Draft Summary of 2001 Award Entries:
Presidential Green Chemistry Challenge Awards Program

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Note: This document does not contain the summaries of the award-winning technologies. These summaries are posted on EPA's green chemistry website at www.epa.gov/greenchemistry/.

Entries from Academia

Affordable Composites from Renewable Sources (ACRES)

Prof. Richard P. Wool
University of Delaware

In the past two years, the ACRES group examined several hundred chemical pathways to convert soy oil 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.

Alternative Solvent Systems for Benign Reactions

Prof. Charles A. Eckert
School of Chemical Engineering, Georgia Institute of Technology

Many common solvents used in the chemical industry bring with them both environmental and economic concerns. These range from the potential toxicity to challenges mass transfer, solvent removal, or catalyst recovery. Professors Eckert and Liotta have applied nontraditional solvents to a variety of reaction processes, and have shown both the environmental and economic advantages. Most of these projects were sponsored or cosponsored by industrial partners who have implemented their advances to the benefit of both the industry and of society.

Examples are shown here of the use of benign supercritical CO_2 to tune reaction rates and products, but also for improved mass transfer and ease of solvent removal. Very hot water, 250-300ºC provides a natural acid or base catalyst which eliminates neutralization and salt disposal, but also leads to ease of downstream separation. Examples of benign and novel synthetic processes include Friedel-Crafts reactions; aldol, Dieckmann, and Knoevenagel condensations; and ester and ether hydrolyses. Gas-expanded liquids are tunable solvents for facile separations, such as chiral separations. Biphasic fluorous systems and ionic liquids permit virtually quantitative separation of very expensive or very toxic catalysts for recovery and recycling.

Professors Eckert and Liotta have formulated an outstanding research partnership. By a synergistic combination of chemistry and engineering, they explore interdisciplinary areas of science and technology. Because they show the economic benefit of their environmental improvements, the results have been implemented.

An Environmentally Benign Asymmetric Epoxidation Method

Yian Shi
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Epoxides are very important chiral building blocks for the synthesis of enantiomerically pure complex molecules. The epoxidation of olefins bearing no allylic alcohol group with high enantiomeric excess has been a long-standing problem with major synthetic significance. Recently we have developed a highly enantioselective epoxidation method for *trans*- and trisubstituted olefins using a readily available fructose-derived ketone as catalyst and inexpensive Oxone or H_2O_2 as oxidant. The reaction proceeds via a chiral dioxirane which is generated *in situ* from the chiral ketone and oxidant. High enantioselectivities can be obtained for *trans*- and trisubstituted olefins, hydroxyalkenes, conjugated enynes, conjugated dienes, vinylsilanes, and enol derivatives.

Generally the epoxidation reaction is quite mild, rapid, safe, environmentally benign, and operationally simple. All these features demonstrate the strong potential of this epoxidation method for practical use.

An Innovative Replacement for Chromium for Aluminum Coatings

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An environmentally benign substitute for Chromium has been discovered which provides excellent corrosion resistance for aluminum surfaces. The material can be formulated both for pigment and conversion coating applications. The material has undergone extensive laboratory tests and demonstrated good adhesion and good corrosion resistance. The material has been patented.

The fundamental goal of this project was to find the pigments that could satisfactorily be substituted for environmentally hazardous chromium coatings in use. From the many possibilities that exist, experimental data led to a successful first formula. Since the lithium salts passivate aluminum, they can serve as viable substitutes for chromium in corrosion preventive systems. Also, they can be used in small quantities as a pigment substitute. Aluminum-lithium provided a base for minimal amounts of corrosion inhibitors as nanostructural cores or bases of other systems.

The results of independent laboratory testing confirmed the effective corrosion protection. Although the steel panels corroded seriously, the aluminum panels only had a few pits, as evidenced by the white powder on the surface. The scribes which exposed bare aluminum did not corrode or undercut, and no blisters on the coating were discovered. Closer inspection showed the pits were caused by lumps of pigment which, after being replaced with preheated and screened pigment, had no corrosion. In addition, the top coated primer had no corrosion, even in the scribe to bare metal. The large unfiltered particles caused a circumstance of pitting corrosion which was reduced by the lithium molybdate passivator, but could be eliminated entirely by screening the lumps out prior to painting.

The mechanism of corrosion protection appeared to be a combination of galvanic action by the lithium and passivation by the reaction products. The inhibitor was a complete success on aluminum. In the case of the four steel panels, the galvanic action probably inhibited corrosion, but the reaction products promoted corrosion on cold rolled steel. The technique of corrosion protection by nanostructural inhibitors is still possible, but the sacrificing pigment must not generate a compound which promotes corrosion. Lithium does not function on steel as it does on aluminum. However, it appears that steel substrates may also be protected by similar lithium systems.

Investigations into the mechanism of corrosion protection by the aluminum-lithium pigment revealed another interesting technique. Water slurries of aluminum-lithium pigments were rubbed on the aluminum panels for one-half hour with a subsequent water rinse. The panel developed a permanent corrosion resistant film and a good base for topcoat application. This was consistent with the results using an aluminum lithium pigment in a paint. It was also considered a unique adhesive and showed possibilities as a sealant.

In addition a chemical film which involves precipitation of lithium, molybdate, and cerium on aluminum alloy surface has been found. The film can be formed by both immersion and brushing at room temperature. Different aluminum alloys, including both low copper content and high copper content, were treated with the chemical film and were tested according ASTM B117. Corrosion resistance of the alloys was greatly enhanced by the chemical film. The chemical film also shows good adhesion to top paint.

Development of Extraordinarily Active Biocatalysts for Highly Selective and Efficient Synthesis of Chemicals and Pharmaceuticals

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Enzymes occupy a unique position in synthetic chemistry because of their exquisite selectivities and high catalytic rates under ambient reaction conditions. Nevertheless, to be used more routinely, enzymes must function in environments that are appropriate for synthesis; key among these is nonaqueous media. Unfortunately, enzymes are poorly active in organic solvents, and this has limited their synthetic and commercial viability, particularly in large-scale processing. Furthermore, the low activity of enzymes in organic media necessitates large reactor volumes and large quantities of solvent in current commercial applications of nonaqueous biocatalysis. By elucidating the mechanisms that underlie the low activity of native enzymes in dehydrated environments, we have developed methods to dramatically activate a wide variety of commercially relevant enzymes in organic solvents. In particular, by engineering the microenvironment of the biocatalyst through lyophilization in the presence of simple salts, we have opened the door for the application of enzymes in many new processes. New enzymatic processes will offer all the benefits of biocatalysis including high activity and specificity, reduced byproduct formation, and environmentally-friendly processing, and thus will provide a green alternative to less efficient synthetic schemes. This technical achievement is particularly relevant for green processing in the chemical, food, and pharmaceutical industries.

Development of Non Fluorous, Highly CO_2-Soluble Materials

Eric J. Beckman

Chemical Engineering Department, University of Pittsburgh

The application of CO_2 to chemical processing continues to elicit significant interest, as CO_2 generally poses fewer hazards than conventional organic solvents. At one time it was thought that CO_2 could simply replace many organic solvents, but subsequent work showed that CO_2 is a rather feeble solvent, and hence unrealistically high pressures are needed to dissolve compounds of interest. The discovery during the 1990's of "CO_2-philes" suddenly rendered a number of applications technically possible, greatly raising interest in CO_2 as a solvent. Fluoropolymers, the most promising CO_2-philes, are unfortunately too expensive to employ commercially and may persist in the environment. Consequently, we have developed a set of thermodynamic heuristics for the design of non-fluorous CO_2-philes. We have demonstrated the applicability of these rules-of-thumb in the design of poly(ether-carbonates), polymers that exhibit lower miscibility pressures in CO_2 than perfluoropolyethers and are biodegradable. The method of synthesis of these materials readily allows generation of surfactants and other functional molecules, opening the economical use of CO_2 to a variety of processes. We have used our simple heuristics to design three types of non-fluorous CO_2-phile, (functional silicones, poly(ether-carbonates), and acetate-functional polyethers); we expect that others will ultimately be found, greatly broadening the applicability of CO_2 as a solvent.

Environmentally Benign Lithography for Semiconductor Manufacturing

Joseph M. DeSimone

Revolutionary processes for high-performance and environmentally-benign patterning of semiconductors are the focus of a collaborative research effort. The technical motivation for this work is the integration of new processes and materials that eliminate environmentally undesirable wet processes used in today's fabrication facilities. The primary goal is to replace conventional processes with superior, "dry" CVD methods and CO_2-based processes. Secondary goals go beyond environmental advantages and address critical challenges facing the microelectronics industry:

1. The high surface tensions and viscosities of organic solvents and water used for current deposition and removal processes damage next-generation < 100-nm-sized structures;
2. The high viscosity of conventionally used solvents makes it challenging to spin uniform, thin films onto large, next-generation >500 mm wafers—the low viscosity of CO_2 allows the deposition of thin films with fewer defects and greater uniformity;
3. The polymers needed for state-of-the-art lithography (157 nm), antireflective coatings, and low-k dielectrics are insoluble in most traditional solvents-novel CVD based processes and liquid CO_2 spin-coating and free-meniscus coating methods eliminate this problem;
4. Solvents and water used today in manufacturing do not lend themselves to integrated "cluster tool" approaches, necessitating expensive clean room facilities-these integrated systems reduce the amount of clean room facilities needed.

Environmentally Benign Preparation and Polymerization of Phosphazene Polymers

Dr. Eric S. Peterson

Idaho National Engineering and Environmental Laboratory (INEEL) Separations Group

Our newly developed, innovative, polymer synthetic method eliminates use of all halogenated hydrocarbon solvents in the synthesis of polyphosphazenes. This synthetic breakthrough offers significant environmental benefit in the preparation of these important inorganic polymers. Polyphosphazenes -- one of the most versatile classes of inorganic polymers known -- are unique in their broad spectrum of properties and related commercial applications. For example, they offer the chemist great flexibility in tuning the polymer physical properties. In addition, polyphosphazenes are well known for their stability when exposed to heat, radiation, and chemicals. The synthesis of polyphosphazenes can occur by three routes: (1) traditional ring-opening synthesis (2) living polymerization, which proceeds through formation of a silylphosphoranimine, and (3) the "DeJaeger" method. Each of these three types of synthesis has advantages and disadvantages. All of them, however, as now practiced by industry, require high-boiling halogenated solvents both for thermal control and dispersal. Our approach eliminates use of all halogenated hydrocarbon solvents and produces phosphoryl chloride, a byproduct chemical having commodity uses within the chemical industry.

Formation of Ene-Diyne Molecules Under Indium Mediated Aqueous Barbier-Conditons

Dr. Thomas Mitzel

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The discovery that natural products containing ene-diyne reactive centers inhibit growth of mutated DNA strands, retarding the development of cancer cells and tumors, has prompted much excitement in the scientific community. Although this research appears promising, it is presently slowed by difficult synthetic routes and low yields of target ene-diyne structures.

This proposal addresses the use of novel synthetic routes which will alleviate this impediment. Use of water as a solvent in the formation of ene-diynes will introduce an environmentally benign methodology allowing for rapid advances in a very stimulating, important, yet untapped area of chemistry.

Use of indium mediated Barbier reactions to form C-C bonds has developed into a new and exciting area of chemical synthesis. Use of water as a solvent in these transformations has become an area of focus for a number of reasons: 1) Water is the cheapest solvent on earth, making it economically favored. 2) Synthetic efficiency may be increased by eliminating the need for traditional protecting groups. 3) Simplicity of controlling reaction conditions. No inert atmospheric requirements, no exclusion of moisture needed. Easier temperature control due to the high heat capacity of water. 4) Elimination of pollution historically caused by use and subsequent disposal of traditional organic solvents.

Indium metal has been shown to form chelates in aqueous solutions, thus allowing for good stereocontrol in the formation of coupling products, an attribute utilized in a variety of procedures. The electrophilic agent has commonly been designed to enhance diastereofacial control in these coupling reactions by placement of a chiral center α- to a carbonyl functionality. While this approach has met with good success giving ratios as high as 13:1 in favor of one diastereomer, it is somewhat limiting by the fact that the nucleophilic species does not project any stereochemical control of newly formed centers.

Previous studies in our laboratories have revealed that α-chlorosulfide species may be used to control stereoselectivity in indium mediated Barbier reactions conducted under aqueous conditions (Scheme 1). The chlorosulfide species used for these C-C bond formations are attainable in one step from purchased materials and expand the scope of indium promoted couplings a great deal. β-Hydroxy thioethers formed in this reaction may be transformed into epoxide functionalities

If a quick, controlled, more environmentally friendly method could be found to form ene-diyne skeletal structures, work in this area could progress at a much quicker rate. It is with this goal in mind, that I propose to utilize the new, exciting, environmentally benign chemistry from our laboratory to form ene-diyne structures in order to elucidate a good skeletal structure for use in targeting mutated DNA to halt the replication of cancerous tumors.

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

M. Mercedes Maroto-Valer

The Energy Institute, The Pennsylvania State University

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

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

Production of Hydrogen Peroxide Directly from H_2 and O_2 in CO_2

Eric J. Beckman

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Hydrogen peroxide is generally considered to be a green oxidant, as it is relatively non-toxic and breaks down in the environment to non-toxic byproducts. Despite its “green” characteristics, H_2O_2 is not produced in a particularly green manner. The current method for production, the sequential hydrogenation and oxidation of an alkyl anthraquinone, is capital-intensive, produces significant volumes of waste, and consumes sizeable quantities of energy during the purification and concentration of the product. There has been great interest over the past three decades in the direct synthesis of H_2O_2 from O_2 and H_2, yet processes developed to date have been unable to resolve the safety vs. productivity dilemma to the point where scale-up has been advisable. We have designed a highly CO_2-soluble Pd^{+2} catalyst, and have successfully generated H_2O_2 from H_2 and O_2 in a biphasic liquid carbon dioxide/water mixture. The use of CO_2 as solvent allows for use of reasonable concentrations of H_2 and O_2 without danger of explosion, and homogeneous catalysis eliminates diffusional limitations to reaction. The H_2O_2 produced is rapidly stripped into water, and hence the degradation of the product commonly observed in heterogeneous systems is minimized. This process configuration eliminates waste streams owing to anthraquinone degradation and use of organic solvent, and also eliminates the need for distillation, reducing energy requirements substantially.

Hydrogen peroxide is an environmentally benign oxidant that has replaced chlorinated reagents in paper processing, is used in drinking water treatment, and is increasingly suggested as a green oxidant in chemical processing. The environmental acceptability of H_2O_2 is a major reason why its production has grown annually by 10% during the 1990's, reaching global production of 1.2 million tons per year in 1995.

Ninety-five percent of the world's hydrogen peroxide is produced via the sequential hydrogenation and oxidation of a 2-alkyl anthraquinone, because it allows continuous production of hydrogen peroxide while preventing direct contact of oxygen and hydrogen. Whereas the anthraquinone route to hydrogen peroxide is commercially successful, it is a process that exhibits several environmental and engineering disadvantages. Because H_2O_2 is produced in organic solvent and is then recovered by stripping into water, the solvent contaminates the aqueous product, a situation that requires downstream distillation – a significant safety hazard and energy sink. The rates of both the hydrogenation and oxidation steps of the synthesis are limited by transport between the gas and liquid phases, and thus by the low solubility of hydrogen and oxygen in liquids. Multiple phases present in the reactors also prevent strict control over anthraquinone residence time, leading to generation of byproducts that must be extracted and disposed. For over three decades, H_2O_2 producers have invested considerable resources in trying to optimize the direct synthesis of hydrogen peroxide from H_2 and O_2, given that this is the most atom efficient route to the product and would eliminate the waste stream derived from anthraquinone degradation. However, H_2O_2 processes described to date have proven unable to circumvent the safety vs. productivity dilemma. Previous work has shown that one can conduct the reaction heterogeneously (over supported palladium) in water, thereby operating safely, yet the productivity of this process is low, given diffusional limitations to reaction and the well-known degradation of the product by the palladium catalyst. The process can be conducted in an organic/aqueous biphasic mixture with an organic-soluble catalyst, yet this creates safety hazards owing to contact between O_2, H_2, and the organic solvent.

We have synthesized a series of highly CO_2-soluble palladium catalysts, and have subsequently generated H_2O_2 from O_2 and H_2 in a biphasic mixture of CO_2 and water. Homogeneous catalysis in CO_2 allows rapid reaction at mild temperatures, and use of CO_2 as solvent permits relatively high concentrations of O_2 and H_2 to be used while remaining outside explosive limits. The product partitions preferentially to water, while the catalyst remains in the CO_2 phase, thus minimizing product degradation. Finally, the pH of water exposed to CO_2 is 2.85, within the ideal pH range for H_2O_2 stability. In summary, production of H_2O_2 directly from H_2 and O_2 in CO_2 reduces waste, eliminates the use of the organic solvent, and eliminates three energy-intensive unit operations (the oxidation reactors, the stripping column, and the distillation train to remove residual solvent and concentrate the product). This process will produce cleaner product using less energy at a significantly lower cost than the anthraquinone route. Further, the direct reaction allows use of smaller plants suitable for on-site production of H_2O_2 for microelectronics manufacture.

Recycling of Scrap Tires Via "High-Pressure High-Temperature Sintering": A Process Involving only Heat and Pressure

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In 1844, Charles Goodyear obtained his patent for the sulfur vulcanization of rubber. His invention created one of the most difficult materials to recycle, as it will not dissolve or melt. Today, studies estimate that there are roughly 2 billion scrap tires in U.S. landfills, with this number increasing at a rate of over 270 million per year. Recently, we discovered a technique for recycling vulcanized rubber. In short, commercially available rubber powder, made from scrap tires, can be "sintered" together without any adhesives through the adhesion of rubber particles with only the application of temperature and pressure. The method takes advantage of the sulfur exchange chemistry that occurs at high temperatures. High-pressure high-temperature sintering works for many different types of rubbers including: natural rubber, styrene-butadiene (SBR) rubber, ethylene-propylene-diene (EPDM) rubber, fluoroelastomers, butyl rubber, silicone rubber, and every possible blend combination attempted. This technique could help solve one of mankind's worst recycling problems, as it can produce a product with good physical and mechanical properties similar to that of many commercial elastomers (2.5 MPa Modulus, 6.0 MPa Strength at Break, 200% Strain to Break).

Charles Goodyear's discovery of sulfur vulcanization of rubber fueled much of the industrial revolution. It paved the way for the development of the rubber tire, and all the various transportation methods associated with it, and overall changed the rubber industry forever. Unfortunately, in discovering one of the most important materials of modern time, he also invented one of the most difficult materials to recycle. Vulcanized rubber will not melt, dissolve, or lend itself to the usual methods of chemical decomposition. Interestingly, Goodyear recognized the need for methods of reuse of his spent rubber articles and in 1853 patented the idea of adding vulcanized rubber powders to virgin material. Today, this is a process known as regrind blending. History has shaped rubber as being a material that one could not recycle in a manner similar to those used for thermoplastics. Charles Goodyear even stated that there are "no means of reworking vulcanized rubber". However, this notion about rubber is simply not true. Our process of "high-pressure high-temperature sintering" confirms this, as it is a means of reworking vulcanized rubber by using heat, pressure, ground rubber powder, and a melt press.

The groundwork for this simple and effective method of producing high-quality rubber goods using only waste tire rubber was discovered in 1944 by Tobolsky et al., but this application was not recognized until last year. Tobolsky realized sulfur–sulfur bonds used to cross-link most rubbers are among the weakest chemical bonds formed, and were responsible for much of the oxidative and other mechanisms that contribute to the degradation of the properties of rubber, including interchange chemistry. Using elevated temperatures, the thermally activated rearrangement of the sulfur-sulfur bonds in many types of rubber was investigated to determine bond rupture and reformation rates. It was found that the rates of bond scission and reformation are essentially equal when the materials are protected from oxygen and other reactive compounds.

Recently in our laboratories, we discovered an application for Tobolsky's work. The application of this work will help to solve the age-old problem of rubber recycling. The technique is done by using a conventional melt press whereby one adds commercially produced rubber powder derived from scrap tires, and subsequently applies pressure and temperature to obtain a solid value-added rubber panel with good mechanical properties. To date, we have investigated many different materials that span the gambit of rubber types used in today's society. These include radiation cross-linked polyethylene, amine cured epoxies, silicone rubbers, sulfur cured (natural rubbers, EPDM rubbers, SBR rubbers), fluoroelastomers, peroxide cured polybutadiene and blends of the above. All of these materials are capable of being sintered together to form a homogeneous material with good mechanical properties. Typical mechanical properties of the sintered panels are 6.0 MPa strength, 200% elongation, and 2.5 MPa modulus. These properties are representative of all types of sintered rubbers and are very similar to the mechanical properties of typical rubber sheeting used in various applications.

The discovery of high-pressure high-temperature sintering will help mankind for many years to come, as it is an answer to the question of "how does one recycle used tires?". The process involves using commercially available rubber powder made from ground tires (an extremely cheap starting material), and with the application of just heat and pressure, one can obtain a value-added part (green chemistry at its best). Work is currently under way investigating the possibility of scaling up to a continuous process where rubber could be extruded like a thermoplastic, or processed by common powder processing techniques such as paste or ram extrusion. At this juncture, these techniques look very promising.

Supercritical Fluid Spray Application Process for Adhesives and Primers

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The objective of this project is to develop low/no-VOC (volatile organic compound), non-structural adhesives to substitute for the current high-VOC, non-structural adhesives used in military applications by substituting supercritical carbon dioxide for conventional VOC solvents and carriers. It is estimated that 8.5 billion pounds of synthetic polymer adhesives are used annually, of which approximately 55 percent are VOCs. While the total DoD usage is not known, it is estimated that approximately 173,000 pounds of VOCs are released annually by Air Force aircraft operations. VOCs commonly used in applying adhesives include aromatics (e.g., toluene), ketones (e.g., acetone, methyl ethyl ketone), and others (e.g.,methanol, chloroform) which negatively impact worker health and safety, adversely affect environmental standards, are ozone depleting, and result in increased hazardous material management costs including permitting and installation of sophisticated emission control equipment.

Conceptually, the UNICARB process is straightforward in that a concentrated solution of polymeric material (in this case the adhesive and adhesive primers), and other additives are mixed in situ with high-pressure (in the range of 1000 psi to 2000 psi) carbon dioxide and then sprayed. In practice, the process is complicated in that one is mixing an incompressible, highly viscous material (polymeric material and solvents) with a highly compressible fluid of very low viscosity (supercritical carbon dioxide). The solvents are mixtures of fast and slow evaporating VOCs which are chosen specifically for their ability to dissolve the polymeric material, reduce viscosity, and aid in atomization and droplet coalescence on the substrate. In the supercritical spray process, supercritical carbon dioxide replaces that fraction of the organic solvent that is needed to give the viscosity reduction necessary for spray atomization. This is also the solvent that is the primary contributor to the high VOC emissions.

For a polymeric material to be adapted to the UNICARB process, the phase behavior of that particular polymeric material (the adhesive in this case) with carbon dioxide has to be known. Mixtures of high-pressure carbon dioxide with the adhesive concentrate must exist as a single phase at elevated pressures for the UNICARB process to work. To date, little is known of the phase behavior of polymer-solvent-carbon dioxide mixtures, and determining the underlying thermodynamic and rheological behavior is an arduous trial and error process.

Additionally, precipitation of solids in solution has been encountered and needs to be avoided when using this process.

This project will adapt the UNICARB spray application process to adhesives in two ways: (1) a continuous process for use in a manufacturing setting, and (2) a portable hand held batch process for use in small jobs or repair scenarios. Each of these processes requires its own unique set of phase diagrams given that the portable device operates in dynamic conditions (the materials and pressures of the system are changing with time), whereas the continuous spray operation operates in a steady state mode (the system pressure and material compositions remain constant with time). Therefore, for each adhesive adapted to the UNICARB process, two different types of phase diagrams will need to be generated.

Two adhesive systems, acrylic and neoprene, to date have been selected for study. We have completed examination of the neoprene system. The work using the neoprene has progressed slowly, due predominately to the crosslinked nature of the polymer and its resistance to dissolving in many solvents. When processed in industrial adhesives, neoprenes are exposed to very high shear, a process we wanted to avoid since it also reduces the molecular weight of the polymer that may change its properties for the purpose of this investigation. To date, we have completed carbon dioxide concentration at 9, 20, 30, 35 weight percent in toluene at temperatures of 45, 50, 60, and 70 C. Equilibrium pressures for the phase boundaries ranged from 700 to 1300 psi.

We have completed the automation of the data acquisition process by including an automated piston controller and modifying the automated data collection computer. These changes will make it possible to increase our testing speed and accuracy by limiting the opportunity for human error.

We have found unforeseen behavior in both systems that requires further investigation. In both the acrylic and neoprene systems, the phase transition measured dynamically occurs at a higher pressure than when measured statically. The presupposition was that the dynamic transition would occur at lower pressures than static due to the time lag for separation of the solvent and polymer. We have found the opposite to be the case and that the dynamic transition found above the static phase boundary reverts back to single phase when allowed to equilibrate. A possible explanation for this phenomenon is the difference between random and nonrandom behavior and that the system in question is showing nonrandom behavior. This finding, once verified, holds important possibilities for understanding phase transitions in multicomponent systems. Our results for the neoprene system with 25% carbon dioxide show a 300 to 400 psi difference between the lower static and higher dynamic results. This is seen from 40EC to 70EC.

Synthesis and Photopolymerization of Monomers Derived from Biorenewable Sources

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Plant derived unsaturated vegetable oils can be readily epoxidized using a novel catalytic method and employing a high yield, solvent-free process to give the corresponding epoxidized triglycerides. Alternatively, naturally occurring epoxidized glycerides can be used as directly obtained from their plant sources. The addition of an onium salt cationic photoinitiator renders these materials photopolymerizable. Further, the use of photosensitizers allows the cationic photopolymerization to be carried out using ambient sunlight. The UV cure of the epoxidized vegetable oils takes place rapidly, with low energy, in the absence of solvents and without any air or water polluting organic volatile emissions. Furthermore, these materials are completely nontoxic. Currently, the epoxidized oils are employed in a wide variety of industrial coating, printing ink and adhesive applications. In addition, we have demonstrated the practical use of these materials as reinforced composites that can be used for such structural, load bearing applications as building and roofing panels, pipe and conduit, boats and for casts and splints. Since a wide variety of unsaturated vegetable oils are available with different structures, a correspondingly large number of materials with specifically tailored properties can be generated to fit specific applications. This technology has the multiple advantages of being very simple, broadly applicable and completely environmentally benign.

Unsaturated vegetable oils produced by American agriculture are an inexpensive and biorenewable resource that are currently in abundant supply. These materials can be converted, using a simple, efficient and nonpolluting process to epoxidized vegetable oils that can be directly used to make polymers. The process used to make polymers involves exposing the epoxidized vegetable oils to either ultraviolet or visible light. A catalyst called a photoinitiator is added to the epoxidized vegetable oil for this purpose. No solvents are employed in the polymerization process that requires a very short time exposure to light and uses no polluting solvents. This technology is already in use for the high-speed fabrication of decorative and protective coatings, printing inks and for adhesives. Work is currently progressing which shows that the technology has particular advantage in such structural applications as housing, boats and sewerage/water delivery systems. Thus, applications of this simple technology range from those employed in the developed as well as the developing world.

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

Professor Tomas Hudlicky
Professor Dennis Wright
Department of Chemistry, University of Florida

The projects described within this document are nominated for an academic award under Focus Area I-The use of alternative synthetic pathways for green chemistry. The prevention of pollution at its source is addressed by replacement of currently used methods of oxidation and reduction (all based on metal reagents) with enzymatic and electrochemical techniques (all performed in water, alcohols, or other environmentally acceptable solvents). The combination of enzymatic transformations with electrochemistry, along with efficient design, yields unprecedented brevity in the attainment of important pharmaceuticals from metabolites of type 1 by oxidative dearomatization, a reaction that has no counterpart in traditional chemistry. Halogenated aromatic compounds, viewed as harmful to the environment, are enzymatically converted to useful synthons and effectively removed from the hazardous waste pool with the added economic benefits of strategic conversion that would not be available through incineration of such compounds, which method would be also a contributor to green-house gases. It must be emphasized here that the enzymatic conversion of the toxic aromatic materials takes place in the very first step of the synthetic pathway and that all subsequent synthetic intermediates are harmless. The residual mass from the enzymatic processes is 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 one of many illustrations of the technology. This document describes the strategy, the logic, the execution, and the future projection of this program of potentially global impact with attendant benefits to the health and economy of society at large through managed processing of aromatic waste to value-added substances. The length of a synthesis and the weight of all reagents and solvents used play a direct role in the attendant accumulated waste mass for the process. A new definition of efficiency, *"Effective Mass Yield"*, is provided as the ratio of the weight of desired product and the weight of all non-benign mass requiring treatment or disposal that is used in the process. Several syntheses of a cyclitol are compared by this criterion in terms of reduced pollution at the source of manufacturing-this indeed is one of the central themes of our design. These projects have been developed in the last five years, and several patents have already been granted on more efficient synthesis of pharmaceutical entities. Several inositols, manufactured by this method, have been marketed by Aldrich Chemical Company since 1997. Since 1998, several diols of type **1** and certain cyclitol intermediates are also catalog items at Aldrich. The overall strategy of this project takes advantage of the best combinations of enzymatic transformations, electrochemical methods, as well as traditional chemistry to achieve unprecedented efficiency in the syntheses of natural as well as unnatural compounds.

The Application of Ultrasound to Catalyze Reactions in Some Industrial Processes

Dr. Finlay MacRitchie
Kansas State University

Ultrasound has potential as a safe and clean methodology for catalyzing reactions. It uses high-frequency sound waves to change reaction paths and speed up reactions, thus reducing the need for added chemicals. The methodology has so far not been scaled up for industrial application to any great extent. The present proposal aims to apply ultrasound to three areas that have the potential to lead to industrial processes. These are (i) the modification of wheat gluten to create value-added products (ii) the clarification of fruit juices and (iii) the purification of water. The gluten industry is suffering from excessive world production. One way of countering this is to produce value-added products. Ultrasound will be used as the central technique to enhance gluten properties such as solubility, gelling, foaming and emulsifying properties. For example, it can be used to increase the solubility, making it suitable for use in fortified beverages. Clarification of fruit juices is a problem that presently is mainly tackled by using enzymes. Ultrasound offers the possibility to deal with the problem without additional chemicals. Water contamination by microorganisms or by chemical pollutants such as pesticides, is another problem where ultrasonics will be applied.

Wastewater Reuse and Zero Discharge Cycles in Process Plants

Miguel Bagajewicz, Ph.D.

The project started in 1996 and is still ongoing. It consists on investigating conditions under which zero water discharge conditions can be implemented in the process industry. The technology can be applied to a wide variety of industries such as: refineries and petrochemical sites, pulp and paper, steel, food, and many others. These zero liquid discharge cycles are based on an efficient use of water through appropriate reuse and decentralized treatment, which lowers the cost and proves them feasible in cases where they have been found too expensive. The research first investigated conditions under which reuse is optimal. These conditions allowed the use of an ingenious methodology to identify the best water use/wastewater reuse system and the appropriate decentralization of water treatment. All this results are now allowing a systematic evaluation of zero liquid discharge cycles at their optimum implementation. The direct impact of the elimination of water discharge in our waterways needs no explanation from the environmental point of view and at the same time eliminates complicated regulatory procedures. The project produced 15 papers and conference proceedings, 23 conference presentations and 4 presentations as a keynote speaker in international conferences. The technology produced is being tested in an industrial site.

End-of-pipe treatment solutions for wastewater cleanup are being replaced by water recycle/reuse and decentralized cleanup systems. Since the first formulations of the problem, which are graphical in nature, there have been several investigators that have addressed this problem using a variety of tools. Some of the limitations of these tools are numerical, but others are conceptual. In addition the issue of zero liquid discharge is not being considered.

The group at the University of Oklahoma has been able to provide several innovative solution procedures for these problems. First, necessary and sufficient conditions of optimality of these problems have been developed. These conditions enable the formulation of linear problems for the single component case and tree searching for multicomponent cases. In addition, forbidden and compulsory cases can be analyzed. The group has been able to develop a methodology to solve this problem globally *by hand*. The interaction between heat integration and water allocation has been rigorously solved overcoming the limitations of other approaches. Finally, methods to perform optimal retrofit have been proposed. Notwithstanding the value of these advances and some of the contributions of other researchers, the problem continues to offer theoretical and practical challenges. The water allocation problem and the wastewater cleanup problem have to be properly merged in a single problem so that decentralized cleanup can be appropriately addressed. Even though good methodologies exist for the solution of both problems separately, the simplifying assumptions of the original work have to be revisited. In particular the issue of fixed load in water polluting processes and fixed removal in wastewater cleanup need reformulation. The mathematical properties of the problem are thus changed and new procedures need to be developed. Procedures to reallocate water dynamically on the basis of existing process-t-o-process connections also need to be developed. The layout of a complex has important impact on the economics of reuse and has been ignored. The impact of mass exchange driving force on capital cost should be considered. Reactors have not been included and the interaction between heat and mass transfer has been ignored altogether. Mass exchanger network technology has not been fully exploited. Alternative locations of pollutant interception, via process modifications need to be developed. Finally, the ultimate goal of exploring solutions that enable zero discharge have not been properly discussed, much less solved. The concept of zero water discharge refers to closed circuits of water, such that water disposal is eliminated altogether. Closed circuits are appealing because end-of-pipe regeneration does not have to be conducted to the full extent required for disposal as water can be reused with higher level of contaminants. Additionally, the absence of a discharge eliminates internal administrative costs associated with the enforcement of EPA and local limits, as well as the interface with government agencies.

The methodology used to address the new posed challenges is the development of necessary conditions of optimum that can simplify the mathematical complexity of mathematical programming formulations, which are otherwise too cumbersome to solve. This project will have a significant impact on water usage and wastewater management for the chemical and petrochemical industry. It follows the guidelines of the DOE and NSF sponsored. Finally, the participation of undergraduates helps disseminating green process systems engineering concepts.

Entries from Small Businesses

440-R SMT Detergent Hazardous Solvent Alternative for Printed Circuit Board Stencil Cleaning
Smart Sonic Corporation

440-R SMT Detergent uses proprietary acidic surfactants which act to buffer the sodium silicate base to bring the useable concentration of 440-R SMT Detergent to within non-hazardous pH limits (11.0 – 12.0 pH). A purple dye and a mild citrus fragrance are added for identity and quality control purposes and to prevent the possibility of unpleasant odors in the workspace.

The surfactant formulations are critical in that they must not only address the flux contaminant, but must also clean effectively at low temperatures (<110^{E}F). It is established that SMT stencils are heat sensitive. The adhesives used to bond the stencil screen to the frame and to the metal etched foil are heat-cured at approximately 160EF. Hot wash solutions will breakdown the stencil adhesive and cause detachment. Temperature fluctuations also cause expansion and contraction of the various metals used to construct a stencil leading to minor distortion of fine-pitch apertures causing misregistration and production misprint problems.

Care was taken not to introduce any additional hazardous or restricted ingredients into an already hazardous cleaning application. By using only non-hazardous and non-VOC ingredients, 440-R SMT Detergent wastewater qualifies for routine liquid evaporation, eliminating the need for drain discharge and liquid hazardous waste disposal.

A Green Revolution with Polyhedral Oligomeric Silsesquioxane (POSS™) Nanostructured™ Chemicals
Hybrid Plastics, LLC

The US plastics industry and its products are primarily based on a limited pool of hydrocarbon feedstocks that were last advanced in the 1950s. Replacing these petroleum-based feedstocks with alternative materials could have substantial environmental benefits. Hybrid Plastics revolutionary green technology is based on POSS™ Nanostructured™ Chemicals that are derived directly from silanes and sand/silica, the most abundant component of the earth's crust. They release no VOCs and thereby produce no odor or air pollution. POSS™ materials can be used both as direct replacements for hydrocarbon based materials or as additives to traditional plastics. They dramatically improve the thermal and mechanical properties of traditional polymers while offering easy incorporation using existing manufacturing protocols. They are biocompatible, recyclable, non-flammable, and competitively priced with traditional polymer feedstocks.

Advanced, Ecologically Safe De-inking Technology to Recover High Quality Pulp from Secondary Fibers/or Recyclable Waste
DeCopier Technologies, Inc.

DeCopier possesses a proprietary chemical formulation capable of removing toner, wax, stickies and other contaminants from secondary fibers without damaging attached materials. The technology consists of a series of ecologically safe chemical formulations that separate the contaminants from secondary fibers without dissolving the polymers. This is a problem commonly encountered by de-inking mills.

DeCopier is developing technology for specific, high growth market opportunities in the de-inking of recycled office wastepaper, the complete destruction of high security documents and the recovery of reusable fibers in the manufacture of disposable diapers.

DeCopier plans to commercialize the following technology:

Chemical formulations for use by de-inking mills to remove contaminants from secondary fibers

Chemical solutions for separating absorbent polymer from diaper fibers, enabling them to be reused in diaper manufacturing

In sum, the advanced de-inking technology is an ideal candidate for the President's Green Challenge Award. It enables paper and pulp mills to:

1. Utilize cheaper grades of secondary raw material to produce high-quality pulp;
2. Reduce the use of virgin pulp (prevent deforestation);
3. Reduce the release of toxic effluents into sewage, and
4. Reduce the waste going into landfills/incinerators.

Biodegradable Packaging Film Incorporating Corrosion Inhibitors

Cortec Corp.

Biodegradable packaging films useful in protecting metallic articles in corrosive atmospheres have been prepared and evaluated. Incorporating volatile corrosion inhibitors in film-forming biodegradable polyester resins improves the corrosion resistance of the films to equal conventional polyethylene packages. These new films not only pass the recently approved ATSM standard and the proposed CEN standard for biodegradability and compostability, but also proved a "green alternative" to polyethylene.

Cadmium Replacement in Mechanical Coating

Madison Chemical Company

Madison Chemical Company manufactures specialty chemical compounds used in numerous applications throughout general industry, and in the metal manufacturing industry. We custom design our products to meet specific needs. Many times these include elimination of highly toxic materials from a customer's facility. In the mechanical plating industry, platers use powdered metal rotated in a barrel with impact media to mechanically plate parts. Frequently cadmium is the metal of choice in mechanical plating applications, because it adheres to the substrate metal to form a corrosion-resistant coating while giving the coated part a lustrous finish. Cadmium is also highly toxic, a proven carcinogen, and listed under Section 313 of SARA. Chemists at Madison Chemical developed a method of replacing large concentrations of cadmium with trace amounts of nickel in zinc mechanical plating. Zinc and nickel exhibit far less toxicity than cadmium, and our product shows greater corrosion resistance than the cadmium compounds generally used. This formula change was considered unique enough to warrant two U.S. patents.

Chrome-free Single-step In-situ Phosphatizing Coatings: Anti-fingerprint Coatings on Galvanized Steel

Dr. Chhiu-Tsu Lin

ChemNova Technologies, Inc.

Current corrosion-inhibiting paints (such as the nominated anti-fingerprint coating for galvanized steel) rely heavily on the use of chromates in surface pre-treatments and primers. These chromates are carcinogenic and must be eliminated. The nominated ISPC technology is a one-step process that uses no chromates, and eliminates a number of expensive and potentially hazardous process steps from the current state-of-the-art technology. This is achieved by pre-dispersing an optimum amount of *in-situ* phosphatizing reagents (ISPRs) in the desired paint system. The ISPRs are designed to produce a metal-phosphate layer *in situ*, and at the same time to form covalent linkages with the polymer resin that ensure excellent coating adhesion and inhibition of substrate corrosion without using chromates. In the nominated technology, a water-borne ISPC acrylic emulsion is developed, free of chrome and hazardous air pollutants (HAPs), and is applied to a galvanized steel sheet with a roll coater to achieve a dry film thickness of less than 1.0 :m. This coating passed all the required alkali resistance and salt (fog) spray tests, and gave excellent results in both fingerprint resistance and earthing property. It thus uses safer chemicals and eliminates enormous amounts of chromates and HAPs from the industrial waste stream.

ClearMate
ClearMate, Inc.

This project aims at extending the process life of a clear chromate bath used in the electroplating industry. The solution is susceptible to iron contamination causing its life cycle to be between 1 to 4 weeks depending on heavy to moderate use respectively. A clear chromate bath can tolerate up to 150 PPM of iron when operating at optimum conditions. The bath consists of trivalent chromium and approximately 70 million gallons of solution are waste treated annually in the United States alone. Worldwide approximately 200 million gallons are produced. The cost to the electroplater is excessive due to the bath's short life cycle. The technology herein uses an additive that inhibits the production of iron during the processing of metal parts in chromate conversion solutions. The rate of formation of iron has been described by a solution's Beta value. The Beta value represents the rate at which iron ions are dissolved in chromate solutions based on surface area of submerged parts and time of submersion. The additive decreases the beta value by a factor of 19. Applications in industry have already yielded reduction factors of 12. This correlates to a reduction in annual clear chromate hazardous waste production of approximately 182 millions gallons.

Computational Design of Corrosion Resistant Steels for Structural Applications In Aircraft
Questek Innovation

The program's objectives are to design, prototype, and characterize a new corrosion resistant steel that can significantly reduce DoD's use of cadmium during rework, maintenance, and the manufacturing of structural steel components for aerospace applications. The new steel will be developed by applying advanced computational tools, models, and design methodology and will demonstrate the potential of a new method suitable to develop alternative processing paths and materials to replace processes and materials posing increasing environmental concerns.

There are four primary technical Tasks within the program. The specific activities within each Task result from the application of *Materials by Design* approach, which integrates processing, structure, property, and performance relations within a multilevel systems structure. The first task, Analysis, will generate a systems flow-block diagram and calibrate models for the design process. The second task, the Design/Synthesis Task, will determine an alloy composition and the processing variables. During the third task a 300 lb. heat of the prototype material will be acquired and characterized; and the during the final task a technical report will be prepared detailing the program activities and analyzing the feasibility of the alloy design and its potential for further development and commercialization. A prototype of an entirely new corrosion resistant steel will be delivered that will posses similar mechanical properties to those of 300M and be compatible with current and emerging aerospace coating processes such as high-velocity oxygen fuel (HVOF) technology.

The benefits of mechanistic computational design technology is that it is now possible to rapidly develop entirely new materials and processes at costs that are orders of magnitude below the historical application of "trial and error" discovery methodology. Use of this alloy will eliminate the need for chromium and cadmium plating for wear and corrosion resistance in sensitive, critical aircraft structural components.

QuesTek is working to develop joint venture agreements with alloy producers and aircraft landing gear manufacturers to execute a "first article" demonstration/validation program. The specifications for the alloy and the protocol for material testing and evaluation have been designed to meet the end-user standards of Boeing and BFGoodrich in the U.S., and of Messier-Dowty in Canada.

Crystal Simple Green
Sunshine Makers, Inc.

Invention and commercialization of new safer family of products for use in the industrial marketplace exemplified by "Crystal Simple Green," the non-toxic, biodegradable degreaser/cleaner.

The use of toxic chemicals in the industrial marketplace exceeds one billion dollars in the United States. These chemical are responsible for environmental and personnel hazards.

Workmen’s compensation claims have skyrocketed due, in part, to the use of acids, high pH solutions, and chlorinated solvents.

Crystal Simple Green utilizes proprietary technology to effectively degrease/clean substrates that are heavily loaded with industrial oils, greases and hydrogenated animal fats. Crystal Simple Green, with a mild 9.35 pH emulsifies, saponifies, and degreases substrates through a process known as micelle creation (Micro Particulate Fractionalization). This unique process breaks oils and greases into small particles, which continues to a molecular level.

Crystal Simple Green is essentially non-toxic, and represents low toxicity hazard to mammals by inhalation, ingestion or topical route of entry. Furthermore, Crystal Simple Green represents no spill hazard and will not be deleterious to microorganisms utilized in the bioremediation process. In fact, Crystal Simple Green has properties that increases the effectiveness of bioremediation.

These attributes, along with Crystal Simple Green’s cleaning efficacy further the use of safer chemical products in the industrial area.

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

Burlington Chemical Company

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.

Development of an Effective, Coordinated Family of Safe, Green Cleaning and Maintenance Products

Rochester Midland Corporation

Traditional cleaning products are often comprised of harsh chemical components selected to aggressively remove deposits from hard surfaces. In many cases these effective products need to be handled very carefully because otherwise they can be very harmful to human health as well as damaging to ecological systems. Rochester Midland invoked a different set of criteria for the development of its ENVIROCARE family of safe, green cleaning and maintenance products. The first priority was that all of the products would be environmentally preferable. The pragmatic definition of “environmentally preferable” is products and related services that have a significantly lower detrimental effect on human health and the environment when compared with competing products intended for the same end-use application. At the same time the products had to perform well in their intended applications and this presented several strong technical challenges since many of the more effective conventional cleaning products contain strong acid or alkaline components not tolerable in the ENVIROCARE products.

An additional important criterion that was invoked was that whenever possible the main components used in the environmentally preferable products would be derivable from renewable resources and with a lesser reliance on petrochemical derivatives.

Dispersit: A Waterbased Oil Despersant for Oil Spills in Salt and Fresh Water
U.S. Polychemical Corporation

Oil spills in marine environment as pose a significant ecological and economic threat. Mechanical recovery methods are ineffective. Petroleum based dispersants, while effective, present their own environmental problems, in addition to, health threats to the user. Other waterbased dispersants, are either ineffective or highly toxic. Dispersit is a breakthrough formula combining effectiveness with safety.

It is an effective and non-toxic oil spill dispersant combining a predominately oil-soluble surfactant with a predominantly water-soluble surfactant. Water is included in the combination to help advance the interaction between the predominately oil-soluble surfactant and the predominantly water-soluble surfactant, as well as, the co-solvent. The water component also helps reduce the viscosity of the dispersant to tallow it to be pumped under pressure. The resulting product performs to a superior degree in both fresh and salt water. It does not pose a threat to human health.

Environmental Advantages Offered by Boric Acid-Promoted Amidation Between a Carboxylic Acid and an Amine to Form Carboxamide, a Basic Unit of Proteins. A Practical Alternative Synthetic Pathway to Carboxamides to Be Used as Oral Delivery Agents of Macromolecular Drugs
Emisphere Technologies, Inc.

A practical and environmentally friendly alternative synthetic pathway has been developed to accomplish the direct amidation between a carboxylic acid and an amine to form carboxamide using a catalytic amount of boric acid as a promoter. Not only are carboxamides important chemicals for the delivery of macromolecular therapeutics via oral administration, but the chemistry of formation of amide bonding (amidation) is also an important chemical transformation in organic chemistry. The amidation promoter, boric acid, is nontoxic, innocuous, stable, resistant to oxidation, environmentally safe, renewable and inexpensive. The conventional methods for making carboxamides require the use of environmentally harmful reagents and generate hazardous wastes. This boric acid-promoted amidation employs only environmentally benign reagents and generates essentially no by-products. The direct amidation between the carboxylic acids and amines with a variety of functional groups was achieved in a simple, single-step process using an equimolar mixture of acids and amines in refluxing toluene for 4 to 16 hours. This new alternative synthetic pathway using only a catalytic amount of boric acid guarantees uncontaminated waste flow, thus assuring a significantly reduced impact on human health and the environment relative to the current state of the art.

Genetic Enhancement of an Anti-Freeze Protein
Aspen Systems Inc.

Traditional anti-icing/deicing agents are either propylene or ethylene glycol. These agents result in excessive biological oxygen demand (BOD) loading and are toxic to humans, mammals and aquatic species. The clean-up of sites contaminated with these deicers is expensive. For example, at Griffith AFB, NY, the use of glycols as a deicing fluid for aircraft has resulted in ground-water cleanup programs costing over $8.2 million. An Air Force policy has been issued banning future purchase of ethylene glycol. The Environmental Protection Agency (EPA) has recently passed regulations that require the construction of on-site collection and treatment facilities for spent deicing chemicals. Under these regulations, waste deicing fluid runoff will be classified as a non-storm water discharge which must have a low BOD and an individual permit if the BOD cannot be eliminated.

This project will develop deicing/anti-icing agents from antifreeze proteins characterized by a BOD substantially lower than the current agents. Initial research has indicated that *Dendriodes canadensis*, a protein found in insects, produces a freezing point depression that is 300 to 500 times the predicted value based on its molal concentration due to non-colligative properties. This project proposes to genetically alter the *Dendriodes canadensis* antifreeze protein (D. can. AFP) gene in order to enhance its freezing point depression capabilities and increase its ability to function as a deicing/anti-icing agent.

Development and use of a deicing/anti-icing agent that is non-toxic and characterized by a low BOD should reduce the costs of the management of deicing/anti-icing operations and minimize the potential environmental impacts from discharge of untreated deicing/anti-icing wastewater to aquatic systems.

Accomplishments to date include the amino acid sequence analysis and binding domain comparisons of the Dendriodes canadensis antifreeze protein with other published AFP sequences. The design, synthesis and conformational sequencing of the mutagenesis DNA oligonucleotides to be used to mutate the D. can. AFP gene. The cloning of the D. can. AFP gene DNA into the pALTER II mutagenesis cloning vector. The confirmation of the mutated sequences by DNA sequencing. The cloning of the mutant D. can. AFPs genes into the yeast, Pichia pastoris, and their insertion confirmed by PCR analysis. These clones have since been proven to be expressing an immunoreactive protein that is secreted into the media which confirms the presence of an AFP.

All Services and the commercial airline industry will be apprized of initial results. Successful candidates will be further tested by Service programs.

Industry-University-Government Partnership for Converting Regional Wastes into Chemical Products
ChitinWorks America

A unique partnership in Maryland is demonstrating innovative approaches to simultaneously solve environmental problems and facilitate economic development. This partnership includes two companies (a composting company and a specialty chemical company), a chemical engineering professor, and a technology development specialist from a state economic development office. The goal of this partnership is to convert food and agricultural wastes into chemical products - thereby reducing nutrient addition to the Chesapeake Bay while creating manufacturing industries based on the state’s renewable natural resources. Beginning with wastes from Maryland’s crab-packing industry, the partners guided research and development, leveraged state and federal resources, and obtained private sector funding to establish a manufacturing operation. The culmination of this partnership is ChitinWorks America, a private company that is converting wastes from Maryland’s crab-packing industry into the specialty biopolymer, chitosan. This manufacturing operation meets the state’s need to cost-effectively manage nutrient-rich wastes, while sparing the state’s crab packing industry the financial burdens associated with landfilling. Additionally, the product of this manufacturing operation is an environmentally-friendly biopolymer for various specialty applications (e.g. oil drilling).

New, Environmentally Protective Aircraft De-icing Technology
Air Force Research Laboratory, Wright Patterson Air Force Base

For flight safety, snow and ice must be removed from airplanes before takeoff. Hot ethylene and propylene glycol, toxic chemicals used to de-ice airplanes at airports, usually run off the airplane onto the pavement and may escape into streams or ground water. Recently ethylene glycol along with other water-soluble organic chemicals such as MTBE have come under increased regulatory scrutiny. When glycol runoff seeps into groundwater, it can contaminate drinking water wells. In surface waters, it can harm wildlife. Some airports are installing multi-million-dollar catch basins to retain and dispose of this glycol runoff. The Air Force Research Laboratory Air Vehicles Directorate (AFRL/VA) and independent inventor, Lee Williams have developed a high efficiency forced air deicer that utilizes compressed air to blow snow and unattached ice off of airplane wings and applies a thin film of hot glycol on the cleaned wing to melt any residual ice. The specialized forced air/glycol application system reduces by 50% to as much as 90% the amount of glycol required to de-ice a jet aircraft. Not only does the technology offer a marked cost savings but also the reduction in glycol use is a tremendous benefit to the environment.

Non-Structural Adhesives Requiring No Volatile Organic Compounds
Montana Biotech Corporation

Polymeric adhesives are used in a variety of joining applications in the military and civilian sectors. Adhesives currently in use generally contain epoxy-polyamides, polyurethane, polysulfides, or alphacyanoacrylates. These adhesives require toxic volatile organic components (VOC) to polymerize, and therefore pose a significant health hazard. The VOCs commonly utilized include toluene, acetone, methanol, ketone, or xylene. Based on Toxic Release Inventory information (1996), it is estimated that 1.6 million pounds of VOCs are released annually through military use of solvent based adhesives. Personnel at manufacturing and repair facilities are at particular risk since the toxic effects of VOCs are evident at concentrations less than parts per million.

The objective of this proposal is to develop innovative, compliant adhesive polymers that have no requirement for volatile organic compounds. The source of these novel polymers will be microorganisms isolated from high temperature waters. Developed compounds will be environmentally safe, thermostable, and water tolerant. The adhesives will meet the minimum requirements of physical property performance and materials compatibility as generally required by MMM-A-121, A-A-1936, MMM-A-139, MMM-A-1058, MMM-A-1617, and MIL-A-5540.

The overall technical approach of this project is to identify natural adhesive compounds produced by microorganisms isolated from high temperature aqueous environments. 500 microorganisms from the Montana Biotech in-house collection will be grown in mini-fermenters and the cells separated from the culture broth. The culture broth containing extracellular polymers will be subdivided into three crude fractions: whole culture broth, exopolysaccharide, and protein components. Each crude fraction will be tested for tensile adhesive properties and compared to adhesives currently in use by the DoD. For example, the Army currently uses Permatex PR1 (Loctite) and Scotch-Grip 1300L (3M) that meets Mil Spec standard MMM-A-121. Polymers in crude fractions with comparable adhesive properties will be purified to homogeneity. The pure adhesive will be analyzed by time of flight secondary ion mass spectrometry (TOF-SIMS) and attenuated total reflectance fourier transform infrared spectrometry (ATR-FTIR). TOF-SIMS will generate information regarding the structure and composition of the adhesive compound and its association with various surfaces. ATR-FTIR data will include the kinetics of adhesion and bond stability on hydrophilic and hydrophobic surfaces. The physical performance of the pure adhesive polymer will be determined using mil spec standards for tensile and shear properties. If the native microorganism proves to be problematic in terms of adhesive production, and the adhesive is a protein product, the gene encoding the adhesive compound will be identified and cloned into a more industrially applicable microorganism.

The Army, Navy, and Air Force apply non-structural adhesives to a variety of systems including gaskets, instrumentation panels, textiles, packaging and labeling. Millions of pounds of VOCs are released annually through use of currently available adhesives. Executive Order 12856, Clean Air Act, Clean Water Act, RCRA, CERCLA, NASHAP demand the reduction of VOC emissions into the atmosphere. DoD use of adhesives identified by this project will directly respond to executive orders for reduction of VOC emissions, and reduce the health risk of military personnel. The potential beneficial uses of these adhesives include molecular sensors, biodegradable plastics and viscoelastic food additives. Medical applications include biocompatible tissue augmentation, wound closure and drug delivery systems. DoD will not only benefit from the reduced costs of implementing non-VOC adhesives, but also benefit from the improved thermostability and water tolerance of these novel adhesive compounds.

70 of the planned 80 pre-selected microbial isolates have been tested to date. Each isolate was used to innoculate nutrient rich and nutrient poor media. Isopropyl alcohol extracts of each microbial culture have been screened in house for adhesive strength using aluminum 2024 and EPDM rubber coupons. Approximately 50% of the tested extracts demonstrated at least 5 psi flatwise adhesive strength. These extracts were used to adhere aluminum 2024 milled bolts for Instron testing by Salient Technologies. Approximately 10% of the original number of extracts have demonstrated at least 10 psi flatwise adhesive strength. Several extracts demonstrated at least 20 psi. This is comparable to the metrics, 3M 1300 and Permatex PR-1, that demonstrate 42 and 12 psi with the same surface respectively. It is estimated that the unrefine extracts are at best 5% pure, and further purification may increase adhesive strength. While further purification will certainly be done, the preliminary extracts already demonstrate strengths which exceed most commercially available adhesives.

The non-structural adhesives will be tested as necessary to qualify for Army, Navy, Air Force, and DOE applications as well as for use in the private sector.

Oxidizer Scrubber Project
Dynacs Engineering Co., Inc.

Dynacs in conjunction with the National Aeronautics and Space Administration (NASA) developed an innovative process that converts hypergolic oxidizer waste to fertilizer for use at KSC and CCAS. The Toxic Vapor Detection (TVD) Laboratory at KSC has demonstrated with laboratory and field tests, a proposed nitrogen oxides (NOx) scrubber system change that is beneficial to KSC and other users of NOx scrubbers. This system will replace the current oxidizer scrubber liquor with one that lowers the NOx emissions. As a result, the spent solution can be used as a fertilizer, thereby eliminating the second largest hazardous waste stream and reducing the overall operation costs at KSC and CCAS. Cost savings attributed to this project relate to the elimination of waste disposal costs ($70,600 per year and a cost avoidance of approximately $16,300 per year in fertilizer purchases. This process was developed to meet Executive Order No. 12856 (Federal Compliance with Right-To-Know Laws and Pollution Prevention Requirements, dated August 6, 1993) and Executive Order No. 12873 (Federal Acquisition, Recycling, and Waste Prevention, dated October 20, 1993).

Solventless Process for Improving Fabric Performance Properties
Nextec Applications, Inc.

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.

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).

Totally Degradable Plastic Additives (TDPA™)
EPI Environmental Products Inc.

In order to be considered environmentally degradable, a plastic must disintegrate by some mechanism to lower molecular weight fragments that are susceptible to microbial attack and, ultimately, elimination as biomass, gaseous byproducts, and water. Polyolefins are usually regarded as environmentally inert. To make them environmentally degradable, mechanisms must be identified to convert these hydrophobic and high molecular weight plastics into water-wettable, friable fragments of very low molecular weight to render them microbially susceptible. It is well known that the abiotic oxidative degradation of polyolefin films produces oxidized molecular fragments of very low molecular weight (work of Profs. A-C Albertsson, C. David and others) in the range of a few hundreds to a few thousands. These products are biodegradable.

EPI Environmental Products Inc. developed and introduced TDPA™ additives to be used at low levels, < 15 weight percent, to specifically promote polyolefin oxidative degradation in the presence of heat and / or near-UV light. Adjusting the components in the TDPA™ additives and the blend proportions with the polyolefin, controls the rate and time for polyolefins to degrade to low molecular weight fragments and hence biodegrade.

Entries from Industry and Government

A New Process for Producing Dimethyl Carbonate
CD Tech

The nominated project is a process at the R&S stage for efficiently producing dimethyl carbonate (DMC) and ammonia from methanol and urea. The reaction is promoted by a novel catalyst-solvent system and is run under reactive distillation conditions. An ability to achieve near stoichiometric yields of DMC and ammonia has been demonstrated. By recycling the ammonia to a urea plant in commercial practice, the net effect is to produce DMC from carbon dioxide and methanol. The commercial potential of the process has been evaluated by estimating capital and production costs for a large-scale plant and comparing the results with current state-of -the-art practice. The latter is based on the reaction of methanol, carbon monoxide, and oxygen in the presence of a copper chloride catalyst. The new process has significant environmental and economic advantages. DMC is a on-hazardous alternative to phosgene currently used to introduce carbonate functionality into a variety of commercial products (e.g., polycarbonates). The projected low cost of the DMC produced by the new process should substantially increase its use as an alternative to phosgene. Further at the projected low price DMC has been proposed as an economic an environmentally benign alternative to MTBE as fuel oxygenate additive.

Biocatalytic Production of 5-Cyanovaleramide
DuPont Crop Protection

The first step in the manufacture of DuPont's new herbicide azafenidin (Milestone®) is the catalytic hydration of adiponitrile to 5-cyanovaleramide. Chemical catalysts were not regioselective for 5-cyanovaleramide production, and generated significant amounts of byproduct adipamide. Rapid catalyst deactiviation when using manganese dioxide required the use of large amounts of this catalyst, resulting in the production of 1.25 kg catalyst waste/kg 5-cyanovaleramide. A flammable organic solvent, toluene, was also required for product separation and recycle of unconverted adiponitrile.

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

Breakthrough NatureWorks^{TM} Polylactic Acid
Cargill Dow LLC

Cargill Dow LLC has developed a revolutionary process for the production of lactide and polylactic acid (PLA). Breakthrough NatureWorks PLA is the first family of polymers derived entirely from annually renewable resources that can compete head-to-head with traditional fibers and packaging materials on a cost and performance basis. The process allows the company to "harvest" carbon that plants remove from the air during photo- synthesis. Carbon is stored in plant starches, which can be broken down into natural sugars. The carbon and other elements in these natural sugars are then used to make polylactic acid. This process relies on basic fermentation and distillation technologies as its core and uses 20 to 50 percent less fossil fuel than is required by conventional plastic resins. In addition, because carbon dioxide is removed from the atmosphere in growing corn, the overall carbon dioxide emissions are potentially lower than with conventional plastics. Initially, Cargill Dow will use the sugars derived from corn. In the future, NatureWorks PLA will likely be made using other sources of biomass such as wheat, sugar beets and even agricultural waste as feedstock which will further reduce dependency on fossil fuel and CO_2 emissions.

DEOXO-FLUOR Reagent
Air Products and Chemicals, Inc.

Deoxofluorination, the conversion of carbon-oxygen to carbon-fluorine bonds for pharma, agro and other chemical synthesis applications, is routinely accomplished at a small scale in the laboratory with DAST [(diethylamino) sulfur trifluoride], usually at near ambient conditions. The thermal instability of DAST has precluded its use at larger scale and at more forcing conditions. Air Products and Chemicals, Inc. undertook a program to render deoxofluorination safer at large industrial scale which led to the discover and development of the Deoxo-Fluor reagent. Extensive thermal analysis by DSC, Radex, ARC, Setaram calorimetry have clearly shown the far superior stability of the Deoxo-Fluor reagent over DAST. *Ab initio* quantum-mechanics calculations on the conformational structures of the reagent have provided a rationalization for this greater thermal stability. The Deoxo-Fluor reagent is effective in the conversion of alcohols to alkyl fluorides, ketones/aldehydes to *gem*-difluorides, and carboxylic acids to CF_3 compounds with, in some cases, superior performance as compared to DAST. Within the past 2 years, Air Products and Chemicals, Inc. has successfully brought the Deoxo-Fluor reagent product from discover to commercial production. Major pharmaceutical companies in the U.S.A., Europe and Japan are currently using the reagent for the synthesis of pharmaceutical products in their development pipeline.

Design for Environmental Health and Safety Through Green Chemistry
Bristol-Myers Squibb Company

The synthetic and semi-synthetic processes utilized in the manufacture of pharmaceuticals at Bristol-Myers Squibb are chemical-intensive and involve the use of many solvents and reagents. The organic chemistry developed at the earliest phases of research and development is essentially geared to producing complex organic molecules through convenient “building block” chemicals. Many of these building block materials are highly regulated chemicals. Process developers use these chemicals because they are widely available and may accelerate the development process and launch of critical life saving and enhancing drug products.

The Process Greenness Scorecard is a tool that helps Bristol-Myers Squibb research chemists and engineers to identify materials of concern and to evaluate potential substitution with environmentally preferable process materials. In addition, the scorecard enables users to consider process conditions that minimize the impact of using these materials. Controlling the use of reagents and solvents, increasing process yields, and reducing waste streams are a few of the factors measured in the scorecard.

The scorecard encourages early product pipeline work to dramatically improve the environmental impact of commercial-scale pharmaceutical operations. It is a means of driving green chemistry by directly measuring progress in designing processes that reduce hazardous solvent use, waste generation, employee exposure, and process hazards.

Designing an Environmentally Sensible Chlorine Alternative
Nalco Chemical Company

Far more chlorine is used to control microbial fouling in industrial water compared to any other chemical. An environmentally sensible chlorine alternative is needed because handling the gas is hazardous, the liquid is not stable, combined residuals are not effective, free residuals do not control biofilms, and disinfection by-products are toxic. STABREX® Microorganism Control Chemical (trademark of Nalco Chemical Co.) is an order of magnitude less toxic, orders of magnitude less volatile, easier to handle, more compatible with other water treatment chemicals, more effective against biofilms, and generates less than half the disinfection by-products compared to chlorine or other alternatives. Three hundred billion gallons of industrial water have been successfully treated since commercial introduction in May 1997. Replacing 80 million pounds of chlorine in the field with STABREX has reduced environmental and human health risks. STABREX is the first biomimetic industrial biocide, having been designed to imitate the stabilized bromine antimicrobials produced in mammalian immune systems. This innovation is original and unique: It is the first biomimetic industrial biocide and it is the first stabilized liquid bromine product ever developed. Scientific validity and commercial significance have been recognized by industry observers and by the press.

Electrometallurgical Treatment of Nuclear Waste
Argonne National Laboratory

Researchers at Argonne National Laboratory have developed an electrometallurgical treatment that can effectively separate toxic, hazardous, or radioactive metals from a wise variety of nuclear wastes. The key step in the process involves the fast, compact electrorefining of large quantities of waste material in an electrochemical cell. Argonne researchers have demonstrated this step by the extraction of more than 200 kg of uranium from spent fuel in one month. The uranium product can be stored, recycled, or converted to an oxide for disposal as a low-level waste. The metal residue, fission products, and transuranic elements from the spent fuel can be immobilized in highly stable waste forms for disposal in a geologic repository. Compared with conventional processing, electrometallurgical technology holds promise for significantly reduced costs, greatly decreased volumes of high-level radioactive waste, and negligible volumes of secondary or low-level wastes. This technology could facilitate the environmentally sound processing of most of the more than 2000 metric tons of spent fuel accumulated within the Department of Energy complex. This technology also has potential spin-off applications for industry, such as the treatment of enrichment tailings from nuclear plants and the disposal of nontoxic wastes (e.g., barium-contaminated slats) from industrial processes.

Electronic and Photonic Polymers from Biocatalysis
U.S. Army Soldier and Biological Chemical Command

An alternative, biocatalytic approach to new conducting and light-actuated polymers has been developed. In this approach, enzymatic polymerization of anilinic and/or phenolic monomers is carried out in the presence of ionic templates to yield high molecular weight, water-soluble complexes of the polymer and the template used. Here the template provides a unique preferential local environment, which serves to both emulsify the monomer prior to polymerization. Metal-like electrical conductivities, Non Linear Optical (NLO) activity and optically driven large amplitude surface relief gratings are obtained from these biologically derived polymeric materials. This approach is particularly attractive because it is completely benign, simple (one step), and uses very mild aqueous conditions. In addition, the process is general as numerous ionic templates and derivatized monomers may be interchanged to build in desired functionalization. This process has the potential to revolutionize the use of electronic and photonic polymers since toxic catalysts or solvents are no longer required for the synthesis or processing of these polymers into useable forms. In addition, templates from renewable sources, such as lignins and even DNA can be used. This technology is expected to have wide technological impact towards the development of new electronic and optical devices.

Eliminating Air Pollution (VOC & HAP) at the Source Through the Use of Ultraviolet and Electron Beam Polymerization
RADTECH International, North America

Paints, coatings, inks and adhesives have historically been based on the dispersion of polymers in solvents. These were then applied to substrates in thin layers. Commercial products, thus treated, were then subjected to heat to evaporate the solvents and convert the polymers to solids. These solvents, volatile organic compounds (VOC), thus became air pollutants and/or hazardous air pollutants (HAP). As such they reacted with NOx to generate ground level ozone, a major air pollutant. Minor changes to the polymers used have allowed some VOC reduction, which has been overcome by rising production levels. The emission levels of volatile solvents remain very high.

The candidate technology described herein abolishes solvents completely. Instead, it provides for oligomers that are dissolved in monomers of similar reactivity. This permits the formulation and application of the above listed products, which are then cured by the application of ultraviolet (UV) or electron beam (EB) energy that causes 100% copolymerization of the oligomers with the monomers forming high performance coatings, inks and adhesives. Since no solvents are used, the emissions are nearly zero. Converters to this technology are therefore free of VOC and HAP regulations even if their production increases substantially. Environmental and health benefits are great. This technology is currently in use in a wide variety of industries and is growing at a 10-12% annual rate.

Eliminating Solvents from Silicon Wafer Manufacturing

Motorola Corporation

The process of plasma dry etching through silicon oxide layers to create sub-micron sized vias for inter-level metal contacts on silicon wafers patterned with photoresist leaves the wafer surface contaminated with polymer residues which must be removed. These residues are called “veils” because of their appearance in the SEM. Conventionally this has been done using special solvents and acids, materials that are very costly, hazardous, and environmentally a burden to be disposed of. Ulvac technologies has developed dry plasma chemical ENVIRO™ processes for treating the polymeric residues which renders them 100% soluble in DI water, along with associated processing equipment for using this capability in manufacturing.

Together Motorola Corporation and Ulvac Technologies Inc. have performed a comprehensive program evaluating the equipment and processes in the manufacturing environment, and developed appropriate methods for employing the technology in the production environment to render it useful and available to the entire worldwide industry.

Process repeatability and reliability, integrity of devices manufactured in terms of electrical performance, yields, and operating lifetimes have been demonstrated to meet or exceed the levels of the conventional acid-solvent technology.

Adapting of this technology by the semiconductor industry is anticipated to have significant impact on reducing the environmental burden associated with this industry as well as offering major manufacturing cost savings.

Environmentally Benign Antibacterial Agents

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

Many effective antibacterial agents for consumer and health care applications on textiles and fibrous substrates are no longer available on the market or are restricted due to their deleterious environmental effects in 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.

Environmentally Benign Enzyme Reactor for Polymer Synthesis
Los Alamos National Laboratory

Most common methods for commercial polymer synthesis use chemicals to oxidize monomers. During this process, large amount of by-products and waste are generated. There has been great interest in development of alternative pathways that would reduce or eliminate waste generation in polymer synthesis, such as using a biological route for polyaniline synthesis, which uses only products of polyaniline and water. However, the current biological techniques using enzyme solution for polymer synthesis suffer from significant limitations. Since enzyme is directly used in solution format in the reaction process, it is hard to recover the expensive enzyme from the final products and almost impossible to reuse it. We have developed a novel technology for polymer synthesis using a biological route, using polyaniline as an example. The technique takes full advantages of the solution enzymatic synthesis method but overcomes its limitations by immobilizing the enzyme on a solid support as a catalyst. The stability of the enzyme is significantly increased through the immobilization process. Furthermore, the catalyst enzyme can be easily recovered and reused with the immobilizing technique. Since a solid support is used, it is possible to fabricate an enzymatic reactor for polymer synthesis. Most importantly, this newly developed technology makes the biological route for polymer synthesis usable and practical in a commercial production process. A patent application for this new technology is under way.

Environmentally Benign Synthesis of Monoglyceride Mixtures Coupled with Enrichment by Supercritical Fluid Fractionation
National Center for Agricultural Utilization Research

This nominated process differs from more conventional synthesis methods or processes utilizing supercritical fluids in that it embodies carbon dioxide as a catalyst or as a transport medium, coupled in one case with a lipase biocatalyst, to produce mixtures of varying monoglyceride content. Further, the same carbon dioxide medium can then be used tin a sequential fashion, to affect an enrichment of the synthesized glyceride mixtures, to yield products having a monoglyceride content in excess of 90 weight percent that have high value as emulsifiers, lubrication aids and as food additives. Using carbon dioxide under pressure, we have shown that metal-based catalysts can be eliminated from the traditional batch, stirred reactor glycerolysis to yield a product that is lighter in color, less odoriferous and having a monoglyceride content between 35-45 wt.%. Alternatively, we have demonstrated and patented a synthesis which uses CO_2 in the supercritical state to dissolve vegetable-based oils prior to transport over a supported enzyme catalyst to produce mixtures having a 90% monoglyceride content.

Environmentally Benign Two Step Synthesis of Fatty Alcohol Mixtures Using Supercritical Carbon Dioxide (SC-CO_2) and SC-CO_2/Hydrogen Mixtures
National Center for Agricultural Utilization Research

The nominated process differs from reported synthetic methods using utilizing supercritical fluids in that it embodies two distinct sequential reactions to esterify vegetable oils followed by high temperature/pressure hydrogenation using a chromium-free catalyst. Transesterification is also accomplished with a “green catalyst,” a commercially-available lipase. The hydrogenation of the methylated oil is much more rapid in the supercritical fluid media compared to traditional technology and produces methanol as a product which can be reused as a starting reactant in the initial transesterification step. Fatty alcohols can be produced in over 98% yield with minimal by-products (n-alkanes) via this process. The described synthesis can be accomplished using only two sequential flow reactors to convert a renewable resource, soybean oil, to a mixture enriched to over 90% in steryl alcohol.

Environmentally Friendly and Readily Biodegradable Chelating Agent
Bayer Corporation, Bayer AG

As part of our commitment to Responsible Care, Bayer manufactures a readily biodegradable and environmentally friendly chelating agent, *D,L*-aspartic-*N*-(1,2-dicarboxyethyl) tetrasodium salt, also known as sodium iminodisuccinate. It is produced by a 100% waste-free and environmentally friendly manufacturing process[1] and characterized by excellent chelation capabilities, especially for iron-III, copper-II, and calcium.

Most classic chelating agents are poorly biodegradable. Some are quite persistent and do not adsorb at the surface of soils in the environment or at activated sludge in wastewater treatment plants. Because of this poor biodegradability combined with high water solubility, classic chelators are readily released into the environment and have been detected in the surface waters of rivers and lakes and in make up water processed for drinking water.

In contrast, Bayer's sodium iminodisuccinate is both readily biodegradable and benign from a toxicological and ecotoxicological standpoint. The material shows an ability to readily and rapidly degrade by OECD 301E and 302B tests.

Excellent chelation and biodegradation properties of sodium iminodisuccinate open the door for its use in environmentally friendly products in a multitude of applications and processes. Some of these include:

agricultural nutrients
detergents
groundwater remediation
household, industrial and institutional cleaners
photographic film processes

Equipment Flushing Agent for the Polyurethane Industry
Huntsman Polyurethanes

The product IFS 283 is designed as a flushing agent for isocyanate contaminated equipment frequently encountered in the polyurethane industry. Any equipment that handles isocyanates can utilize IFS 283 as flushing agent. This includes tanks, hoses, vessels, piping, flow meters, pumps and other equipment. Equipment contaminated with isocyanates, especially polymeric methylene diphenyl diisocyanate, is subject to the formation of solids due to the reaction of the isocyanate with moisture, forming intractable polyureas. These solids can effectively destroy sensitive flow meters, block hoses and necessitate rebuilding of pumps. ISF 283 reacts preferentially with the isocyanate, eliminating the chemically hazardous moiety and generating a water washable urethane liquid. Equipment flushed with ISF 283 is decontaminated and thereby much safer to handle. The contaminated flush material, if used properly, will not have residual isocyanate species and can be discarded at a saving of about $500 per drum compared to disposal of a hazardous waste material. The total volume of more hazardous solvents that IFS 283 can replace is uncertain, but estimated to be about 2 to 4 million pounds.

Innovative Green Chemistry for Sustainable Manufacture of Caprolactam
Evergreen Nylon Recycling LLC

Evergreen Nylon Recycling LLC (ENR) has developed an innovative green chemistry pathway for producing nylon 6 using sustainable, renewable feedstock. The process chemically renews nylon 6 by manufacturing caprolactam (the base monomer of nylon 6) from post-consumer nylon 6 carpet and other nylon 6 waste articles.

This is the world's first, large-scale, sustainable (closed-loop) nylon recycling process, and it eliminates the annual use of 700,000 barrels of crude oil, 83 million pounds of benzene, 120 million pounds of cumene, and 86 million pounds of phenol as the source feedstock for caprolactam. Additionally, numerous direct environmental benefits are gained. Over 200 million pounds of nylon wastes (post-consumer & post-industrial) are diverted from landfills each year. There is zero use or generation or emissions of toxic materials in the Evergreen process. Air emissions are significantly lower as compared to traditional caprolactam manufacturing, and the feedstock for the process is indefinitely renewable because nylon 6 can be recycled by Evergreen over and over again without ever degrading product quality.

The technology has been implemented through a $100 million investment in the ENR plant in Augusta, GA. Start-up occurred in December and full-rate production is expected by mid-2001.

Low VOC Chemical Agent Resistant Coatings
U.S. Army Armament Research, Development, and Engineering Center

This project developed a low volatile organic compound (VOC) Chemical Agent Resistant Coating (CARC) system suitable for use on military equipment in which the materials and processes for the reformulation/application, stripping, and disposal are optimized and in compliance with current and anticipated regulatory requirements. The primary focus was to reduce the VOC of the polyurethane topcoat from 3.5 lb/gal to 1.8 lb/gal. Additionally, this CARC will eliminate the hazardous air pollutants (HAP) and toxic solvents used in the current topcoat formulation.

At current annual usage, a CARC targeted to a 1.8 lb/gal VOC limit would save at least 5 million pounds of VOC per year, proportionately reduce photochemical smog generation and avert Notices of Violation (NOV) at user facilities including depots, air logistic centers (ALC), bases, and original equipment manufacturers. VOCs which would be reduced or eliminated include: methyl isobutyl ketone, methyl isoamyl ketone, toluene, xylene, and butyl acetate, all of which are HAPs. The technology developed by this project will also eliminate the need to install emission control devices for approximately twelve facilities for a total cost avoidance of $60 million for equipment installation and $3 million in annual operating costs. By developing one CARC topcoat for use by all the Services, substantial savings will result in procurement and logistics operations. While this formulation was developed specifically for military applications, its demonstrated durability and enhanced performance properties will make it ideal for “hard use” civilian applications.

After successful development of the new CARC formulation, the FY99 efforts focused on stripping tests using chemicals which have been used recently at various depots. The most recent data acquired in the wheat starch, laser and chemical stripper tests yielded results similar to those obtained from stripping with steel shot, flash jet, plastic media, and garnet. The recent data indicate that the new CARC strips at a rate similar to that of the current CARC topcoat.

Nalco ACT™ – Advanced Condensate Treatment for Boiler Systems
Nalco Chemical Company

Nalco’s ACT™ program is a great innovative advancement in the global condensate treatment market (total market of approximately US$ 200MM). It is the first new approach to condensate corrosion protection in over 40 years. It provides improved safety, environmental friendliness, and performance benefits versus the long-standing use of amines. For customers concerned with providing a safer workplace to their workers, in minimizing the risk in storing chemicals, and reducing regulatory compliance issues, ACT™ offers them a perfect answer. Furthermore, for the food and beverage industries that may not feed any treatment due to concerns with amines, ACT™ is a perfect fit due to its full FDA compliance, its lack of odor, and its performance as a corrosion inhibitor.

Within the Chemical Industry, it is important for research to drive innovations aimed at safer alternatives to established chemistries. Chemical research must live up to our commitment of improving the environment and to the health and well being of every person. The innovative ACT™ program truly meets this goal of providing a safe, environmentally friendly, and yet cost effective alternative to amines that have been fed to boiler systems throughout the world for nearly half a century.

New Generation Adiponitrile Technology
E. I. DuPont de Nemours & Co., Inc.

A new generation nickel catalyst system has been discovered and taken through pilot plant demonstration for the hydrocyanation of butadiene to adiponitrile. This new catalyst, developed through a molecular architecture approach to the design and construction of homogeneous catalysts, is dramatically more active, more selective and more robust than the current commercial catalyst operating in our Joint Venture Butachimie plant. These properties result in the reduction of organic byproducts from this process by more than 35% and reduction of inorganic byproducts by more than 50%. In addition, they result in the concomitant reduction in energy requirements for this process while also providing additional capacity from existing investment. Moreover, process simplifications enabled by this technology dramatically reduce the capital requirements for grassroots facilities planned in the future to support growth in the Nylon-6,6 and Nylon-6 marketplaces. Overall this technology results in improved environmental performance, lower manufacturing costs and increased capacity from existing investment through source reduction rather than tailpipe treatment.

Non-Destructive Testing of Corrosion Under Coatings
Northrup-Grumman

Surface corrosion on aluminum aircraft skins and around joints and fasteners is often the precursor to buried corrosion. Aircraft paints are routinely removed to reveal the presence of corrosion on the surface of metal structures and the aircraft is subsequently repainted. Aircraft painting and repainting operations result in significant emissions of volatile organics, organic and inorganic hazardous air pollutants, and hazardous waste. The objective of this project is to develop nondestructive inspection techniques to detect the presence of corrosion under an organic film in order to reduce the amount of painting and depainting that is performed and thus reduce the release of VOC and the generation of hazardous waste. This project will develop: (1) a spectral NDE technique employing an optical reflectance probe in the near/mid IR region combined with Directional Hemispherical Reflectance (DHR) and FTIR integrated detector; (2) Wide-area spectral imaging (WASI) using spectral filters and high-resolution focal plane cameras to allow rapid initial assessment of sub-paint corrosion; and (3) a Scanning Kelvin Probe (SKP) electrochemical method employing a calibrated capacitance probe to indirectly measure corrosion potential across a surface. Challenges to be overcome include probe positioning and electrical noise.

The project consists of five tasks over four years: (1) baseline measurements of unexposed coatings and typical corrosion products to build up a database of standards; (2) evaluation of aged aircraft components; (3) optimization of measuring systems at varying levels of corrosion and their modification for field use; (4) prototype verification (in conjunction with NAWCAD); and (5) preparation of a transition plan for cost-effective applications.

Minimizing the number of times the aircraft exterior coatings are stripped and reapplied provides substantial pollution prevention and cost saving opportunities. The inspection and measurement techniques can be used to target and map specific areas that require maintenance due to corrosion, thus eliminating the need to completely strip and reapply the exterior coatings. The inspection and measurement techniques provide a means to verify the condition of coating thus allowing for a switch to a condition-based rather than schedule-based maintenance. The inspection and measurement techniques provide a means to verify the condition of the primer and surface preparation once the topcoat has been removed thus eliminating a portion of the rework that now routinely occurs.

Non-Polluting Composites Remanufacturing and Repair for Military Applications
Army Research Laboratory

This program will create technologies that enable out-of-autoclave processing as well as reduction of emissions from adhesive bonding operations. Used in tandem, these techniques can substantially reduce pollutants and waste in composite repair and re-manufacturing. These technologies offer the additional benefit of significantly decreasing the need for recycling scrap and waste materials by enabling efficient material use and reducing the number of processing steps required for the manufacture of multi-functional PMC components (e.g., Crusader and AEMSS) by up to 80 percent. In AEMSS alone, cost savings in excess of $10M over the next 6-7 years are anticipated.

The technical objective is to research, develop, and demonstrate a unique, affordable, environmentally friendly family of polymer-matrix composite (PMC) manufacturing and repair technologies for stand-alone repair of current, soon-to-be-fielded, and future DoD structures. Repair concepts and technologies will be demonstrated on DoD-specific problems, including the design and implementation of a non-autoclave repair procedure for the Army's complex integrated polymer composite lightweight armor designs used on the Composite Armored Vehicle and the Crusader Self-Propelled Howitzer (SPH); the development, demonstration, and documentation of a repair-friendly processing method for the remanufacture of the Navy's FY02+ fielding of the Advanced Enclosure Mast Sensor System (AEMSS) including multifunctional material development; and the development of several advanced concepts for non-autoclave manufacture and repair of thin composite skins for aircraft and Army rotorcraft.

This program investigates a variety of novel composite processing and cure methods, including vacuum-assisted resin transfer molding (VARTM), the multi-resin co-injection process, electromagnetic PMC curing techniques, and novel portable radiation (ultraviolet and electron beam) cure techniques to solve pollution problems in composites re-manufacturing and repair for military applications. A key to success is tight control over temperature during processing, reducing residual stresses and providing a consistent glass transition temperature (Tg) and consistent mechanical properties using recently invented composite manufacturing techniques and optimizing them for repair of complex DoD PMC structures.

PARIS II Solvent Design Software
Environmental Protection Agency

Industrial solvents whose continued use raises concern for worker health and toxins in the environment need to be replaced cost-effectively. We created PARIS II to address this need. PARIS II is an acronym for Program for Assisting the Replacement of Industrial Solvents, Version 2. This software tool identifies pure chemicals or designs mixtures that can serve as alternatives to more hazardous substances currently in use. The "greener" solvents formulated by PARIS II have improved environmental properties, but can perform as well as those they were designed to replace. The theoretical basis for the PARIS II program is the observation that the mathematical expressions governing solvent behavior are universal, and that the performance of each solvent is quantified by a number of coefficients representing various physical and chemical properties, e.g., viscosity, diffusivity, etc. The solvent's features used by PARIS II include dynamic and equilibrium properties, environmental behavior (VOC index and environmental index), and performance and safety requirements. By applying this representation to solvent design, PARIS II can identify alternative solvents by matching coefficients rapidly. A ranked list of replacement solvents can be created within minutes. PARIS II provides a cost-effective approach to pollution prevention because users do not have to change equipment or modify their chemical processes in order to adopt safer, "greener" solvents.

Patterned Channel-constrained Process for Additive Electroless Metal Deposition
Naval Research Laboratory, Center for Bio/Molecular Science & Engineering

Channel-constrained metallization (CCM) is described as a process for the fabrication of patterned metal features useful as etchmasks and electrical interconnects for microelectronics applications. The method creates a reactivity template through patterned exposure and development of a photoresist film to uncover an underlying ligand self-assembled monolayer (SAM) coating the substrate to be plated. A Pd(II) catalyst, selectively and covalently bound to the uncovered ligand sites, initiates additive, patterned electroless (EL) metal deposition of the substrate. Because the photoresist channel walls confine lateral EL metal deposition, the deposited metal film faithfully replicates the pattern of the mask used to expose the photoresist. Adhesion of the EL deposit, which is controlled by the strength of the Pd(II)-ligand bond, is sufficient to pass an ASTM tape peel test even on flat, unroughened surfaces. Consequently, the use of adhesive Sn(II) salts is not required for CCM, avoiding environmental problems associated with the use and disposal of Sn, accelerators, and substrate surface etchants currently employed with standard subtractive EL processes. The additive nature of catalyst and metal deposition characteristic of CCM further minimizes both reagent use and the generation of plating waste relative to subtractive methods, providing additional environmental and cost advantages for the process.

Pesticide Reduction Through Precision Targeting
U.S. Department of Agriculture

The Department of Defense (DoD) presently uses approximately 1 million lbs of pesticide active ingredient annually, excluding pesticides used during major deployments. In each of these settings, these pests and disease vectors affect the health of DoD personnel by transmitting pathogens, contaminating foods and surfaces, and producing allergens. The overall goal of this project was to reduce pesticide use and associated risks through the use of precision targeting and comparative risk reduction. This project resulted in the development of a comprehensive, standardized, verifiable, and documentable system for protecting troops, DoD supplies, and DoD facilities from disease vectors and pests in a manner that reduces pesticide use and risk. This novel approach to integrated pest management (IPM) is applicable to three major settings: (1) military deployments and training exercises, where vector-borne diseases, such as malaria, leishmaniasis, dengue, and tick borne illnesses, cause direct loss in troop combat effectiveness; (2) the DoD supply system and supply depots, where pests cause losses to war stocks of military rations and other material such as uniforms and blankets; and (3) military installations, where a wide range of pests cause damage to buildings, structures, and vegetation.

Successful execution of this research provided standardized procedures for achieving comparative risk reductions associated with the broad scope of disease vectors, pests, pesticides, and pesticide resistant populations in military theaters of operation as well as on military installations. Specific payoffs included reduced use of pesticides by as much as 40-80 percent via a comprehensive, standardized, verifiable, and documentable system, and reduced direct and indirect costs of pesticides.

Primerless RTV Silicone Sealants/Adhesives
U.S. Army, TACOM-ARDEC – Picatinny Arsenal, NJ

Room temperature vulcanizing (RTV) silicones, developed in the late 1940's, have played an important role in the design and superior performance of weapon systems (airplanes, missiles, electronics, ammunition, vehicles and nuclear weapons) developed by the DoD and DOE. A unique combination of properties has made them the material- of- choice for designers wanting to improve and increase weapon performance. RTV silicones are used as adhesives, sealants, coatings, heat insulators and encapsulating materials. For RTV silicones to achieve a high level of consistent adhesion to various substrates, a saline primer is applied prior to silicone application. These primers contain 90-98% volatile organic compound (VOC) solvents, which evaporate into the air. The objective of this project is to develop, evaluate, and transition a primerless self- bonding low temperature curable addition cured silicone, which eliminates the use of high VOC primers without compromising durability, compatibility, thermal resistance and long term stability.

The project will be conducted in four phases. In phase I, current addition cured silicones available off the shelf will be modified with a bifunctional adhesion promoter compound. In phase II, a less inhibiting adhesion promoter, based on structures defined by molecular modeling will be utilized in an attempt to develop room temperature curing systems. Laboratory adhesion evaluations will be used to establish “go/no go” criteria for technology development in phase II. To expand adhesion capability to a variety of substrate materials, including plastics, novel adhesion promoting concepts will be evaluated in phase III using guidance from molecular modeling predictions. Phase IV will demonstrate the use of a new primerless silicone formulation.

By eliminating the use of the traditional primers, development of this technology will provide several benefits: a reduction of over 500,000 lb/yr of VOCs; avoidance of costs from waivers, deviations and fines associated with the use of non-compliant materials; savings derived from reduced hazardous waste disposal costs; improvement of throughput; reduction in inventory management costs; and cost savings from reduced purchasing, material handling and specification consolidation.

Recycling Propellants in Non-Polluting Supercritical Fluids: Novel Computational Chemistry Models for Predicting Effective Solvents

U.S. Army Research Laboratory – Aberdeen Proving Ground, MD

Waste solid explosives and gun propellants are destroyed primarily by open pit burning and detonation or incineration. However, extraction and recycling of such explosives and propellants using a non-polluting, inert supercritical fluid (SCF) solvent such as carbon dioxide (CO_2) has economic and environmental advantages. Although the ingredients in composite propellants and explosives demonstrate varying solubility in CO_2, solubility is enhanced when trace amounts of simple polar modifiers are added to the SCF solvent.

The objective of this project is to determine the optimal physical conditions and chemical makeup of an effective SCF CO_2 solvent with added polar modifier using well-established computational chemistry techniques.

The investigation focused on determining modifier properties and physical conditions that enhance the solubility of energetic materials in the SCF solvent using classical molecular simulation. Two complementary theoretical investigations on the properties and effectiveness of polar modified CO_2 SCF solvents were pursued in parallel. The first investigation focused on the actual dynamic event for dissolution of a hexahydro-trinitro-triazine (RDX) crystal in an SCF solvent. Solvation dependence on the physical conditions of the system (far from or close to the critical point of the SCF) were examined. The second investigation focused on determining modifier properties that enhance the solubility of RDX in the SCF solvent using rigorous quantum mechanical methods. A written report detailing predicted optimal conditions for extraction of energetic components from propellants and explosives in SCF CO_2 was developed. In addition to receiving data, the user was supplied with recommendations based on the data analysis from the development of the SCF CO_2 extraction system. Additionally, a program package that allows for prediction of solubility of energetic materials in multi-component SCF CO_2 was developed along with a users manual and a table of recommended parameters for use in applying the model to various types of modifiers and solutes.

The principle benefits resulting from this research include the prevention of pollution associated with disposal of Army and Navy explosives and gun propellants and an associated reduction of life-cycle cost of munitions. Recycling is an alternative to open burning/incineration of gun propellants, which increasingly is restricted, and to incineration, which is not widely available and requires size reduction preprocessing.

Replacement Non-Toxic Sealants for Standard Chromated Sealants and Repair

Air Force Research Laboratory

The objective of this work is to formulate and test candidate non-chromated sealants that will provide equivalent or improved properties as compared to the existing chromated sealants while meeting the requirements of MIL-S-81733C. Additional goal is to reduce the volatile organic compound (VOC) content of the materials by 65 percent.

Sealants are required in aircraft systems and on weapons to provide protection against corrosion, prevent moisture entry, provide a fuel barrier, and provide electrical insulation. Traditionally, sealants use chromium as the primary corrosion inhibiting substance. Chromium has been designated as hazardous and is targeted for elimination in order to comply with either current or pending Occupational Safety and Health Administration (OSHA) requirements. Most sealants also contain VOCs such as methyl ethyl ketone (MEK) and toluene. Under this project team’s guidance, a chromate-free corrosion inhibiting sealant has been developed, tested and transitioned to the field. A new polymer has been developed that is characterized by properties beneficial to corrosion-inhibiting sealants: rapid cure times without a reduction in work life; a pleasant odor; excellent rheological properties; excellent cure at low temperatures; and high solvent resistance. The proposed work is directed towards use of this new polymer to formulate corrosion inhibiting sealants for all the types and classes of MIL-S-81733.

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

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.

Sol-Gel Technology for Low-VOC, Non-Chromated Adhesive & Sealant Applications
Air Force Research Laboratory

The primary objective of this project is to develop and transition to the Department of Defense (DoD) and other organizations processes that eliminate the volatile organic compounds (VOC), chromates, and strong acids typically found in the metal surface treatment and priming steps conducted prior to application of adhesives and/or sealants. Secondary objectives are the reduction of hazardous wastewater streams associated with current processes and improved performance compared to these processes.

This project will develop, evaluate, and field demonstrate nonchromated, zero VOC sol-gel processes for adhesive and sealant applications. The sol-gel processes developed will replace the current approaches that are high-VOC and/or chromates. They will also eliminate the current use of strong acids and reduce the waste streams associated with the existing processes. This project will build on recent work using sol-gel technology to deposit thin organic-inorganic coatings on metal surfaces to develop good adhesion between the metal and subsequently-applied polymers (primer, adhesive, or sealant) via covalent chemical bonding. A main feature of the effort is the extensive leveraging of previous, ongoing, and proposed research.

Development of new non-chromated, zero-VOC adhesive and sealant surface preparation and primer technologies will have a major impact on both cost and performance of military and commercial aircraft. Eliminating VOCs and chromates from these processes will result in considerable cost savings due to avoiding the need for hard controls and/or fines for non-compliance. At the Naval Aviation Depot (NADEP) North Island alone, the installation of VOC-control equipment for these processes is expected to cost $15M and the installation of chromate control equipment is expected to cost $2-3M, with operation costs of approximately $250K per piece of equipment annually. However, the majority of repairs at NADEP North Island are conducted on aircraft; thus, a mandate for hard controls will incur additional costs for removal of parts and increased aircraft downtime. Consideration of cost savings from other NADEPs, U.S. Air Force air logistics centers (ALC), Army depots, and commercial usage will multiply these cost avoidance figures many-fold.

Solvent Waste Reduction via an Acetic Acid Bowl Cleaning Process
IBM Burlington (IBM Microelectronics Division)

Photoresist, a photosensitive resin mixed in a carrier solvent, provides the base upon which the semiconductor circuit pattern is built on a silicon wafer. When resist is applied to the semiconductor wafer, it also gets applied to the equipment (the coater bowl). A variety of solvents have traditionally been used to periodically remove this resist buildup. A new chemistry has been developed by IBM process engineers that uses glacial acetic acid instead of the more traditional organic solvents. This provides two primary benefits. It reduces the quantity of chemical, and the quantity of waste, required to clean the bowls by 97% (87,000 gallons of solvent per year) and it allows treatment of the waste solvent in the Burlington on-site biological wastewater treatment process. These chemical use reductions and process improvements will save approximately $296,000 per year in chemical purchase and waste disposal costs and $64,000 in space and process efficiencies. Since the acetic acid and resist byproduct waste can be broken down via bacterial action at the site biological treatment plant, the new process eliminates the need to ship this wastestream off-site for treatment and disposal.

Vegetable Oil Based Printing Inks and Their Environmental Advantages

U.S. Department of Agriculture, ARS, NCAUR

A technology has been developed for preparing ink vehicles using vegetable oils, in the complete absence of petroleum products. 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, that is on the order of about 0.5-3.0% 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.

Water Based Synthesis and Purification of Mannich Base Modified Polyphenols

Henkel Surface Technologies

Mannich reaction products of polyphenols with formaldehyde solutions and secondary amines produce unique chelating polymers. These have replaced many hexavalent chromium containing treatments and continue as quired amine functionality allows dilution with water before application. At this point, the organic solvent component serves no apparent useful purpose. Since phenols can be ionized, and thus be solubilized in water, by a strong base such as sodium hydroxide, a water-based synthesis process was developed. These reactions proceed with paraformaldehyde (eliminates methanol content) and amine at lower temperatures and higher yields than the solvent -based processes. Dilution and acidification, followed by deionization through a strong-acid type cation-exchange column quantitatively removes the sodium, residual amine, monomeric Mannich reaction products (small ethylphenol content from the precursor polymer) and other cationic impurities - resulting in a highly purified 100% aqueous polymer solution. Additional benefits realized include: improved shelf-life and hot/cold stability of the concentrate, elimination of flash points, BOD/COD and residual formaldehyde reductions, and the elimination of worker exposure to organic volatiles during manufacture.