bottoms of all ocean-going boats. Every ocean-going boat must have its anti-fouling paint removed and reapplied every year. Current technology mandates that the paint be sanded off. The resultant powder is dangerous; it is blown into the water and inhaled by the people sanding the bottom of the boat. Every year, 1.5 million pounds of copper oxide paint dust are dumped into the ocean in the United States alone.

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

Radiance Services Company

The Radiance Process: A Quantum Leap in Green Chemistry

The Radiance Process is a novel, dry, nontoxic cleaning technology for surface preparation. It employs the quantum mechanical effects of laser light in combination with an inert gas, ordinarily nitrogen, to clean surfaces. The light lifts the contaminant from the surface and the flowing gas sweeps it away without the pollution now associated with surface cleaning. The process has potential application in the manufacturing of semiconductors, photomasks, flat panel displays, storage media, and optics. Radiance cleans without emissions, discharges, or wastes, thus preventing pollution and conserving natural resources. It is designed to supplant the use of wet chemicals in surface cleaning and preparation.

Nextec Applications, Inc.

Solventless Process for Improving Fabric Performance Properties

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

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

Arkenol, Holdings, L.L.C.

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 uses innocuous and renewable feedstocks. The Arkenol process utilizes concentrated sulfuric acid to break down the cellulosic structure in lignocellulosic feedstocks and then, with water, complete the new formation of individual C6 and C5 sugars for further processing into chemicals and fuels. The lignin is processed for soil amendment or solid fuel. Silica, uniquely present in rice straw, can be recovered and converted to high value precipitated silicas or zeolites. Trace amounts of sulfuric acid in the sugar solution are converted into gypsum for soil amendment or ammonium sulfate for fertilizer. The sugars can be converted into alcohols and carbon dioxide, acids, ethers, solvents, or surfactants either by direct chemical conversion or through fermentation or a combination of both.

The successful implementation of Arkenol's technology will lead to decentralized and economic production of fuel ethanol and other biobased chemicals. Arkenol's ability to use a wide variety of feedstocks will enable placement of production facilities (or "biorefineries") near the market for the products. Large scale conversion of waste materials into fuels and chemicals is a novel solution to waste management, pollution prevention, and economic development.

Total Impact Program—An Environmentally Preferable Program for Laundry

Anderson Chemical Company

Anderson Chemical Company's Total Impact Program® employs chemistry with a more positive environmental profile for human health and the environment than that used in conventional laundry systems. The TIP® program incorporates a neutral pH detergent enhanced with enzymes and surfactants that pose low environmental concerns, oxygen bleach, and biodegradable softeners. The program also saves water and energy and extends fabric life. The program targets three main impact areas: user safety and health, environmental impact for pollution prevention via source reduction, and efficiency through resource consumption reduction by decreasing processed pound costs (decrease in water consumption, energy costs, and reduced effluent costs resulting from volume and pH factors).

Waste Oil Source Reduction Through Extended Oil Service Life

AMSOIL Incorporated

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. Used oil generated by households, however, is currently disposed of improperly at an alarming rate nationally—220 million gallons per year as estimated by the U.S. Department of Energy.

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

Zero-Waste Dry Plating of Cadmium

IonEdge Corporation

Electroplated cadmium is widely used in the defense and aerospace industries for the corrosion protection of steels. Cadmium, however, is a known toxic material. In addition, the electroplating process generates large quantities of toxic sludge and effluents. A typical medium-sized electroplating shop, for example, discharges well over 100,000 gallons of effluents daily and disposes 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% 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 compounds, 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 environmentally 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 eliminate significant solvent use, satisfying environmental, health, and safety concerns. Watershield eliminated hazardous materials in an 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.

Entries from Industry and Government

Morton International, Inc.

ADVAFLEX™ Organic Stabilizer

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

ADVAFLEX™ is an entirely new concept in PVC heat stabilizer technology that offers numerous advantages over conventional stabilizers. First and foremost, these are two-component systems containing new organo-sulfur chemistry and low levels of metal activators such as zinc. The performance advantages include excellent thermal performance, competitive costs, good secondary performance attributes, compatibility with co-additives chemistries, and simplicity of PVC formulation. The environmental and health benefits include very low metal content (as low as 0.4%); low odor and volatility; and the absence of barium, cadmium, lead, phosphorous, alkylphenol, and other aromatic chemicals that are used in conventional technology. ADVAFLEX™ has undergone a thorough toxicity screening that demonstrates the product is essentially nontoxic, and not mutagenic, carcinogenic, or environmentally hazardous. The metal activators in ADVAFLEX™ formulations are generally required at catalytic levels and the preferred metal, zinc, is a required element of the human diet. ADVAFLEX™ technology is a commercially attractive alternative that improves on all aspects of conventional technology, especially with respect to human and environmental safety.

IMC-Agrico Company

AGROTAIN–(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% in 1962 to 37% in 1986 for urea. There are many reasons for this increase. Urea is a source of nitrogen for crop fertilization that is easily handled and transported, higher in nitrogen content than other common solid nitrogen fertilizers, and can be readily bulk blended with other fertilizer components such as potassium chloride, diammonium phosphate, and other materials to prepare multinutrient fertilizers. While urea has many advantages over other nitrogen sources and has already captured a greatly increasing market share, a major drawback to the use of urea is its tendency to lose a substantial portion of the nitrogen values by ammonia volatilization. These losses can easily exceed 30% 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 (BNPO, 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 lb/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.

Air Liquid PFC Recycle Process

American Air Liquid

Perflourocompounds (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 lifetime 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. This amount could 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 or (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 and demonstrated both the capture and concentration of the PFCs above 95%. In summary, this technology improves the environment by reducing PFC emissions that are targeted by 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

American Society for Testing & Materials (ASTM)

The laboratory-based elemental analysis of nonaqueous 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 five 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.

Ciba Specialty Chemicals Corporation

Ashless Friction Modifier/Antioxidant for Lubricants

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

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

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

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

Pacific Northwest National Laboratory

Biocatalytic and Biomimetic Process for the Synthesis of Nitroaromatic Intermediates and Destruction of Nitrocompounds, Including Explosives

Nitroaryl and nitroheterocyclic compounds—found in antibiotics, radio sensitizers, explosives, dye intermediates, herbicides, and pesticides—require a technology to synthesize and destroy nitrocompounds. The massive stockpiles of explosives alone and the contamination they cause in water, soil, and sediment around the world pose a serious threat to humankind, health, and the ecology. Currently, there are no acceptable technologies or resources to demilitarize aging stockpiles and clean up their contamination. Current stockpiles of energetic materials requiring resource recovery or disposition (RRD) weigh in at about 449,308 tons. Through 2001, over 1.2 million tons will pass through or reside in the RRD account (Joint Ordnance Commands Group, 1995).

A totally different, but significantly similar challenge exists in cleaning up the sites where soil and ground water are contaminated with TNT, RDX, HMX, and other nitro-based explosives. Today technicians use incineration, open burning, and open detonation technologies to eliminate explosives. The cost of incineration is beyond our means and resources, and open burning and detonation are environmentally unacceptable. Researchers at Pacific Northwest National Laboratory (PNNL) have developed a technology solution that is environmentally friendly, offers economic benefits, and can be easily implemented over incineration, open burning, open detonation, and several other technologies.

The PNNL destruction technology uses enzymes (biocatalysts) and biomimetic processes; the synthesis technology uses biocatalysts. The enzymes for these applications were discovered to be ubiquitous in plants, microorganisms, and dairy products. Nitro reductase enzymes from these sources are used to synthesize nitroaromatic intermediates such as hydroxylamines and aminophenols, and were used successfully to synthesize phenylhydroxylamine and p-aminophenol from nitrobenzene, an important industrial chemical for dye and headache medicine using nitroreductase enzymes from spinach.

Spinach enzymes also were used to synthesize 4-hydroxylamino-2,6-dinitrotoluene from 2,4,6-trinitrotoluene, TNT, which can be used in the production of antioxidants. This TNT conversion process provides a "zero" cost alternative for disposing of unusable TNT stockpiles located worldwide. Unlike incineration, the PNNL biomimetic process, based on potassium superoxide, destroys explosives under mild reaction conditions. Contrary to other processes, this technology synthesizes and destroys nitrocompounds at room temperature—without leaving and using organic solvents. These emerging enzyme and biomimetic technologies provide an environmentally benign, safe, and cost-effective method to synthesize and destroy nitrocompounds—including explosives.

The Chemical Kinetics Program

Almaden Research Center, IBM Corporation

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 at IBM for three years for process research and development. Since May 1996, the package has been available globally for a no-cost license through the World Wide Web and is used in many other industries for process research and development because of its exceptional ease-of-use and functionality. It also has been frequently licensed by environmental researchers in universities, corporate and government laboratories, and environmental regulatory agencies to develop models and evaluate hazards.

Albany Research Center, U.S. Department of Energy

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% magnesium (Mg). Because the specifications for most diecast aluminum alloys call for a Mg level of less than 0.1% Mg, the charge must be demagged. The excess Mg is removed through the addition of chlorine (Cl_2) gas, or occasionally through the addition of AlF_3. Most of the demagging reaction schemes use Cl_2 and in practice require 6 lb of Cl_2 gas to remove 1 lb of Mg as $MgCl_2$ (approximately 4,500 lb of Cl_2 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 that 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 Cl_2 gas or AlF_3 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 ($Li_2Ti_3O_7$) 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.

Argonne National Laboratory

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

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

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

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

Designing an Environmentally Friendly Copper Corrosion Inhibitor for Cooling Systems

BetzDearborn, Inc.

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

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

The use of HRA resulted in a five-fold decrease in the amount of copper released to the environment, compared to TTA. Since HRA does not react with oxidizing biocides, considerably less chlorine or bromine is required for prevention of MB activity. A reduction in chlorine usage of 10 to 20% was observed at the above nuclear power plant, and reductions of 35 to 40% have been observed at other industrial sites. Lower chlorine usage means lower amounts of chlorine- or bromine-containing compounds ultimately being released in discharge waters. In addition, substantially lower concentrations of HRA are required for copper alloy protection compared to TTA. At the nuclear power plant trial, the five-fold reduction in the copper discharged was obtained with 2.0 ppm HRA compared to 3.0 ppm TTA. Furthermore, a mass balance showed that only 9% of the TTA was recovered (compared to 90% of the HRA). The TTA loss was due to the reaction with chlorine and the formation of a chlorinated azole. Thus, the use of HRA resulted in a net reduction in the amounts and types of azole and halogenated azole compounds that were released into the environment. Finally, direct measurement of LC50 acute toxicities for fathead minnows, done on site in the plant effluent at the nuclear facility, showed a reduction in toxicity when TTA was replaced by HRA.

Nalco Chemical Company

Designing an Environmentally Sensible Chlorine Alternative (STABREX)

Industrial water treatment is necessary for energy conservation and to ensure a sustainable global supply of freshwater. 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—far more chlorine is used to control microbial fouling in an industrial water treatment compared to any other chemical. An environmentally sensible chlorine alternative is needed because the gas is hazardous, the liquid is not stable, chlorine is too volatile, free residuals do not efficiently control fouling biofilms, combined residuals are not very effective, reactivity with scale and corrosion inhibitors is counterproductive, and disinfection byproducts are toxic.

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

The design and performance benefits of STABREX Microorganism Control Chemical have been proven in 100 billion gallons of successfully treated industrial water since introduction in May 1997. The product is useful wherever industrial water is reused such as in recirculating cooling water, in all sorts of light and heavy manufacturing processes, airwashers, pasteurizers, and in hydrostatic sterilizers. STABREX has replaced 20 million pounds of chlorine or its equivalent in the field, worldwide. Compared to chlorine, the new product is more than 10 times less toxic, generates 50% less disinfection byproducts, is much more effective in controlling microbial biofilms, is many orders of magnitude less volatile, is much simpler to handle and feed, is 50% less reactive with other water treatment chemicals, and degrades an order of magnitude less in storage or transport. STABREX works better, is safer, and is easier to use than current chlorine alternatives.

Tektronix, Inc.

Designing Safer Chemicals: Spitfire Ink

As the information age enters a 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 10 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, solvents, 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 nonreusable 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.

Durable AMPS® Antimist Polymers for Aqueous Metal Working Fluids

The Lubrizol Corporation

The generation and accumulation of metalworking fluids (MWF) mists in the plant environment during metalworking production gives rise to worker health and safety concerns. It is estimated that about 1.2 million workers are potentially exposed to MWFs annually. In response to increasing worker health concerns from MWF mists, the United Auto Workers Union has petitioned the Occupational Safety and Health Administration to lower the permissible exposure limit (PEL) of oil mists in the workplace from the current PEL of 5 to 0.5 mg/m^3. The current mist control methods being used for mist exposure controls have drawbacks. For instance, engineering mist controls based on machine enclosures and mist collection are exorbitantly expensive to install and maintain. The second chemical mist control methods based on using high molecular weight polymers as antimist (AM) additives for aqueous MWFs have found limited acceptability because AM polymers lose their performance due to shear degradation, requiring frequent additions to maintain performance.

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

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

Akzo Nobel

A Durable Hydrodechlorination Catalyst for Selective Conversion of CCl_4 to $CHCl_3$

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 are 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 byproduct 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 to 2% 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.

U.S. Department of Agriculture Forest Service

Effluent-Free Process for Use of Oxygen in Place of Chlorine Compounds in Wood-Pulp Bleaching

NOTE: This project is a partnership between the U.S. Department of Agriculture and Prof. Craig Hill of Emory University. This entry was submitted by each party of the project and therefore was judged in both the academic and industry categories. The project summary appears in the academic entries section on page 12.

Revlon Consumer Products Corporation

ENVIROGLUV™: A Method for Decorating Glass with Radiation Curable Environmentally Friendly Inks

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

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

Envirogluv technology, developed by Revlon, fills the gap in the glass decorating industry for a decorated glass container that is aesthetically pleasing, durable, and obtained in a cost-effective, environmentally friendly, and energy-efficient manner. Envirogluv provides an expensive look similar to that found with ACL, but without the undesirable health and environmental concerns. Additionally, Envirogluv decorated glass containers are completely recyclable.

The ink compositions used in the Envirogluv processes contain no heavy metals and minimal or no VOCs. All of the pigments used are organic and biodegradable. The Envirogluv inks are cured directly on the glass by exposure to ultraviolet radiation, rather than by baking at high temperatures in lehr ovens. The elimination of lehr ovens from the glass decorating process provides many safety and environmental benefits, such as reduced energy consumption, reduced chance of worker injury such as burns or heat exposure, and more efficient and economical use of plant space. Envirogluv is inexpensive on a unit cost basis, making it a commercially viable alternative for glass decorators.

Environmentally Benign Antibacterial Agents

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

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

Such agents have been synthesized and patented. These new environmentally benign antibacterial agents, magnesium hydroperoxyacetate (MHPA) and magnesium dihydroperoxide (MDHP), are prepared by heating aqueous solutions of the two reactants under carefully controlled conditions to yield a water-dispersible product. These new compositions have active oxygen or peroxide contents of 1 to 30%. These new compounds exhibit antibacterial activity against representative gram-positive bacteria (*Staphylococcus aureus*) and gram-negative bacteria (*Klebsiella pneumoniae*), are hydrolytically stable at ambient temperatures for extended periods (at least 60 days), and thermally stable below 350 °C.

Fixation of aqueous dispersions of these agents to a wide variety of fiber types and fabric constructions has been demonstrated, as well as the long-term durability of these agents to laundering to retain antibacterial activity. Because of the unique surface characteristics of cotton fibers in woven fabrics, antibacterial activity (99.3% or greater reduction in growth) against representative gram-positive and gram-negative bacteria was observed even after 50 launderings. These agents have also been applied to a variety of cotton and wood-pulp cellulosic nonwovens. Thus, these agents have the additional benefit of being more suitable for renewable fibers such as cotton and cellulosic fibers derived from wood pulp than the nonrenewable synthetic fibers (such as polyester and polypropylene). Moreover, since cellulosic fibers are bleached with hydrogen peroxide, these agents have compatible chemistry with prior purification processes. The agents themselves may also be used in other applications (e.g., skin disorders, toothpastes, virus inactivation) yet to be evaluated.

United States Postal Service

Environmentally Benign Pressure Sensitive Adhesive Program

Every year the U.S. Postal Service (USPS) sells about 42 billion stamps. These sales bring in revenue of up to $7 billion. In all, the USPS spends about $200 million to produce about 50 billion stamps annually. Due to public demand, the USPS has issued different non-lick (self-adhesive) stamp products. The removal of pressure sensitive adhesives (PSAs) from recovered paper is a major problem facing the paper recycling industry. Because the USPS currently purchases about 12 to 15% of domestic PSA production and produces a high percentage of self-adhesive stamps (82%), and due to the public demand for convenience as well as hygienic considerations, environmental issues have to be addressed. With the development of these new stamp products, concern has been raised by a certain segment of the industry and by the general public about the environmental impact of PSA stamp products. Neither the adhesive nor the release liner backing are repulpable or recyclable.

The Environmentally Benign PSA Program was initiated by the USPS as part of its commitment to develop stamps and postal products that do not adversely affect the environment. The purpose of this program is to develop a PSA that is benign to the environment and is able to meet the USPS requirements. This means that each component of the pressure sensitive construction (i.e., the face stock, the adhesive layer, and the release liner backing) will not only be able to perform to the USPS requirements for postage stamps, but will also possess those properties that are capable of being defined as environmentally benign. Once the adhesive is developed, demonstrated, and implemented, the USPS intends to expand the use of its application to other postal products.

The USPS takes a leadership role in addressing this complex problem because of popularity and high visibility of PSA postage stamps. USPS is also one of the largest single PSA materials purchasers. Identification and development of improved PSA materials to meet stringent postage stamp performance requirements allows USPS to mandate use of these materials for all postal products in future purchases and helps resolve contaminant issues in recycling postal/consumer waste paper.

Polaroid Corporation

Environmentally Benign Supramolecular Assemblies of Hydroquinones in Polaroid Instant Photography

NOTE: This project is a partnership between the Polaroid Corporation and Prof. John Warner of the University of Massachusetts, Boston. This entry was submitted by each party of the project and therefore was judged in both the academic and industry categories. The project summary appears in the academic entries section on page 14.

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

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

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

Studies conducted at the National Center for Agricultural Utilization Research have produced two alternative syntheses for producing monoglyceride-containing mixtures, via glycerolysis, that employ CO_2, 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% that have high value as emulsifiers, lubrication aids, and food additives. Using carbon dioxide under pressure, metal-based catalysts can be eliminated from the traditional batch, stirred reactor glycerolysis to yield a product that is lighter in color, less odoriferous, and has a monoglyceride content between 35 to 45 weight%, depending on botanical oil source.

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

Environmentally Responsible Liquid Polymers

Nalco Chemical Company

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% 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 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.

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

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

ABB Power T&D Company Inc.

Fully Biodegradable Vegetable Oil-Based Electrical Insulating Fluid (BIOTEMP™)

The electrical industry uses millions of gallons of petroleum-based insulating fluids in transformers and other electrical apparatus. These fluids have low biodegradability, and in recent years, environmental concerns have been raised regarding the use of these fluids in equipment located in housing areas, shopping centers, and major water-ways. Spillage of the fluid by leaks and other means would contaminate the surrounding soil and water, posing a threat to living organisms. A safer, environmentally friendly fluid has been sought by electrical utilities.

To meet this challenge, ABB, a major worldwide electrical equipment manufacturer, initiated a R&D program in 1995. Agriculturally based oils were considered the best choice. However, none of the vegetable oils commercially available were found to be suitable for immediate use because of the presence of undesirable components, poor oxidation stability, and high level of conducting impurities. The research project focused on 1) selection of a suitable base oil, 2) refining of the oil to electrical-grade purity, and 3) providing oxidation stability for long-term use when exposed to air periodically.

High monounsaturated oils with more than 75% monounsaturated content were selected. These oils are mostly high oleic oils derived from genetically modified oil seeds. They are inherently more stable than oils with significant di- and tri-unsaturate content. Further refining was achieved by the use of adsorbents derived from high-surface-area clays. Oxidation stability was the hardest to achieve because many antioxidants that are available are also highly conducting. A three-component system of antioxidants that would not significantly increase the conductivity was developed by extensive testing. The level of additives is below FDA regulatory limits, and these were food grade additives.

The newly developed fluid was tested extensively. The biodegradability was 97% or more, comparable to pure vegetable oil. The fluid is stable at elevated temperatures due to high fire point (above 300 °C), adding more safety. The beneficial environmental impact of the new fluid, now commercially available, would be significant. For the first time in the last 100 years of use of insulating fluids, a truly biodegradable fluid has been developed for use in electrical apparatus with emphasis on environmental safety.

Green Card: A Biopolymer-Based and Environmentally Conscious Printed Wiring Board Technology

T.J. Watson Research Center, IBM Corporation

Printed wiring boards (PWBs) have become ubiquitous in our society and are found in an ever-expanding range of industrial and consumer products including computers, VCRs, cameras, and automobiles. The demand for PWBs is increasing rapidly—the world market for PWBs has increased at an average rate of $2 billion per year since 1983 to a current value of over $25 billion. PWBs are composites that are generally formed from an epoxy or novolac resin coated on fiberglass or paper sheets that are laminated in multilayer stacks that are interleaved with suitably patterned copper sheets. PWBs provide both the substrate for physically attaching electrical components, as well as copper traces that provide electrical connectivity between the components. Due to the use of highly crosslinked thermosetting resins, the laminates form intractable composites that cannot be recycled by melting and reforming in the same manner as thermoplastic polymers.

Of increasing concern is the manufacture and disposal of the more than 150 million square meters of laminate that are produced globally each year. The resins currently in use for PWB manufacture are generated entirely from petroleum-based stocks. Natural products, especially if used in a form similar to that in which they occur in nature, generally take less energy to produce than their petroleum-based counterparts, hence replacement of part or all of the current raw materials could result in significant energy savings. Both energy and effluent (solid, liquid, or gaseous) reductions may be possible by choosing appropriate biobased raw materials.

New resin compositions that incorporate wood or plant resources (available in commercial quantities) were investigated. The technical objectives of this program culminated in the development and optimization of the use of lignin—a waste byproduct of paper manufacture—for the fabrication of several PWB demonstration vehicles to prove manufacturing feasibility. Resins that included as much as 50 to 60 wt% lignin were formulated to meet the primary requirements for printed circuit board physical and electrical properties. The utility of lignin in epoxy-based resins was demonstrated for a range of current and advanced applications. Pilot scale manufacture of resin and laminates using these formulations was accomplished on standard manufacturing equipment using current processing techniques and chemicals. In addition, the lignin/epoxy formulations have financial incentives that increase their desirability due to the inexpensive nature of lignin as a raw material.

A lifecycle analysis was performed, showing that the environmental benefits of a lignin-based resin system included reductions in energy usage, solid wastes, air and waterborne emissions, and "greenhouse gases" such as CO_2 from petroleum based sources, methane, and nitrogen oxides. Due to the lower energy requirements for production of natural raw materials, fuel usage for resin production can be cut by up to 40% by converting from standard epoxies to lignin-based resins. Lignin resins can be cast from ketone/alcohol or ketone/propylene glycol methyl ether acetate solvents, which would reduce the usage of methyl ethyl ketone (a SARA listed chemical) and acetone in PWB manufacture. Disposal concerns are also reduced, as incineration will produce reduced levels of greenhouse gases, and boards submitted to compost/landfill will have increased opportunity for biodegradation due to fungi potentially present in that environment that can break down lignin.

Solutia Inc.

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 that 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% 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 Boreskov 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 CO_2 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 and eliminates the emission of massive amounts of greenhouse gases, while greatly reducing the production of organic wastes.

Hydrofluoroethers (HFEs)—The Right Balance of Properties

3M Center

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

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

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

Hydrogen Sulfide Elimination from the Substances Not Precipitated by H_2S Test

Mallinckrodt Baker, Inc.

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

Imation No Process Plates

Imation Corporation

Although the principles of lithography were first applied to printing in 1796, aluminum plates precoated 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, this 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 roll up 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.

The Geon Company

Increased Utilization of Raw Materials in the Production of Vinyl Chloride Monomer

Commercial catalytic oxidation processes have been adapted for disposal of organic solvents, ground-water pollutants, synthetic co-products, incinerator flue exhaust, and automotive exhausts. In the large-scale catalytic oxidation of chlorinated hydrocarbons, fuel value is typically recovered as steam and chlorine is recovered as HCl and/or Cl_2. Various approaches are disclosed in the patent and scientific literature. Studies of the deactivation of commercial catalysts over long-term exposure of streams of chlorinated and nonchlorinated hydrocarbons found that during long-term use the reaction temperature needed to be increased in order to maintain high conversion rates and reduce catalyst deactivation. In commercial scale catalytic oxidation of chlorinated materials, the maximum operating temperatures are limited by the optimal temperature range for the chosen catalyst as well as the corrosion resistance inherent in the metals used for the equipment. For example, certain economical nickel alloy steels undergo catastrophic corrosion in the presence of HCl at or above 530 °C. Increasing the operating temperature of the reaction approaching 530 °C will lead to higher corrosion rates. It would therefore be desirable from an economic standpoint to maintain very high conversion of 99% or higher of feedstocks over long periods of time without risking increased rates of corrosion.

Geon developed Catoxid™ as a catalytic process for the recovery of chlorine and energy from chlorinated organic materials. Typically, such materials are co-products of the production of useful chemicals such as vinyl chloride monomer (VCM), or other chlorinated and nonchlorinated products. The recovery is accomplished by catalytically reacting the organochlorines and an oxygen containing gas such as air to produce hydrogen chloride (HCl), carbon dioxide (CO_2), and water in a fluidized bed reactor. No additional fuel is required to sustain the exothermic reaction, and the chemical energy of the materials is recovered as steam. The HCl produced is fed directly to an oxychlorination reactor and recovered as 1,2-dichloroethane (EDC). The EDC is subsequently converted to VCM and ultimately PVC. The Catoxid™ process thus reduces the amount of chlorine required to produce a specific amount of the desired product VCM, and also reduces the fuel requirements of the production facility. Unlike incineration, which is the only acceptable alternative, the Catoxid™ process has no vents to the atmosphere. In addition, since no aqueous hydrochloric acid is generated (as is usually the case for incinerators), there is no need to utilize caustic or limestone to neutralize the acid. The Catoxid™ process was developed for the EDC/VCM/PVC industry and is directly applicable to many technologies used to produce VCM.

An Innovative Process for the Manufacture of Caprolactam from Postconsumer Nylon 6 Carpet and Other Nylon 6 Waste Articles

Allied Signal Inc.

A proprietary depolymerization and purification process developed by Allied Signal and DSM Chemicals North America converts an alternative feedstock, postconsumer nylon 6 carpet, to high-quality caprolactam, the monomer for nylon 6. The innovative technology is presently being commercialized through a manufacturing joint venture, Evergreen Nylon Recycling LLC, in Augusta, Georgia.

It is estimated that in 1996, more than 1.3 billion pounds of postconsumer nylon 6 carpet was disposed of via landfilling or incineration. At full production, approximately 20% of this waste stream, or 230 million pounds per year of waste carpet, will be diverted from landfills and converted into 100 million pounds of caprolactam at the Evergreen facility. The recovered caprolactam is polymerized into nylon 6 polymer and used in such critical applications as carpet fibers and engineering resins, demonstrating that quality products can be regenerated from waste carpet sources indefinitely. Additional environmental benefits include reduced oil dependency of 700,000 barrels per year, reduced energy consumption of 4.49 Btus, and reduced global warming gas emissions (67% CO_2 and 100% N_2O).

To secure the required supply of postconsumer nylon 6 carpets, Allied Signal created an infrastructure to collect, sort, and deliver waste nylon 6 carpet to the commercial facility in Augusta, Georgia. The infrastructure, together with the breakthrough depolymerization technology, has resulted in a recycling process that is both economical and environmentally beneficial. Landfill diversion, energy savings, and reduced greenhouse gas emissions are examples of the environmental benefits.

In Situ Chemical Stabilization of Lead-Based Paint Waste from Abrasive Blasting

U.S. Army Construction Engineering Research Laboratories

A team of researchers from the U.S. Army Construction Engineering Research Laboratories (USACERL) and the TDJ Group developed, demonstrated, and patented an innovative technology for the removal of lead-based paint from structures at a significant cost savings compared to traditional methods. The engineered abrasive combines a traditional abrasive media with a calcium silicate-based material (commercially known as Blastox™) which chemically stabilizes the lead in the residual abrasive blast waste. The stabilized waste will not show the toxicity characteristic for lead (EPA Method 1311, Toxicity Characteristic Leaching Procedure) and can be disposed as a nonhazardous waste at a much lower cost (up to 30% savings on total project costs for potential DOD-wide savings of $5 billion). The method enjoys the same high production rate of traditional abrasive blasting and requires no equipment modification. The key technological breakthrough combines a traditional abrasive media (such as silica sand or coal slag) with a calcium silicate-based material (CaO at 65 wt%, SiO_2 at 22 wt%) which chemically stabilizes the lead in the residual waste. The chemically stabilized lead-containing waste will not leach lead at a rate greater than 5 ppm and will not be characterized as hazardous waste.

U.S. Bureau of Engraving

ISOMET: Development of an Alternative Solvent

The U.S. Bureau of Engraving and Printing, 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%), toluene (25%), and acetone (20%). 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%), propylene glycol monomethyl ether (10%), and isopropyl alcohol (35%). 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.

Mobil Oil Corporation

Membrane Separation in Solvent Lube Dewaxing

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

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

As a result, a single commercial facility could reduce fuel oil consumption by 36,000 bbl/yr. This equates to a reduction in greenhouse gas emissions of about 20,000 tons/yr for each plant in which the technology is installed. The same plant would reduce cooling water use by nearly 4 million gal/day, or about 1.5 billion gal/year. The use of membranes allows more solvent to be recirculated in the dewaxing operation, which in turn leads to higher lubricant yields and a reduction in the amount of undesirable byproducts generated in the process. The higher process yields reduce by about 5% the volume of crude oil required to produce a given volume of lube oil. For a world-scale plant, this equates to a savings of about 2 million barrels of crude oil per year. Finally, the loss of dewaxing solvents, which are volatile organic materials, into the environment could be decreased by 50 to 200 tons/yr per plant depending on the age and mechanical condition of the dewaxing equipment. This results from a reduction in the number of pieces of equipment required to refine a given volume of lube oil.

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

Metabolic Engineering of Crops for Commercial Production of Biodegradable Plastics

Monsanto Company

Poly(hydroxyalkanoates) (PHAs) are a class of polymers accumulated by numerous bacterial species as carbon and energy reserves. These polymers have thermoplastic properties that make them attractive as biodegradable alternatives to petrochemical plastics. One polymer of this class, poly(ß-hydroxybutyrate-co-ß-hydroxyvalerate) (PHBV) is currently produced by fermentation of the bacterium Ralstonia eutropha; however, the process is not economically competitive with polymer production from petrochemicals. PHA production in green plants promises much lower costs, but producing polymer with the appropriate monomer composition is problematic.

The goal of Monsanto is to produce PHBV by transferring the *R. eutropha* biosynthesis pathway to plants and modifying the plant's intermediary metabolism to generate the appropriate metabolic precursors for copolymer synthesis. Metabolic engineering of Arabidopsis and Brassica to redirect intracellular pools of both short-chain fatty acids and amino acids resulted in the production of PHBV. This process required transformation of plants with four separate transgenes, and a novel application of one endogenous plant enzyme.

This technology provides a novel biosynthetic route to plastic using atmospheric CO_2 as the carbon source and sunlight as energy. The project is intended to utilize green technology from cradle to grave. The energy for polymer extraction and processing will ultimately be provided by the residual biomass derived from the polymer production crop. Key environmental benefits include utilization of atmospheric CO_2 (rather than petroleum) as a chemical feedstock, reduced combustion of fossil fuels for polymer production, and reduced consumption of landfill space because the polymer is biodegradable (compostable). Additionally, economic benefits to the agricultural sector will be associated with production of the new or modified crop.

This project is one of the first and most complex attempts to metabolically engineer green plants to produce novel chemicals. Agriculture already provides a large number of chemical raw materials for industry, including sugars, oils, fibers, and many small molecules. The power of this new technology lies in the ability to manipulate plant metabolism, thereby creating new pathways leading to new products. Therefore, this project serves both the specific aim of PHBV production in plants, and opens the use of green plants as factories for the commercial, environmentally sustainable production of biodegradable plastics.

Minimizing Environmental Emissions by Using Different Solvents in Manufacturing Processes

Eastman Kodak Company

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

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

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

Nalco Chemical Company

Nalco Fuel Tech NOxOUT® 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 (NOx), the pollutant targeted in NO_XOUT® technologies, is a "primary" pollutant, and reducing it directly reduces acid rain, particulate matter less than 2.5 microns in diameter, and greenhouse gases and mitigates nitrogen eutrophication sensitive watersheds. NOx also is a precursor in the formation of ground-level ozone that, along with NOx, 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 NOx reduction from fuel combustion sources. NO_XOUT® can reduce NOx emissions by 75% compared to the 20 to 50% 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 NOx reduction, elimination of byproduct disposal, toxic use elimination of Superfund Amendment and Reauthorization Act Title III chemicals, and increased energy efficiency.

Nalco LAZON Technology

Nalco Chemical Company

The U.S. paper industry suffers more than $1 billion per year in lost production alone due to biological contamination problems. Nalco LAZON Technology gives papermakers 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 nonhalogen 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 onsite. 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

Nalco Chemical Company

Stricter NPDES discharge limits for effluent metals impact both metal and nonmetal 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 pretreatment 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%, product overfeed is reduced, environmental releases of treatment chemical are reduced, a less toxic treatment chemical is used, and 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 PORTA-FEED®

Nalco Chemical Company

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% of our annual sales ($659 million) were shipped in 500,000 nonreturnable drums. Fifteen percent of 1996 annual sales ($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 Chemical Company

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% 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.

Albright & Wilson Americas Inc.

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% 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 byproducts. 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.

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

Ciba Specialty Chemicals Corporation

The coatings industry in the United States has had to focus their efforts to develop products that are compliant with an ever expanding set of federal, state, and local regulations, all designed to reduce or eliminate materials that pose a threat to either human health and safety or more broadly, environmental safety. The Irgacor family of organic corrosion inhibitors was designed and developed specifically to replace the standard anticorrosive pigments that are based on heavy metals such as lead, 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 anticorrosive 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). Irgacor corrosion inhibitors are typically used at levels (based on total solids) of 0.5 to 4% compared to 10 to 20% or more for anticorrosive pigments. The volume of Irgacor necessary to replace the 11.0 million pounds therefore will 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%, 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 anticorrosive properties as well as excellent protection against flash rust. This provides the coatings industry with effective materials to further the development of waterborne coatings as replacements for solvent-based, higher VOC products.

New Technology Converts Waste to Valuable Intermediates

Dow Corning Corporation

Methylchlorosilanes, intermediates for the growing silicone industry, are produced by the reaction of elemental silicon with methyl chloride in a fluidized bed reactor. As with most chemical processes, conversion of reactants to products is not 100%; and while the percentage of waste is small for this process, these waste streams become more significant as the production volume of this industry continues to grow.

A significant fraction of the wastes produced by this "direct process" reaction are high-boiling methylchlorodisilanes that have been disposed of in the past by quenching them to form a nonhazardous landfillable material. In pursuit of reducing wastes and recovering value from the fed raw materials, Dow Corning has developed a process that provides for the conversion of these waste materials into valuable monosilanes by reacting the methylchlorodisilanes with hydrogen gas to form methylhydrogenchlorosilanes. Thus not only are the wastes associated with the production of chlorosilanes reduced, but the value of the raw materials are recovered as intermediates important to a wide range of siloxane products.

Once this new technology is implemented in Dow Corning's basic silicone plants, total cost savings will be $3 million per year. This number can be expected to rise significantly as the production capacity of these plants increase.

Akzo Nobel

Next Generation Fire-Resistant Fluids

Triaryl phosphate esters constitute a major industrial product category for fire-resistant hydraulic fluid and lubricant applications. Tertiary butylphenyl phosphate (TBPP) esters, a more specific class in this category, have a growing share of these markets due to their greater stability and lower toxicity compared to phosphate esters derived from naturally occurring cresols and xylenols. Current production methods yield TBPP esters with 10 to 45% triphenyl phosphate, a less stable component and a known esterase enzyme inhibitor that also is known to degrade the hydrolytic stability crucial for hydraulic fluid and lubricant applications.

Two synthetic approaches were developed to produce TBPP esters in high yield with less than 5% triphenyl phosphate. Both use commercially available raw materials and existing technology for production. The processes do not adversely impact environmental emissions or effluents. Most importantly, these new TBPP esters will be cost-effective to produce, given the performance advantages they bring to the marketplace.

These next generation TBPP esters are more stable and less hazardous for many applications reducing environmental concerns about recycling and disposal, as well as reducing potential worker exposure hazards with much lower esterase inhibition properties. A patent has been filed on these TBPP esters and on the methods to manufacture them. Plans are in place to implement production of these novel products in 1999.

Roche Colorado Corporation

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

The design, development, and implementation of environmentally friendly processes for the large-scale production of pharmaceutical products is one of the most challenging aspects of business operations in the pharmaceutical industry. Significant efforts toward developing new and efficient synthetic processes for the preparation of Cytovene®, a potent antiviral agent for the treatment of cytomegalovirus (CMV) retinitis infections in immunocompromised patients, have been made since the discovery of Cytovene® in 1980. Patients who are particularly at risk for developing CMV include those with AIDS and patients who are transplant recipients. In the early 1990s, Roche Colorado Corporation developed the first commercially viable process for the production of Cytovene®. In 1993, chemists at Roche's Boulder Technology Center developed a novel commercial process for the manufacture of Cytovene®, which at the time had an estimated commercial demand of about 50 metric tons per year.

The Guanine TriEster Process (GTE), which was registered with the FDA as the current manufacturing process for the world's supply of Cytovene®, achieved several environmental and economic goals through technology-based designs for pollution prevention. These achievements include a reduction in the number of chemical processing and isolation steps from six to two steps, a reduction in the number of reagents and intermediates from 22 to 11, recovery and reuse of three out of four major reagents, a reduction in the number and quantities of byproducts and waste generated, doubling of the processing throughput of the process, and at the same time, an increase in the overall yield of the product by more than 25%.

The new GTE Process for the commercial production of Cytovene® clearly demonstrated the successful implementation of the general principles of green chemistry. The development of environmentally friendly syntheses—including the development of alternative syntheses utilizing nonhazardous and nontoxic feedstocks, reagents, and solvents, elimination of waste at the source, and elimination of the production of toxic waste and byproducts—established a new and innovative technology for a general and efficient method for the preparation of Cytovene and other potent antiviral agents for the treatment of CMV retinitis and AIDS-related diseases.

Oxidizer Scrubber Project

Dynacs Engineering Co., Inc., Kennedy Space Center

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

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

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

Oxygenation of Hydrocarbons by Photocatalysis: A Green Alternative

National Risk Management Research Laboratory, U.S. Environmental Protection Agency

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

The chemical manufacturing industry generates more than 1.5 billion tons of hazardous waste and 9 billion tons of nonhazardous waste annually. Roughly half of the releases and transfers of chemicals reported through the Toxics Release Inventory and 80 to 90% of hazardous waste generation reported through the Resource Conservation and Recovery Act are due to chemical manufacturing. Organic chemicals constitute the largest source of the toxic releases. Many of these releases can be minimized by improving the conventional housekeeping methods and pollution prevention techniques. Some of these techniques include better management of material and energy, more efficient process control, optimizing process conditions, and recycling and reusing waste and byproducts. However, cleaner production methods can be achieved by adopting "green synthetic" methods.

In recent years, there has been considerable work aimed at utilizing semiconductors photocatalysts for a variety of applications. High-value oxygenated organic compounds have been successfully synthesized from linear and cyclic hydrocarbons by a low-temperature photocatalytic oxidation using the semiconductor material titanium dioxide (TiO_2). Various hydrocarbons were partially oxygenated in both aqueous and gaseous phase reactors using ultraviolet light and titanium dioxide at mild conditions. The conversions and selectivities obtained for the partial oxidation of hydrocarbons have been comparable to those achieved with the conventional method.

Vapor phase photocatalytic oxidation of toluene with air, using a continuous reactor at 160 °C and 27 mW/cm^2 irradiation, resulted in 12% conversion per pass to benzaldehyde and benzoic acid, with a 95% selectivity to benzaldehyde. Gas phase oxidation of cyclohexane achieved up to 6% conversion per pass, and the major products obtained were cyclohexanol and cyclohexanone, with no detectable formation of CO_2. The gas phase photocatalytic reactors eliminated the separation step involved with liquid solvents and catalyst slurry mixtures, and minimized the adsorption of products to the catalyst.

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

PARIS II Solvent Design Software

National Risk Management Research Laboratory, U.S. Environmental Protection Agency

There is a great need to replace solvents used in industry whose continued use presents environmental difficulties, such as worker health concerns and environmental impacts such as ozone depletion and environmental toxicity. To address this need, a research program has been underway to create the solvent design software PARIS II (Program for Assisting the Replacement of Industrial Solvents, Version 2). PARIS II designs solvents by matching the physical properties and behavior of undesirable solvents to that of environmentally better replacements. The theory embodied in PARIS II is based on the observation that the mathematical expressions governing solvent behavior are universal, and that the identity of the solvent is represented by coefficients (e.g., viscosity, diffusivity, activity coefficients). It is, therefore, possible to design entirely new replacement solvents by mapping one solvent into another using these coefficients, and the resulting replacement will mimic the behavior of the original solvent irrespective of intended application. PARIS II embodies a sophisticated algorithm using property prediction and phase equilibrium calculations to design mixtures with specific properties and behavior. These properties include general, dynamic, and equilibrium properties, environmental requirements (i.e., a VOC index and an environmental index), and performance and safety requirements. The result is general and robust solvent design software.

It is worth emphasizing that PARIS II is capable of not only designing solvents that mimic the behavior of another solvent, but it can actually design solvents with improved technological and environmental properties over the existing solvent. The reason is that the algorithm allows one to actually request a solvent with, for example, 10% lower viscosity, 20% higher density, or 50% lower vapor pressure. This is most useful when the replacement solvent is a mixture so that different components can be added and the composition adjusted by the software. With the PARIS II algorithm, improving environmental performance is automatic because the algorithm looks for solvents with environmental indexes as close to zero as possible. Improving the technological performance of the solvent, however, is at the discretion of the user.

PVC Replacement Technology

Chemecol, L.L.C., Forbo International, and McDonough Braungart Design Chemistry, L.L.C.

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 nonvolatile 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 multiphase 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 with 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.

M.A. Hanna Color—Technical Center

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 cleanup), 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 pyrolization. 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 22.4 million pounds (11,200 tons) annually, conservatively assuming an average solvent content of 30%. M.A. Hanna Color estimates that within the first two years of use, the new color laser marking technology could effectively replace approximately 10% of the plastics decorating processes that involve inks. Within ten years, this figure could rise to 50%. Meeting the 10% projection would eliminate approximately 1,120 tons (2.24 million pounds) of VOC emissions from the production of plastic parts in the U.S. annually.

DuPont Company

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

Phosgene is an important intermediate in the synthesis of polycarbonate plastics, high-performance polymers, agrichemical intermediates, and urethane foams. Current global production is about 10 billion pounds per year. Although the process chemistry is selective, the byproduct carbon tetrachloride, CCl_4, is generated at a rate of 300 to 500 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 scale-up of greater than 250,000 times. The catalyst was purchased, shipped from Siberia, and implemented in less than one year after the start of the program. After one and a half years of commercial production, the new catalyst has consistently demonstrated high phosgene production rates and achieved a 90% 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.

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

Mallinckrodt Inc.

The removal of oxides of nitrogen (NOx) by in situ addition of hydrogen peroxide to a metal 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 NOx emissions are generated. A study was completed to determine the best method for reducing NOx emissions from the dissolving process. The literature states NOx is required to catalyze the dissolution reaction. This theory was challenged; Mallinckrodt Inc. proposed to oxidize the NOx back to nitric acid by adding hydrogen peroxide directly to the process, thus completely eliminating NOx emissions. This proposal was demonstrated in the laboratory. Next, two trial runs using this technology were completed. In both cases the formation of NOx was completely eliminated. Based on the information from the trial runs, manufacturing, with help from research and development, designed a hydrogen peroxide addition process, which was successfully introduced. The new process has eliminated the generation of 30 tons per year of NOx while at the same time reducing nitric acid usage by approximately 109 tons per year. Also, 13 million gallons per year of scrubber waste water were eliminated since the scrubber is no longer needed.

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

PPG Industries, Inc.

PPG has developed the Tephram® nonasbestos diaphragm for use in diaphragm electrolysis cells for the production of chlorine and caustic soda (NaOH). Approximately 75% of the chlorine and caustic soda produced in the United States is made by the electrolysis of salt brine in diaphragm electrolysis cells. In these cells, salt dissolved in water is supplied as analyte to an electrolysis cell consisting of an anode, cathode, and a diaphragm. The Tephram® diaphragm uses nonhazardous materials to replace asbestos, reducing complexity in the safe handling of raw materials and in the disposal of diaphragm materials at the end of their useful lives. The Tephram® diaphragm is not only easier to handle safely and is more environmentally friendly, it also lasts longer than does asbestos and operates with greater energy efficiency. These advantages of greater durability and efficiency combine to reduce expenditure of cell renewal labor and consumption of both materials and energy.

Viasystems Technology Corporation

Solder Waste Reduction Environmental Project

One operation in the manufacturing process of printed wiring boards (PWBs), Hot Air Solder Leveling (HASL), applies solder to the copper circuits on the PWB as a solderability preservative for subsequent component assembly operations at customer locations. As the PWB passes through the molten solder in the HASL process, some copper dissolves from the PWB into the solder bath. The maximum allowable copper contamination level in solder for PWB applications is 0.30%. To maintain the solder bath below the maximum copper contamination level, a fraction (1/3) of the solder bath was routinely removed from the process and replaced with fresh solder. This spent solder, due to its lead (Pb) content, was classified as a hazardous waste.

In 1991, 372,800 pounds of solder hazardous waste was generated at Viasystems Corp.'s Richmond facility from the process for disposal. This was reduced to 261,720 pounds in 1992 through optimization of process parameters to minimize the copper dissolution rate. Although this was a significant waste stream reduction, this level of hazardous waste generation was still unacceptable from an environmental and cost standpoint. In addition, the required bailout of spent solder created productivity and process control issues within the process.

In 1993, a specific waste minimization project was undertaken to further reduce the solder hazardous waste generation in the HASL process. An online solder skimmer device was developed that allows preferential removal of the copper from the HASL solder. The solder skimmer functions by continuously circulating a small portion of the solder from the HASL solder pot (480 °F) through the skimmer, which is maintained at a temperature 100 degrees lower (380 °F), then returning it to the main solder pot. A portable solder pot was developed to work in conjunction with the solder skimmer to eliminate solder waste generation when routine maintenance was performed. As a result of this solder waste minimization project, solder dross hazardous waste shipments were reduced from 261,720 pounds in 1992 to 29,920 pounds in 1996. The solder waste generation was reduced from 199 pounds in 1993 to 31 pounds in 1996 on a per 1,000 panels processed basis. An overall waste reduction of over 80% was achieved. The reduction of solder waste also resulted in fresh solder cost savings of over $250,000 per year. There are now more than 50 solder skimmer devices in use on HASL processes throughout the world.

Dow Polymers LLC, Cargill Dow Polymers LLC

Solvent-Free Process to Produce Biodegradable Polylactic Acid Polymers

Polyactic acid (PLA) is a highly versatile biodegradable polyester derived from 100% renewable resources that offers great promise as a replacement for petrochemical-based plastics in a wide range of commodity applications. The environmental benefits of PLA have long been appreciated. However, the commercial viability of PLA has been limited by high production costs leading to resin prices above $2/lb. Yet PLA may well be considered the "sleeping giant" of biodegradable, renewable-resource based polymers.

Cargill Dow Polymers, in conjunction with its parent companies, has developed a novel solvent-free process for the production of lactide and polylactic acid (PLA). This process allows the manufacture of an environmentally friendly, biodegradable polymer that is positioned to effectively compete with petrochemical-based, commodity plastics. PLA is made in a multistep process from lactic acid, a fermentation product derived from 100% renewable resources. First, aqueous lactic acid undergoes a condensation polymerization to produce low molecular weight PLA pre-polymer. Next, PLA pre-polymer is thermally depolymerized into a mixture of L- and meso-lactide diastereomers, lactic acid, and water. The lactide isomers are isolated with high purity by a patented vacuum distillation process. Finally, PLA high polymer is produced via a tin-catalyzed, ring-opening polymerization of lactide in the melt.

The advantage of this new synthetic process is that costly and environmentally unfriendly solvent purification steps for lactide and PLA are completely avoided. Another environmental benefit of PLA is the fact that it could be 100% recyclable once the commercial volume warrants its own collection system. Articles produced from PLA can be conveniently hydrolyzed with water back to lactic acid quantitatively and reused in the process. Additionally, one of the unique features of PLA is its ability to rapidly biodegrade. Furthermore, PLA is a low-impact greenhouse gas polymer since the CO_2 generated during its biodegradation is exactly balanced by CO_2 taken from the atmosphere by renewable resource feedstocks. Petrochemical-based polymers contribute to the VOC emission and greenhouse warming problem when they are incinerated. For every ton of petrochemical-based polymer that is incinerated, more than 3.7 tons of CO_2 are emitted to the atmosphere.

This process has been in operation for more than a year at a semiworks facility in Savage, Minnesota, the world's largest PLA plant having a capacity of 8 MM lb/yr. A planned 250 million pound commercial PLA plant, with a targeted PLA price of $0.50/lb, has the potential to eliminate up to 1 billion pounds of CO_2 emissions annually if the product replaces disposable hydrocarbon products that are incinerated. The combination of versatile production capability and advantaged economics, while simultaneously practicing sound green chemistry, uniquely positions EcoPLA™ brand polymers to be competitive with petrochemical-based plastics in a variety of commodity applications.

Solvent-Free Semiconductors Manufacturing Process

Conexant Systems, Incorporated, ULVAC Technologies, Inc.

The U.S. semiconductor industry utilizes over 300 million pounds of solvents and other chemicals annually in the manufacturing of computer chips. In addition to the costs of initial purchase of these chemicals, the industry must bear the cost burden of waste disposal of these hazardous and polluting chemicals. Ultimately the consumer must pay for these costs when purchasing a new computer or any other product (e.g., cellular phone) which utilizes these chips.

The major uses for solvent cleans in the industry are for Post Metal Etch (the application here) and for Post Via Etch. These are known as "back-end" processes in the industry. Approximately equal consumption is for each application; metal alone would total 125 million pounds annually. This is equivalent to 18 million gallons of solvent used annually in the U.S. territory. It is estimated that the Conexant Systems, Inc. facility uses approximately 20,000 gallons per year for solvents related to post-metal stripping applications. Purchased at $40 per gallon (not including waste disposal costs), this is a cost of $800,000 annually.

A new generic process for accomplishing the above objectives was developed by ULVAC Technologies, Inc. that incorporates plasma chemical processing to replace hazardous, costly, and polluting wet solvents in the manufacture of metallized patterns on silicon wafers. This process is adapted to the specific chemistry of the manufacturing process for each semiconductor manufacturer. Initial experiments established the process adjustments to obtain satisfactory performance with the Conexant Systems, Inc. 0.25u metal product. This included testing for electrical performance, inspecting all process steps for cleanliness and stability, confirming that corrosion will not be a problem, and generally verifying that overall device performance is satisfactory. The result has been a new multilevel metal-manufacturing line that incorporates no solvents.

Union Carbide Corporation

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 nontoxic 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.

Sequa Chemicals, Inc.

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 nonformaldehyde 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 nonwoven mat. This provided a binder system that eliminated formaldehyde emissions and maintained good performance and reasonable economics.

These starch graft emulsion polymers are water-based, nontoxic and nonirritating. 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% free formaldehyde. Approximately 1 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 workplace 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 midpoint 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 Polyol

Stepan Company

Stepan Company's Polyester Polyol product, manufactured using the Phthalic Anhydride Process Light Ends (PA Lites), uses a previously categorized waste as a raw material in its manufacture, thereby eliminating the material's disposal via incineration. This Polyester Polyol is the basic raw material for 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

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 the 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 that 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.

Antelman Technologies, Ltd.

Superior Replacement for Chlorine in Water Treatment

Chlorine is today the most commonly used product for the treatment of industrial and recreational water. Its use, however, has been accompanied by a host of personal complaints and environmental risks. Chlorinated waters often find their way into natural waterways, destroying the organisms that sustain the food chain of aquatic life. Environmental interactions have been shown to facilitate the evolution of highly carcinogenic chloramines that find their way into the food chains of higher animals and humans. Sildate® provides a practical remedy to an environmental dilemma—how to sanitize water without using chlorine or other halogens, such as bromine.

Sildate® is an entirely new, nontoxic, environmentally friendly, complete water treatment system which is virucidal, bactericidal, and algicidal in parts per million. Each molecule of Sildate® is a single molecular diamagnetic semiconducting crystal that kills hazardous germs by direct electrocution and chelation rather than conventional poisoning. Because of this action modality, it is totally nontoxic to higher life forms. The Sildate® monomolecular device is a unique, inexpensive, patented, marketed product that effectively fills a significant public health need without the serious environmental problems associated with other products now in use. It is safe to humans, wildlife, pets, aquatic creatures, and to the earth's environment.

Bayer Corporation, Bayer AG (Germany)

Two-Component Waterborne Polyurethane Coatings

Two-component solvent borne polyurethanes have long been considered in many application areas the benchmark for high-performance coatings systems. The attributes that make these systems so attractive are fast cure under ambient or bake conditions, high-gloss and mirror-like finishes, hardness or flexibility as desired, chemical and solvent resistance, and excellent weathering when aliphatic polyisocyanates are used. But the traditional carrier has been organic solvent which, upon cure, is freed into the environment as VOC and hazardous air pollutants (HAPs) material. Use of high-solids systems ameliorates this problem but does not go far enough.

Aqueous polyurethane dispersions (PUDs) can impart the properties of polyurethane coatings from a waterborne system containing less organic solvent. They are fully reacted, high-molecular weight polyurethanes, which are most commonly ionically modified for water dispersibility. Because of low levels of crosslinking, chemical and solvent resistance is generally not equivalent to films based on two-component solvent borne polyurethane. Additionally, manufacturing procedures used for polyurethane dispersions frequently dictate inclusion of cosolvent.

Bayer's introduction in 1992 of high-quality two-component (2K) polyurethane coatings using water as the carrier amazed the coatings industry because, at that point, it was considered that 2K polyurethanes required scrupulous protection from water. Developing waterborne formulations that produce films equivalent to solvent borne counterparts was not a trivial matter. It was accomplished with the invention of water dispersible polyisocyanates and much work to develop practical formulations for a variety of market areas. New spray equipment has been developed that makes implementation of this environmentally friendly coating simple and inexpensive. The work done on the 2K waterborne polyurethanes over the past several years has resulted in a technology that provides several health and environmental benefits. VOCs are reduced by 50 to 90%, and HAPs by 50 to 99%. The amount of chemical byproducts evolution from films in interior applications is also reduced. In the United States, 2K waterborne coatings are now being sold into such market areas as industrial finishing, wood finishing, floor coatings, military coatings, and automotive interiors.

Use of Solid Catalysts in Pollution Prevention in the Nitration of Aromatic Compounds

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

Nitration reactions of aromatic substrates are important for the industrial production of a wide variety of essential chemicals, chemical and pharmaceutical intermediates, and explosives. The most widely used practical nitrating agents are mixtures of concentrated nitric and sulfuric acids. These homogenous systems are very corrosive and present serious environmental problems caused by spent acid disposal. This traditional nitration process is a notoriously unselective reaction resulting in statistical distribution of ortho, meta, and para substituted nitro isomer products. Also, this process requires an aqueous washing stage to remove oxidized byproducts that result in a waste stream that is environmentally unsuitable and costly to treat.

Therefore, there is a great need for a new nitration method that can overcome problems associated with the current mixed-acid nitration process widely used in the industry. An attractive nitration process has been developed to provide para-nitro isomer with high regioselectivity in alkyl and halo benzenes under mild conditions using concentrated nitric acid and a solid catalyst. Several aromatic substrates were nitrated using industrial grade nitric acid as the nitrating agent and commonly available, cheap zeolite solid acid catalyst to yield commercially valuable para-nitro isomer in good yield. The increase in the regioselectivity of the commercially more desirable para-isomer is due to the shape selective characteristics exerted by the solid catalyst.

This process has a number of practical advantages: significant improvements in regioselectivity favoring para-isomer in aromatic substitution in good yields, ease of separation and recovery of products, and low cost. The solid catalyst can be easily regenerated and reused by recalcination. It represents an attractive method for the clean synthesis of a range of nitroaromatic compounds. For example, this process eliminates the formation of unwanted meta-nitrotoluene isomer and other byproducts in the production of 2,4,6-trinitrotoluene (TNT) thus preventing the Red Water pollution problem. Regioselective formation of commercially more desirable p-nitro isomer has unique applications in the polyurethane and dye industry. In this respect, the polyurethane division of Bayer Corporation is currently evaluating this technology to implement in their polyurethane and dye production facilities.

Vegetable Oil Based Printing Inks and Their Environmental Advantages

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

The current United States market for news inks is greater than 500 million pounds, for sheetfed inks is greater than 100 million pounds, and for heatset inks greater than 400 million pounds. Conventional printing inks used in these applications are multicomponent systems comprising a hydrocarbon and/or alkyd resin, a hydrocarbon solvent, a pigment, and optional additives. The large amount of petrochemical resins and solvents, used in these formulations, are presenting environmental problems and pollution during the production and disposal of these inks. In recent years, the industry has been able to substitute soybean oil for a portion of the petroleum fraction, although news ink can contain as little as 40% vegetable oil (including soybean oil), sheetfed ink as little as 20% vegetable oil, and heatset ink as little as 7% vegetable oil of total formula weight.

In comparison to the formulas, the USDA developed news, sheetfed, and heatset lithographic inks, by using vehicles consisting of 100% soy or other vegetable oils, eliminating all petroleum products from the ink formulations. Ink vehicles were prepared by the polymerization of vegetable oils. By controlling the polymerization conditions, the desired viscosity, color and molecular weight could be achieved for a variety of vegetable oils having a broad range of iodine value and fatty acid composition. These vehicles were used to formulate news inks in four primary colors (black, cyan, magenta, and yellow).

For sheetfed and heatset ink vehicles, heat polymerized vegetable oil was mixed with monoester of an unsaturated fatty acid or a blend of unsaturated fatty acid monoesters. In the formulation of the vehicle, unmodified vegetable oil was used as a third component. Esters were incorporated at a relatively low level—on the order of about 0.5 to 3.0% by weight of the vehicle. Heat polymerized and unmodified oil constitutes the major fraction of the vehicle, and thereby primarily is responsible for the rheological properties of the formulated ink.

Physical properties (i.e., viscosity, tack, drying time, printability) and performance of these inks meet or exceed the industry standards. Biodegradation and volatile organic chemical tests once again showed the superiority of our inks over commercial inks.

Dow Corning Corporation

Volatile Methyl Siloxanes: Environmentally Sound Solvent Systems

Linear Volatile Methyl Siloxanes (VMS) are a class of mild solvents having an unusual combination of environmentally benign qualities. They are low in toxicity, make little contribution to global warming, do not contribute to urban ozone pollution, and do not attack the stratospheric ozone layer. They do not accumulate in the atmosphere, but rather are rapidly transformed to naturally found species, and they have received SNAP approval and VOC exemption from the EPA.

VMS solvency can be tailored to specific applications by use of cosolvents and surfactants. Eleven U.S. patents, 26 new azeotropes, 5 commercial solvents, and several formulated products have resulted. The underlying phenomena related to their use to replace less benign solvents in coating formulations or to remove particulates, oils, fluxes, and aqueous contaminants have been extensively studied. Their mild but selectable solvency, environmental benignancy, and odorless character commend them for many uses. Highly purified grades leave no surface residue, and many of their applications require such purities. They have potential value for precision Water Displacement Drying during the many aqueous processing steps of Flat Panel Display and semiconductor manufacturing.

Supratech Systems Inc.

Water Washable Flexo Photopolymer Plate "Flexceed" and Washout System

Flexography (Flexo) is a method of direct rotary printing that uses resilient relief image plates and the fastest growing printing process in the world. The conventional flexo photopolymer plates can be washed out only by using organic solvents to make relief images. Concerns for solvent use include the emission of VOCs, flammability because of lower flash point, hazardous waste, and influence on human health. Flexo photopolymer plate "Flexceed" is designed to be washed out by water to eliminate the use of any organic solvents. Both "Flexceed" plate and its washout system are designed as a total system to make treatment of its washout solution pass waste management regulations at reasonable cost using a user-friendly concept. The newly developed washout system can provide wider latitude for developing new types of "Flexceed" plate, which can satisfy the requirements of new flexo market segments for "Flexceed," while maintaining this environmental benefit. It has been positively demonstrated that the total "Flexceed" system is acceptable for each market segment of flexo printing industry due to not only print performances but also economic benefits as compared with the conventional solvent washout flexo photopolymer plate systems.

Zero Effluent Photographic Processing in the Printing Industry

E.I. duPont de Nemours & Co., Inc.

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 that 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 million 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 million gallons of photographic developer containing thousands of tons of noxious chemicals like hydroquinone are similarly dumped on the POTWs. Further, 15 million gallons of photographic fixer containing high levels of ammonia and silver are 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%. 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% 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% 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%. In addition, the analytical capability and control at a recycling center allow about 90% 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 million 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.

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