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NETI Project Profile # 1

Building a Better Mousetrap

UMass Engineers Use "Crystal Captors" to Eliminate VOC Emissions

By Deborah Parker

Every molecule of matter has a chemical shape, a pattern that sets it apart from every other. Sometimes the differences are so slight, only the most trained eye, using state of the art computer magnification and simulation equipment, can tell them apart. A team of researchers at the University of Massachusetts Amherst has recently engineered a "molecular sieve," that can capture specified molecules attempting to pass through its portals, sight unseen. The work of chemical engineers W. C. Conner and R. L. Laurence holds enormous promise for both reducing the costs of hundreds of chemical manufacturing endeavors, as well as drastically reducing the potential release of dangerous Volatile Organic Compounds (VOCs) into the environment.

According to Conner and Laurence, the delicate science of mixing and separating different molecular components are what form the crux of every chemical engineering process in the world, the technology that brings us everything from gasoline for the car to the specialty coatings that make safety glass safe. No matter how beneficial the desired result, however, chemical plants have always had to deal with the expense and environmental impact of the resulting by-products and emissions. For instance, the group of solvents known as VOCs are one of the leading by-products in thousands of chemical and manufacturing plants around the nation; the treatment and safe disposal of VOCs alone cost industry billions each year.

Michael Nikolakopoulos, Chief Product Engineer at Chem Design Company, a Bayer Subsidiary based in Fitchburg, Massachusetts, explains just cleaning up VOCs after a typical days work has always involved numerous steps and enormous expense. "Every time we complete a process, we have to purge our systems with nitrogen. All the VOC emissions - the left over raw materials from our reactions - are thus condensed into a single storage system. From there, they have to be taken off-site to be treated and/or burned," Nikolakopoulos explains. "That is why the experiments done by Dr. Conner and Dr. Laurence are so important to us, to the industry as a whole. They have used their crystals to capture and separate these extraneous solvents while they are still in the raw material stage, before they become by-products. They were able to prevent the emissions, to save the raw materials, in the first place. The VOCs not only did not have to be cleaned, or disposed of, they could be put right back through the system to be used as fresh product."

The crystals engineered like these industrial chemical sieves at UMass are a member of the silicate family called zeolites. Under intense scrutiny by the UMass Amherst Chemical Engineering Department for almost a decade now, zeolites have demonstrated several remarkable qualities. The first is that each type always forms in exactly the same shape, forming an equally exact '"pore" at its center. The researchers at UMass soon learned they could engineer these structures - imagine "solid snowflakes"- into sheets capable of serving as a chemical mesh or gatekeeper, allowing only molecules that perfectly matched the specific zeolites "pore" pattern, to pass through. These zeolite traps also proved capable of functioning in extreme temperatures, unlike some of the synthetic versions already in use.

NETI funded Conner and Laurence in their attempt to engineer test sieves that would remove Chem Designs VOC by-products, as part of the process. "To do that, the zeolites were engineered with pores of molecular dimensions that could selectively remove the specific VOCs in question, as they passed through," Conner explains. The first advantage, Conner stresses, is that the zeolites are so precise at capturing the desired shapes, all of the targeted VOCs are removed as they pass through the sieve, resulting in virtually zero PPM (parts per million) at the end of the line. What's more, when the solvents are selectively removed in such concentrated form tainted by no other substance, as no other substance may even slip through the pores - "it is possible to envision a process where the potentially polluting solvents are never present as a contaminant," Conner concludes. "They would simply be reused over and over again, captive to the process." Ongoing studies at UMass are now underway to test the efficacy of using microwave radiation to rapidly heat and thus speedily clean/unclog the crystal membranes themselves, allowing for their rapid and repeated use during the manufacturing process.

"The potential benefits of this research are fairly enormous," Nikolakopoulos concludes. "Not only will the environmental benefits be far-reaching, but the potential savings in raw materials, and the reduction of disposal costs, could be extraordinary." The researchers will soon turn to exploring other applications for these chemical captors as well. "The obvious applications are the control of air and exhaust quality for any number of industrial environments," Conner concludes." With the right combination or layers of these crystal filters, you could theoretically put smog in one end and get nothing but clean air out the other."

NETI Project Profile # 2

Smile . . . You're on VSEAT Camera!

By Deborah Parker

Getting a good strong whiff of an industrial strength-solvent will make almost anyone instinctively pull back at least an inch or two from the source. Whether its perchloroethylene a commonly used dry-cleaning fluid or one of the many other solvents used in the printing, painting or even lead abatement industries, the sharp odor associated with these volatile organic carbons often serves as its own warning signal for those in close proximity to back off. But what happens to people whose sense of smell is acclimated to solvent odor? Many people who work with these chemicals on a day-to-day basis report they no longer are even aware of the odor after a short time on the job. If ones job duties and work stations change frequently during a given day, as is the case in a growing number of job descriptions, how does the average dry cleaning worker know when his or her personal exposure may be exceeding, say, the limits of 25 parts per million set by the American Conference of Governmental and Industrial Hygienists (ACGIH)?

"They can't know," says Certified Industrial Hygienist and Environmental Health Sciences Professor Salvatore R. DiNardi. "That's why it's incumbent on business owners to train employees very carefully about the safest way to perform their assigned tasks. And, in this day of liability concerns and regulatory crackdowns, I'd say its also vitally important for the same employers to be in the position of documenting that this training occurred, and that they actually know what their exposure may be." That's why DiNardi, head of the Environmental Health Sciences Department in the School of Public Health and Health Sciences at the University of Massachusetts Amherst, and a team of colleagues and students have refined a combined video camera/vapor sensor apparatus that can be used in virtually any environment where solvents may pose a threat to worker safety. With funding from NETI, DiNardi and his colleagues have created and tested a prototype of the system they call VSEAT, short for Video Source Emission Assessment Technology. "Basically, the system has three components: a video camera that records the worker going about his or her job, a vapor sensor that is worn on a backpack by the worker during the same period. And finally, there's a computer program that ties the video footage to the vapor readings and portrays them on a bar graph, right there on the screen," DiNardi explains.

"Using this system, workers can see, right there on the TV, that when they leaned into a dry cleaning machine to unload an armful of clothes, the vapor reading went sky-high. They can also see that when they stood back even six inches and tossed the same garments in a few at a time, the exposure was significantly lower.' When the researchers used the test system to test for tetrachloroethylene exposures in four different dry cleaning establishments in the region, 'workers were startled to see how much their own specific behaviors affected their own exposure levels, that even making minor modifications in how they did something had a dramatic impact," DiNardi stresses.

While VSEAT was primarily intended as a training tool to support workplace safety initiatives, environmental safety consultants like Richard Cahaly of Cahaly Environmental believe any company that has air-born solvent exposures in the work environment would be well-advised to use one of the systems as a self-diagnostic and ongoing documentary tool. "I have personally seen the VSEAT in action, and I think its potentially one of the most exciting tools ever made available," Cahaly notes. "Whether a company has employees working around tanks of chemicals, or simply stripping paint, this should be basic, on-site equipment to ensure that vapors or particulate are monitored, and that safe, standard operating procedures are developed and used." G. Edward Burroughs, a Certified Industrial Hygienist with the National Institute for Occupational Safety and Health (one of the Centers for Disease Control) concurs. Burroughs says a portable system like the VSEAT would mimic technology used for several years by NIOSH investigators with dramatic results. "NIOSH recommends people minimize exposure to workplace solvents, especially any of the potential occupational carcinogens," he notes. "While there may be some disagreement in the industry as to exactly what is harmful to humans and what is not, you can be certain that if organizations like the ACGIH have set exposure limits for something, then they believe there to be a possible threat. And OSHA, the Occupational Safety and Health Administration, is currently reevaluating its own Permissible Exposure Limit for Perc. From that vantage point alone, I think implementing a self-monitoring system, and a worker-training plan using a device like the VSEAT, would be an excellent exercise in good stewardship of ones resources, both human and economic."

While the estimated costs for an entire VSEAT package may be a bit high at approximately $2,000 per set for small dry cleaning shops to absorb, DiNardi is hoping regional trade associations could buy a system or two and loan them out to their members. Large companies that could more easily afford to own a system certainly should, he adds, and these firms could loan them out to smaller companies, or even as a training aid to their local volunteer or municipal fire departments. Because the apparatus can be modified to give an audible signal when worker exposure reaches proscribed limits, the apparatus can be used as a behavior modification tool as well, helping to alert firefighter or industrial emergency team trainees about maintaining the proper posture in smoke or vapor-dense conditions.

"While VSEAT should not be considered the end all in worker training and safety programs around health and environmental hazards, I think the technology could be an important tool in a comprehensive educational program, and should be available to one and all," DiNardi concludes. "I guess I like to liken using VSEAT video demonstrations to the video crash dummy commercials used for years to encourage seat belt use in automobiles. While it may be hard to document exactly how seeing those dummies go through the windshield impacted a driver or passengers later decision to fasten a seat belt, or not, I don't know anybody who has ever seen the demonstration even once, who ever forgets what they saw. And, for anyone working around volatile organic compounds, the vapor read-out in VSEAT is just as dramatic."

NETI Project Profile # 3

Keep Your Eye on the Prize

UMass Helps Chemical Industry Perform Fine-tuned "Simultaneous" Reactions and Separations

By Deborah Parker

Polyesters - those plastics that everything from clothing to beverage bottles are made of - start their lives out as fairly simple, individual chemicals, reacted with one another to form something far more functional than a liquid in a barrel. Most of the pharmaceuticals we use in everyday life started out as individual powdered or fluid chemicals as well. Michael F. Doherty, a professor of Chemical Engineering, says chemical plants are actually industrial-sized kitchens. In them, manufacturers whip up a huge array of products by using basically the same few ingredients, transformed through enormously complex recipes.

"Take methyl acetate, used in polyesters," Doherty begins. "First you take some methanol, and you take some acetic acid, carry out a reaction, and you've taken the first step on your way toward making plastic." Unfortunately, Doherty explains, not all of the methanol molecules and acetic acid molecules react during the normal process. "So, while you are indeed turning valuable raw materials into product, you are also turning them into a mixture of junk. You may end up with extraneous, mingled chemicals, or you may even end up with something toxic. In either event, you have to strain out or evaporate what you wanted from what you don't want, and then process and/or dispose of the rest. You get your prize, the molecule you wanted, but at what cost? It's always been a terrible waste of raw materials that held enormous value just minutes before."

Both Doherty and colleague Michael F. Malone knew that it was fundamentally possible to design a chemical plant that would bring together in the exactly correct amounts the raw materials needed for some types of reactions. Eastman Chemical had already proven that when the company built a huge plant fine-tuning the production of the methyl acetate described above. "They designed a process so precise, one that used all the raw materials so efficiently, that no one else can now compete with them," Doherty recalls. Doherty says Eastman Chemicals great success is what led the UMass Department of Chemical Engineering to explore whether or not the same methodology of simultaneous reaction and distillation could be applied to other chemical recipes. "And basically, we knew we had to work it all out on paper and test it here," Doherty adds. "Simply trying this and that, even on a small scale in an industrial lab, would have been enormously expensive." In 1995, the team received funding from NETI to explore the possibilities. Industries supporting their research included Eastman Chemical, Dupont, Union Carbide Corporation, Dow Corning, Shell International Chemical and ICI-England.

Much to the excitement of every major chemical company in the world, Doherty and Malone and their students have indeed documented a new way to use an old methodology to pinpoint, with enormous precision, exactly where prize ends and unwanted by-products begin in many interactions. Using their extensive knowledge of the mathematical equations that come into play during any reaction, the researchers have successfully predicted exactly how and when the desired prize molecule will be formed in a given reaction chamber, and how and when these and other molecules will continue to react from that point on. Armed with this knowledge, manufacturers may soon be able to bring their raw materials together far more selectively, rather than in the mix a lot, separate a lot method currently employed in most reactions. In fact, Doherty and Malone's tests indicate that its entirely possible to design reactors that can allow a desired molecule to be grabbed the millisecond it is actually created simultaneously reacted and separated allowing the unreacted raw materials to pass along unaffected and available to be sent through the reactor again.

Using a high-pressure apparatus built with NETI funding, the UMass team succeeded in a demonstration using one of the most complex and hard to pinpoint reactions: the creation of isopropyl acetate. "It has so many features common to other chemistries, and yet, such a narrow range of actual reaction conditions, that we figured if we could demonstrate our theory worked on this, we could apply it to just about anything," Doherty says. Other reactions of a more proprietary nature have now been tested in their sponsors labs as well, and Doherty says the results are the same: the reactive distillation technology appears capable of giving engineers an ability to predict, and thus intervene and exert control, in even the most subtle of reactions.

Eastman Chemical says the long-term potential of these simultaneous chemical reaction and separation technologies can result in dramatic benefits. "In the right circumstances, simultaneous separation can markedly improve reaction conversion, resulting in higher yields and lower costs, or reaction selectivity, resulting in less wastes," says Technology Fellow Jeffrey J. Siirola. "Likewise, simultaneous reaction can sometimes markedly simplify separation and purification systems by more completely reacting raw materials, so that none is left over, or by reacting difficult to remove impurities into more easily separated compounds. Where this reaction and separation synergism is successful, the result can be to reduce the cost to build and operate a chemical plant by one-half, or even more." Siirola says the methodologies being developed at the UMass Process Design and Control Center are critical to enabling engineers to both predict in which specific situations combined simultaneous reaction and distillation (the most common separation technique in large scale chemical processes) are in fact synergistic, and also to appropriately design equipment and systems to achieve the expected synergistic performance. The UMass research, he concludes, "is rapidly approaching a solution to some serious industrial problems."

Doherty says all the financial and environmental benefits aside, the sheer magic of the new system is a joy to those in the chemical engineering industry. "Using the new method, we are now able to get answers we could never, ever have expected to come upon using the old ways, he concludes. Now we know exactly where and when to look, instead of playing chemical hit or miss."

NETI Project Profile # 4

A Cure for the Cure

UMass Researchers Perform Ground-Breaking Research in the Ultraviolet Curing of Polymer Coatings

By Deborah Parker

If it's glistening and smooth today, chances are it started out sticky and wet in a manufacturing plant somewhere. That's the bottom line on all the coated products Americans use in their homes and offices every day. From orange juice cartons to counter tops, from photographic film to the paint job on the vehicle in the driveway, there is barely a moment that goes by in which specialty coatings don't play some kind of role in modern-day life. Unfortunately, drying or curing all those coatings has played a significant role in the overall energy consumption and its resulting pollution in the nation's manufacturing plants as well. While the Clean Air Act has already had a major impact on reducing the use of solvent-based coatings that once released enormous amounts of volatile organic compounds into the atmosphere, the switch to water-based coatings did not address the energy-intense procedures still required to dry them. According to a team of polymer scientists at the University of Massachusetts Amherst, however, ultraviolet light may soon offer the cure.

"The demand for high-quality, durable coatings is reflected in almost every manufacturing industry today; these coatings offer numerous benefits, from the time-release coatings on medicine capsules to the coatings that allow data to be transcribed onto a computer disk," Dr. Shaw Ling Hsu explains. "But for those industries wishing to be more environmentally conscious, as well as those now mandated to be, that's made finding alternatives to current curing procedures quite essential." Hsu and co-investigator Dr. Jacques Penelle believe radiation curing may be the alternative industry requires. Using custom-engineered formulations designed to be particularly sensitive to ultraviolet frequencies, a furniture manufacturer, for instance, may soon be able to flash dry the finish on an intricately carved hutch in a fraction of a second, rather than blow-drying it for several hours, or even days. Hsu and Penelle are in the midst of documenting the possible of radiation curing for the nation's coating manufacturers with the help of funding from NETI. Exploring the relative strengths and weaknesses of using UV technology to replace the energy-intense combination of high temperatures and fan-driven air now traditionally used to cure coatings, the team hopes to provide data that will benefit every industrial coating user in the world and to dramatically impact the environment while they're at it. The early findings at UMass suggest that more than 50 percent of the products treated with conventional curing methods could be efficiently cured with radiation instead. "The technology switch," notes Hsu, "could result in one of the singularly most dramatic decreases in energy demand ever seen by the American coating industry."

"Radiation curing is not new," Hsu continues. "European industries, which have more stringent environmental guidelines than we do, already use ultraviolet radiation to cure some 20 percent of their painted products," Hsu notes. "Yet, even though the United States uses more paint than Europe and Japan combined, fewer than one percent of American painted products are UV-cured. Thus, one of our goals has been to generate the first scientific data about UV curing to offer to American manufacturers. This data is something they need to consider now, and will need to understand even more in the future, as environmental mandates become more stringent. At the same time, we believe we may also be able to suggest solutions to some of the problems once associated with UV curing."

Hsu explains those historical problems were threefold. One has been that pigments in paints have sometimes absorbed the radiation faster than the rest of the paint molecules, resulting in inconsistent formation of the final coating. Unfortunately, making the rest of the paint as UV-sensitive as the pigments themselves rendered it so reactive that it became virtually impossible to use. "The coating would harden the second that the container was opened, and often, even while the container was still closed," Hsu notes. A second problem has been that even pigment-free polymers dried so quickly when the radiation was administered, surface stress sometimes resulted in a coating that would buckle or crack. And finally, the acrylate monomers traditionally used to elicit good radiation-sensitivity have created allergic symptoms in many chemically sensitive workers. Penelle explains that's because humans react to these chemicals the same way they react to freshly cut onions, "Their eyes sting and water. And some people are extremely sensitive to these polyacrylates," Penelle notes. "Fortunately, we have already solved that problem. We have successfully synthesized some new monomers that the body appears not to respond to, and yet are quite acceptable for UV curing."

The pigment problem -and the hard-as-a-rock-in-the-can problem - are also well on their way to being solved, at least in the UMass labs. "We are developing a special class of photo initiators that work through a double-trigger process," Hsu explains. "This new coating, sprayed on its host surface at ambient temperatures, will just sit there, looking smooth and wet until the UV apparatus is turned on. When the worker throws the switch, the new molecule the researchers have developed instantly absorbs the radiation and reacts by heating up. The increase in surface temperature, in turn, activates the second, heat-sensitive components of the new coating. When the temperature reaches 50^{o}C (122^{o}F), the surface immediately dries. It's all over in a minute." The final deliverables that Hsu and Penelle hope to turn over to the industry will be data that demonstrate the relationship between certain components, the surface itself, and the UV radiation - to create a chart of how monomers link into polymers to make a coating and how and when the resulting stresses are created. In fact, using a laser measuring apparatus developed in their lab, Hsu and Penelle have already successfully produced the first-ever concrete measurements of monomer conversion and the resulting impact upon a surface.

The research has already generated significant interest among the leaders of paint, adhesive and other specialty coating producers across the nation. Loctite Corporation, makers of Super GlueTM and other specialty adhesives, is one industrial partner supporting the UMass project. "A growing number of Loctite's products, used in the manufacture of engineering and automotive equipment, electronic components, optical devices and medical equipment, are already UV-cured, thus we are very interested in supporting and promoting academic research which may have an impact on this business," notes company spokesman John Woods. Noting the absence of solvents, the low energy required to cure the new adhesives and the rapid curing rate of the UV products, Woods explains these qualities make them particularly suitable for high speed automated assembly operations, where high production throughout can result in significant reductions in manufacturing costs. "The precise cure control is also a major benefit because radiation curable products are completely stable until exposed to light of an appropriate wavelength and intensity. This allows components to be precisely aligned prior to curing, making them especially suitable for a range of imaging applications, including photoresists, optical data storage, printing plates and rapid-3D-prototyping."

And, despite the company's existing record of industrial success with UV products, there is much that manufacturers do not understand at a fundamental level about these systems, Woods concludes, which is why the UMass research is so important. "The Hsu-Penelle research on radiation curing should enhance our understanding of the relationship between the radiation curing conditions and the material properties of the final polymer. In addition, it proposes to lay the groundwork for the development of even more reactive systems, with even less toxicity. We expect this will lead to development of new applications for radiation curing into areas traditionally served by less environmentally acceptable products."

The one obstacle for manufacturers, Hsu admits, is that the UV technology will probably increase manufacturers costs by about 15 percent as new high-tech raw materials will be required, as well as the need to purchase and maintain UV apparatus. "But all indicators are pointing to the fact that these costs will simply have to be born, that the environmental guidelines will mandate the switch," he stresses.

NETI Project Profile # 5

Sticky Business

Introducing "All Natural" Adhesives

By Deborah Parker

Anyone who's ever watched a medical show on TV has seen a green-suited surgeon calling "Sutures!" as he or she reaches to stitch up a wound. According to a team of polymer scientists at the University of Massachusetts Amherst, there may come a day when that same surgeon will be calling out "Glue stick!" instead. The same all-biodegradable glue may be used to seal envelopes and packages, too, and be grown on an actual plastics farm coming soon to a field near you. It's not science fiction; it's a new kind of adhesive discovered by Robert Lenz, a professor at the Conte Polymer Research Center at the University of Massachusetts Amherst, and Steven Goodwin in the Department of Microbiology at the University. The pressure-sensitive adhesive is actually manufactured with polymers made by bacteria, and determined to be entirely biocompatible. "In the tests done to date, the body has shown no immune response to these polymers; they have slowly and totally been absorbed into the body," says Lenz. "What's more, the glue is perfectly capable of being used in everyday packaging adhesive applications as well. Most importantly, and unlike most current glues, it will biodegrade entirely when buried in a landfill." Invention of the new all-purpose adhesive is just the latest discovery emanating from research on these bacterially produced plastics, which Lenz and colleagues have been studying for about ten years. Working with a particular species of bacteria *Pseudomonas oleovorans* they discovered that the organisms would create granules of polymer within their bodies if their food supply were threatened. The microorganisms then feed on this polymer as needed, converting it back to nutritional fuel.

"Since the exact type of polymer they produce is based on the specific chemical compounds they are ingesting at the time," Lenz explains, "we found that by bringing the bacteria into the lab and offering them compounds not normally found in their environment, we could make them adapt and produce polymers with unusual compositions." With funding from NETI and support from a handful of interested polymer manufacturers, Lenz and his colleagues began exploring the potentially valuable characteristics of some of these compositions. "Stickiness," Lenz notes, "turned out to be one of those valuable characteristics." Normal polymer-based adhesives, such as the ones used in making adhesive tape, are made from petroleum-based products and do not biodegrade, he explains, and that non-biodegradability has been one of the challenges that has faced researchers attempting to invent things like totally biodegradable diapers. Interestingly enough, Lenz says some of the compounds fed to the bacteria are about as renewable as you can get. "Corn oil, palm oil, soy bean oil - and even waste cooking oil - have all proven effective," he notes.

So what's stopping companies from making the switch? "The petroleum-based compound costs $1.50 per pound to make, and the bacterial version would cost over $2.00 a pound, so not too many companies have been interested in producing it in bulk yet," says Lenz. "But I haven't given up hope. Should we suddenly have another oil crisis, or should environmental guidelines be enacted that require total biodegradability of given products, then this adhesive could be a big deal." Other countries may beat the United States to commercial development of the new products, Lenz notes, since municipal composting facilities - requiring total biodegradability of the rubbish left curbside - are already growing in popularity in Sweden, Norway, Germany and Japan. But a Massachusetts based company, Metabolix, Inc., is actively developing these types of bacterially produced polymers, and is seeking investors who might have an interest in developing products made from them.

The 3M company was one of Lenz's early industrial partners, and the firm says they stand fully ready to put the research to use when market conditions are right. "3M's interest in biodegradable adhesives stems from a long standing goal of offering innovative new products," says Dr. Denise R. Rutherford, Technical Manager for the Bonding Systems division of the Minnesota-based company. "We strive to support development of new products which are suited to changing environmental regulations and needs. Biodegradable adhesive technologies are of developmental interest to 3M and Professor Lenz has provided us with an opportunity to obtain additional information about such technologies." Meanwhile, back at the lab, additional research has been performed that might allow these polymers to be produced in agricultural crops, bypassing the bacteria altogether, "to actually be grown as part of an oil-producing plant instead," Lenz says with a smile. "In fact, one company has already been successful. They, too, however, are waiting for an economic demand before pursuing this avenue. Lenz says in the end, while we now possess the technology to create totally environmentally sound products, we may need legislation that requires the use of such products for the technology to advance any further. "If we ever enacted such a law, one that said containers or such must use only biodegradable materials, and if oil prices became high enough to make the use of renewable resources more attractive? Then," he concludes, "we'll be on a roll here."

NETI Project Profile # 6

On the Road Again

Recycled Plastics Will Soon Add Flexibility and Strength to the Nation's Highways

By Deborah Parker

The proverbial bend in the road may soon have a little bounce to it, thanks to polymer scientists at the University of Massachusetts Amherst. Alan J. Lesser of the Department of Polymer Science and Engineering at UMass has discovered a way to take discarded plastic milk jugs and soda bottles, melt them down, and use the resulting polyolefin "goo" to add a little give to the asphalt used to pave highways. The result is a stronger, stretchier highway that can better survive the freeze and thaw cycle of a New England winter. What’s more, the poly-goo seems to make asphalt more impervious to the heat of a Texas summer as well. The new technology promises safer driving conditions, reduced costs for contractors - and the municipalities that pay them - and last, but not least, a significant reduction in the amount of traditional asphalt required to maintain the nations roadways.

Rich in environmentally threatening napthenes and asphaltines, asphalt is basically left over oil that cannot be refined further for any other useful purpose. "It's a toxic mess," Lesser explains. "Yet contractors put more than seven million tons of these materials on Massachusetts highways and roads each year. We've had to tolerate the toxins because asphalt is all we had to work with. And, quite simply, people really wanted roads."   The roads people got, however, often left much to be desired. Federal Highway Administration specifications required only that a certain grade of asphalt be used to pave its roadbeds; contractors in New England thus used the same AC-20 that contractors in Texas did. In New England, the material grew brittle in the cold, cracked, and eventually caused the potholes that wreak havoc on the suspension systems of cars. In hotter climates the asphalt would melt, causing waves in the road that didn’t do the suspension systems much good either, not to mention releasing more of those napthene fumes into the environment.

Scientists had tried using plastics to address some of these problems, but the resulting mixes just didn’t work. The plastic would rise to the surface - "Think no traction," Lesser says with a smile - and the composites would eventually crumble. Lesser wanted to know why, and what polymer science could do about it. Armed with funding from NETI and the corporate support of Shell Oil and Morton Chemical, Lesser launched an investigation into the polymer/asphalt failure. The answer? "Size counts," says Lesser. The researchers discovered that if the recycled plastics are ground to the correct particle size - much smaller than the particles tried in earlier experiments - the polymers would stay in solution within the asphalt blend, while offering a significant increase in road surface strength and flexibility. The team is now continuing its research so that exact recipes for the additives can be given to meet the diverse roadbed demands of the nation.

"Basically, here in Massachusetts, we're figuring we can replace about five percent of the asphalt now used with the polymer additive, which has no toxicity associated with it. While five percent may not sound like a lot, when you realize that some seven million tons of asphalt is now used in roads and on roofs just in Massachusetts each year, you’re talking about a meaningful reduction," Lesser notes. "And when you multiply that by 50 states, you've got a significant reduction in toxic impact. You’re also increasing the life span of all these roads by many years, reducing the need to repave them, and all the energy consumption that goes into that."

Lesser’s research has also attracted the attention of some companies that don’t have anything to do with asphalt at all. Solutia - which makes the nylon fiber for carpets - wants to know if discarded carpets could be melted down and used to fill the nations roadbeds. Which got Lesser to thinking that the manufacturer also produces the nylon filaments used to strengthen radial tires. "So now I'd be delighted to undertake further research on behalf of a tire company, if any are interested," Lesser concludes. "If we can melt down tires? Not only would the fire hazard, the environmental hazard posed by tire dumps, be addressed, but the concept just appeals to me, he notes. Ashes to ashes, tires to roads, it just has a nice ring to it, don’t you think?"

NETI Project Profile # 7

Reducing the Impacts of Toxins and Shopping Carts

Using Ground-Up Polyurethane Flashing to Reduce the Demand for Iso-Cyanide

By Deborah Parker

What do car fenders and many children's toys have in common? They both need to be impact resistant, whether to survive a mechanical force of two tons all told, or a human one of two years old. And, in the 1990s, anyway, they're both manufactured from the cross-linked polymers known as polyurethane. Polyurethane, for all its many strengths, has always had two inherent weaknesses, at least as far as manufacturers and the environment go. One is that the reaction-molded products made from it can never be melted down and reused; the second is that making these products involves the use of iso-cyanite. This highly lethal solvent caused the Bhopal, India disaster a decade ago, where an accidental release of the chemical killed thousands. Reducing the demand for iso-cyanite has been high on the list of environmental checklists ever since - and a polymer scientist from the University of Massachusetts Amherst has recently discovered a way to make a significant contribution toward that end.

Alan J. Lesser, from the Department of Polymer Science and Engineering at UMass Amherst, is a specialist in the micro-mechanics of polymers - the way polymers break and absorb energy when loaded. With funding from the National Environmental Technology Institute, Lesser recently experimented with grinding discarded polyurethane castoffs or flashing from a manufacturing plant into pieces so small, they could be reintroduced into the product stream as raw material. "As far as manufacturers see it, however, grinding the materials is just another expense," Lesser notes, "so we had to demonstrate that they could recoup the expense by producing a product that was actually better than one they could make with all virgin feedstock. I'm delighted to report we've been at least moderately successful."

The first part of Lesser's research involved coming up with a theoretical model that would explain and predict just how small the optimum particle size would have to be to have the ground-up polyurethane flashing properly bond with the virgin material. "Really, really small - about ten microns - was the answer," notes Lesser. The second part of the research involved introducing the ground poly to virgin materials in different ratios, scientifically charting the points at which the additive actually served as reinforcement to an existing product, and at which point it created a defect and reduced performance instead, the way large pebbles in a concrete mixture might cause a dried block to fragment under pressure. "We've determined that its possible to both increase fracture toughness by about five percent, while concurrently reducing the need for virgin material by up to ten percent," Lesser notes.

Several major players in the industry are watching the research closely. Shell Chemical Company supported both stages of the research, since the new composite might serve as a component in some new products they have in the wings. Industry partner GE Plastics is also interested, always looking for ways that their Novel GTX thermoplastic can be used to help automobile fenders deflect things like baseballs and shopping carts and ways to make it stronger, more cheaply, and with the least possible impact upon the environment.

"More research is obviously called for, but so far we've demonstrated the potential to get an improved product, reduce the demand for iso-cyanite, and reduce a company's flashing disposal costs," Lesser concludes. "We anticipate that many different industries producing these products, using them or charged with disposing of them will be interested in these results."

NETI Project Profile # 8

Beyond Benches

Thanks to a Process Discovered at UMass, a Soda Bottle Discarded Last Week May Soon Come Back as a Car

By Deborah Parker

Americans love soda. In fact, some 450 million pounds of plastic soda bottles are collected at the nations recycling centers every year. "While most consumers probably think that those bottles are washed and melted down and turned into soda bottles again, that's actually not the case," says University of Massachusetts Amherst polymer scientist William J. MacKnight. "Because the recycling industry can't guarantee that a consumer didn't store insecticide or gas and oil for the lawn mower in one of those two-litre bottles before it ended up on curbside, reusing the plastic for continued food storage has always been out of the question. There was also a very slight degradation of the plastic during recycling, just enough that reusing it in a thin-walled container might render it not quite as strong a second time around, not strong enough to hold liquid under pressure."

That's why the traditional fate facing these hundreds of tons of used polyester has been reuse in the manufacture of items requiring only low-end raw materials used in thick applications, things like the hardy park benches now dotting the nations parks. "But this soon begged the question, just how many park benches does the world need? MacKnight continues. We wanted to explore if there wasn't some way we could learn to reuse these polyester molecules, trapped inside as it were, in more high-end products, products that were currently requiring virgin raw materials," MacKnight notes. "We recognized that any success would thus both reuse and reduce two of the environmental maxims."

With funding provided by NETI and the corporate support of G.E. Plastics, MacKnight and his students at the Silvio Conte Polymer Research Center at UMass Amherst soon learned that indeed, soda bottle polymers could be depolymerized treated and melted back down into a plastic syrup. The consistency of the new syrup was identical to that of the various polymer liquids manufacturers blow into the molds used to make everything from computer consoles to vehicle dashboards. The soda bottle team was soon confronted with a serious, chemical engineering dilemma. They discovered that while one of the polymer components the trimer could indeed be melted back down, it did so only at 500^{o}F, a temperature that destroyed the only existing re-hardening catalyst. Preliminary research into various methods of filtering out that one component, allowing manufacturers to use the rest, was immediately explored, but the idea was soon discarded as too expensive. "Nobody was going to switch to the new material if it had a whole new set of costs associated with it," MacKnight acknowledged. A year later, however, the research team is grinning ear-to-ear. "We discovered a new catalyst, one that will work at the higher temperatures" MacKnight says cheerfully. "Our patents are pending."

Roger Kambour, a research scientist with General Electric, says the ramifications for the plastics industry are fairly enormous. "Every manufacturer of vehicle components be they cars, airplanes or boats should soon be knocking on MacKnight's door, since the new thermoplastic components appear to be as hardy as the fiberglass material currently in use as car fenders and vehicle cross-beams," Kambour notes. "For starters, the current manufacturing processes require the use of solvents that are both toxic and expensive," Kambour explains. "This has meant that different manufacturers have had to safeguard their employees during the manufacturing process to begin with. Then, they either had to incorporate the solvent into the product, and thus lose it not to mention having to worry about the potential release of toxins should the impregnated material be involved in a hot-enough fire. Or, they had to go through various steps to evaporate the solvent off, and attempt to reclaim it. Both are expensive," Kambour concludes. "The amazing thing about the new catalyst is that it allows scrap polyesters to be melted down, into a low viscosity fluid that can be injected molded and reacted in place, without the use of any toxic solvents at all."

What’s more, at the end of the life span of the traditional thermoset resin components, end products can only be discarded, they can't be melted back down, period, Kambour notes. "MacKnight's new thermoplastic, however, seems to hold the promise of being capable of repeated meltdowns. This means it could be salvaged in an auto yard, and used to manufacture things like shipping pallets. Then, if those were damaged, they could be returned, melted down, and remolded, again and again." MacKnight says the Polymer Center is now simply waiting for some major players in the polyester industry to step forward with some R&D pilot projects to test the properties of the scrap poly goo. He doesn’t expect to have to wait too long.

"The problem facing us is that most companies are doing fine with the processes they have in place, and unless something changes new environmental mandates banning their current solvents, they think, why rock the boat? The answer is, we have developed a new chemistry that will allow plastics manufacturers to use their current plants, give them significantly lower cost, produce a superior product, and have zero environmental impact," MacKnight concludes with a smile. "It won't be long before somebody says, hey, we'd be crazy not to."

NETI Project Profile # 9

The Squeaky Wheel's Grease Goes Green

By Deborah Parker

Without grinding, we'd be living in the Stone Age. That’s how University of Massachusetts Engineers Stephen Malkin and Changsheng Guo sum up the importance of this one mechanical application, used in hundreds of thousands of metal working plants around the world. If you think about it, grinding is at work in almost every precision manufacturing process anywhere, explains Malkin, Distinguished Professor in the Department of Mechanical and Industrial Engineering and Director of the Grinding Research Program at UMass Amherst. Every bearing company depends on it, the makers of almost every engine component, the makers of gears, ceramics, optics, even the razor blades used by millions of people every morning. If something is precisely machined, you can pretty much count on the fact that grinding has played a part in it by making rough edges smooth. Grinding, and the application of some kind of oil, make it all possible.

Why oil? "The process of bringing the rough edge into contact with a grinding surface has always required the anointing of the grinding surface with a lubricant capable of reducing the friction and subsequent heat produced at the interface," Malkin notes. "Without it, the metal reaches too high a temperature - well over a thousand degrees - and the product itself will sustain irreparable damage." Unfortunately, the emollients that have long protected the product in the machining industry have taken a toll on both its workforce, and the environment. Traditionally, copious amounts of petroleum-based lubricants have been required to lubricate and cool during the grinding process. Cleaning and/or disposing this used oil, laced with billions of metal slivers or swarf, shed in the grinding process, has been an arduous task for all involved, requiring numerous steps along the reuse-recycle-disposal journey. "It had to be mixed with biodegrading agents, and filtered. Then, at the very end of the line, there were always the disposal costs related to any used oil product of the water-soluble variety," Malkin continues. All of these costs can be enormous, when you take into consideration that one large manufacturing plant might have several thousand gallons of oil in their grinding tanks at any one time. In fact, the annual expenditures related to grinding operations in the United States alone are estimated to exceed 25 billion dollars.

Protecting workers from the ever-present oil-laced vapors has been another challenge. "While we all use petroleum-based lubricants in many aspects of our lives without ill-effect, breathing in petroleum vapors over a long period of time has been implicated in a variety of ailments," says Robert Myers of ITW Fluid Products Group, based in Tustin, California. ITW is the company that, in 1996, sent UMass a small container of a new product that needed testing for the marketplace. Generically referred to as an ester oil, its an industrial strength version of the vegetable oil people use in meal preparation every day. Since UMass has one of the only internationally recognized public and impartial grinding research labs in the world, Accu-Lube R asked Malkin and Guo to answer the question: Could its corn oil replace petroleum on the grinding wheels of the world? Malkin and Guo, who were about to embark on testing liquid nitrogen as a possible coolant/lubricant for the grinding industry, agreed to test the oil as one of many emollient controls included in their studies.

NETI gave the team funding to begin its research; industrial giants like General Motors, Norton Company, Torrington/Ingersoll-Rand, SKF, and Landis Gardner immediately stepped forward with offers of additional equipment and supplies. "We were eager to take part, as what the NETI researchers are doing is of vital interest and importance to the industry as a whole," notes Dr. Chi-Hung Shen, manager of Machining Systems for General Motors Global Research and Development Operations. "The health hazards and environmental impacts of existing metalworking fluids have been major and ongoing concerns for our industry. Having a non-toxic alternative would have a profound impact on our industry."

Within only a few months, Malkin and Guo had abandoned the liquid nitrogen part of their study after documenting that, while the substance did indeed cool effectively, it was poor at preventing surface damage - and was going to be too expensive for use on an industrial scale. What they were documenting about the ester oil, however, continued to amaze them. "Ester oil is proving not only an effective grinding fluid, but it is also used in almost ridiculously small amounts. You have to apply only a few drops! In our test machines, we used far less than an ounce per hour," Malkin notes. And as for non-toxic, as producer Myers, from ITWs Accu-Lube Division likes to explain with delight: "It's vegetable oil. No matter how much your body ingests, it processes it as just another food."

The relative costs of using ester oil are also encouraging. According to Malkin and his colleagues, the cost of using water-soluble grinding fluid in a 60-gallon tank, 8 hours a day, 5 days a week, 50 weeks a year, would be $1,125. "Add on the required replacement fluids, disposal costs at even $2 a gallon, and labor, and the overall annual cost would be $1,970," Malkin notes. The UMass research documented that using liquid nitrogen in the amounts required to cool an identical operation would cost $7,000. "Meanwhile, while the original start-up costs for the ester oil would include an expenditure of about $900 for the micro-lubrication applicator, after that, the cost of buying the oil required would be only $215 a year," he concludes. "Best of all, disposal is greatly simplified and is far less expensive."

Today, General Motors is about to start testing the new coolant lubricant in its own laboratories, and UMass is embarking upon tests that will use jets of cold air to blow the swarf away from the interface and provide additional cooling. The team is also interested in identifying corporate sponsors for future research into the new lubricants possible applications in the drilling, reaming, tapping and sawing industries. As for the UMass teams current corporate partners, well, they couldn't be any happier. "We have all been trying so hard to be environmentally conscious and protective of our workers, but alternatives just didn't seem to exist on the horizon," concludes Steve Reder of Torrington/Ingersoll-Rand. "If this UMass research plays out as it seems that it may, even having the new technology available for limited applications will have an enormous and far-reaching impact. This is a big deal, because its going to make such a big difference, for so many."

NETI Project Profile # 10

Plotting the Possible

New Computer Software Allows Chemical Engineers to Abandon Off the Shelf Designs for Something with an Optimum Fit

By Deborah Parker

Almost every man-made product, from modern fabrics to pharmaceuticals, comes from oil, the primordial fluid of chemical engineering. To produce those fabrics and aspirin, chemical plants separate parts of the oil from other parts, and then recombine the desired components in new and useful ways. The cast off raw materials, and the by-products created accidentally in the chemical reaction and separation procedure, has long been one of the biggest environmental challenges facing industrialized nations. And with more stringent environmental guidelines to contend with, and the cost factor of product loss and/or by-product disposal, reducing or eliminating by-products has become a major focus of the chemical engineering industry.

Scientists from the University of Massachusetts Amherst are about to hand industrial chemists a new and impressive tool to help them on their way. Ka Ng, a professor in the Chemical Engineering Department at UMass, has recently unveiled a new computer program that will allow companies to optimally design new chemical plants in such a way that unwanted components and by-products are eliminated or significantly reduced in the very process of creating the products they want. "The problem has always been that chemical engineers, the people designing plants, were used to shopping for available models when it came to procedures, the machinery used to produce a given product," Ng explains. "A good parallel in every day life would be the building of a prefab house. The potential owners have a catalog of tested styles to choose from, and that would be it; choose this roof style, and you get a door here, one there, and one full bath." In chemical engineering circles, that meant if you wanted to produce A, you built a reactor just like the one everyone else had built to produce A, Ka continues, "even though that reactor might have some significant problems associated with it, be it waste or cost. Why, there is one reactor out there that, to do what it must do, is operated at 450^{o}C, at pressures of 50 atmospheres. It is like operating a bomb, 24 hours a day! But it was the only off the shelf technology, the only sure thing that designers were familiar with."

What Ng and his colleagues have done at UMass is create a computer program that allows designers to scratch the off the shelf approach to building reactors. With funding from NETI, Ng and his colleagues are creating and testing programs that allow designers to custom design their reactors and simultaneously weigh all the major factors involved in modern chemical plant design, including process and product safety, environmental impact, waste minimization, overall costs and ease of management and control. With the same ease that a customer might expect shopping the Web page catalog of an international retailer, the chemical plant designer using Ng's program can now make hundreds of adjustments to reduce reactor pressures by lengthening this, reduce the temperatures by adding that, "or remove the toxic by-products by doing a reaction this way, and preventing their formation in the first place," Ng explains.

How does it work? Well, sticking with the house analogy, Ng explains, "we ask you to begin by entering the ages, sizes and genders of family members. The computer will then ask for more information your occupation, hobbies, and daily schedules. And then, it goes to work!" In seconds, the screen might suggest that, with five children in the house, three bathrooms are in order. But the cost of that! Not to worry, the computer continues, if you build them on top of each other like this a schematic appears the plumbing costs will be reduced 40 percent and you can have three for the price of two. Oh, wheelchair access makes a second-floor bath a concern? Then how about nesting all three on the first floor, with access like this? (Another schematic appears.) And, since you're building from scratch, why not install a solar water preheating system along the southern exposure, and save on your fuel costs as well?

Ng's computer software does exactly this, using all the known reactions and reactors, separations, and separation technology. Enter the product or products you wish to produce and the computer begins, step-by-step, to help plot the available choices, ever cueing for environmental and cost management concerns. A page of reactor styles to choose from appears first and then, step-by-step, the computer offers up the next realm of possibilities - and alerts the designer to what is not possible as well, should a novice make a mistake along the way. "If you select a device or procedure that allows a small amount of product to escape into the atmosphere and the product you are dealing with is hydrogen cyanide, which will instantly kill anyone who even smells it the program will alert you to your error," Ng says with a smile.

For other vital factors, the computer jumps far ahead of the designer, accessing its enormous database of chemical attributes, interactions and relative sensitivities; desired by-products, undesired ones, the constituent parts and technology available, and the relative costs. It presents a variety of choices, and alerts the designer to problems, and possible ways to circumvent them, even if it means going back and choosing Reactor Design C, when you started with Reactor Design A, Ng notes. The computer will instantly reapply all the data entered to that point to the new choice. It does not even utter a sigh.

Ng has been taking the "show" on the road. Many major chemical producers - Rohm and Haas, Dupont, Morton International, Solutia, Searle, and Mitsubishi Chemical America - among them have expressed interest in helping to fine-tune the technology and test it in their R&D laboratories. "Professor Ng's research on multi-phase chemical reactors provides engineers with practical tools that can be used to design reactor systems capable of producing proportionately fewer undesirable materials," says Alan Leviton, a Technical Fellow with the Rohm and Haas Company. "Chemical manufacturers who use these procedures stand to gain a competitive advantage by reducing the complexity and cost of new plants. Reducing the production of undesirable by-products also supports industry goals of sustainable growth and contributes to improving the industry's public image, a goal of the Responsible Care program."

The beauty of having it all on computer for the first time is that the software can be updated as required, allowing chemical engineers to redesign when the technology is improved and to apply new knowledge as it is revealed. Ng concludes, "This will allow us to change as fast as the possibilities do, as fast as the world changes. And sometimes, the world can change very fast."

NETI Project Profile # 11

UMass "Crystal Sieves" Hold Enormous Promise
For Chemical Plants, Communications, and Bio-Medical Industries

By Deborah Parker

You can't put a square peg in a round hole, not if that peg and the hole are of comparable size, anyway. It's a lesson in mechanics that most people learn in the playpen. But some University of Massachusetts Amherst chemical engineers have recently taken the lesson to a whole new plane; one so high that their molecular sieve membranes and films may soon change the entire chemical industry - and then some. Chemical engineers Michael Tsapatsis and Jan van Egmond, have succeeded in creating a membrane of inorganic crystals that join together in a geometric pattern so precise, only specific molecules of the exactly right shape can slip through. Early tests by the chemical engineering giant BP/Amoco have confirmed that this exclusionary molecular sieve is proving highly successful at separating even closely related molecules of hydrocarbons poured through this membrane of the crystal formations known as zeolites.

Why is this so important? "Because separations form the crux of almost every single chemical engineering endeavor," Tsapatsis explains. "The chemical industry spends billions of dollars each year separating mixtures of hydrocarbons into their many components, just to meet the demand for different types of fuel and chemical feedstock. Most of the expense involved in completing industrial processes usually lies in bringing together enough of the right combination of materials to get at least a small amount of what you're aiming for." Disposing of unwanted products and solvents is not only expensive, it has also been one of the most pressing environmental problems facing the chemical engineering industry since its inception.

In 1996, NETI provided Tsapatsis and van Egmond with funding to investigate whether zeolites could be grown into an industrial-strength material capable of allowing only the right chemical components - and in the right amounts - to come together in the first place. Tsapatsis says the answer is now an emphatic "Yes". The membrane has proven 100 percent successful at separating ethanol and methanol mixed into water - leaving only pure, untainted water behind. What's more, by virtue of its exclusionary mechanics, the zeolite membrane may soon render some even highly complex reactions virtually by-product free.

Take the process involved in producing para-xylene, a highly desirable substance used in the manufacture of polymers and resins. The challenge is that there exist three xylene isomers of the same mass, boasting the same number of "arms," Tsapatsis explains. The only characteristic that identifies whether an isomer is an "ortho", "meta", or "para" isomer is the location of those arms, and only the "para" isomer has the desired result. With the membrane sieve, the zeolites don't even allow the "metas" and "orthos" through the gate. And, because the left behind isomers instantly chemically reorganize to maintain a nearly equal proportion of the meta, ortho, and para isomer shapes, the excluded solution can react, "until there is virtually nothing left," Tsapatsis says. "The environmental management by-product obstacle is simply eliminated."

Technically known as microporous aluminosilicates, the zeolites are a family of crystals that always grow with certain-shaped holes or pores, and Tsapatsis has spent the past five years both identifying new possible shapes and sizes and getting them to grow uniformly enough to form sheets of the material. What's more, the zeolite membranes appear to tolerate highly corrosive environments and temperatures of up to 800^{O}C, unlike the polymeric membrane technologies currently in use, which can be used below 200^{O}C.

Dr. Ruth Ann Doyle, Senior Research Scientist at BP/Amoco, an industrial partner in the UMass project, says the results to date hold enormous promise. "While there have been incremental improvements to the critical separations processes used by the chemicals and petroleum refining industries over the years, there have been no significant breakthroughs. This could be that technology breakthrough. If precise control of the pore structure and its adsorption properties can be documented; if long term stability of the membrane can be documented; using this shape-selective membrane could result in substantial yearly energy savings, and even improve the yield in many processes," Dole notes.

Indeed, the next challenge faced by Tsapatsis and van Egmond, and their colleagues Dion Vlachos and Scott Auerbach - who are working on a related, NETI sponsored project - is determining the industrial life span of any given membrane sheet. Will it be three years, or thirty? That, and finding ways to make the now flawless process an even faster one, to match industrial rates of production. The new technology is already piquing the interest of those in numerous other industries, including the manufacturers of specialty films for sensors, electronics and optical components. Industrial safety firms may also jump on board to find out if zeolite membranes can filter out dangerous gases; firms manufacturing technology for clean rooms may wish to ask Tsapatsis and his colleagues to investigate the membranes ability to screen out a variety of microscopic hazards. Tsapatsis believes the mesoporous molecular sieve may possibly hold enormous promise for the biomedical industry as well if they can be managed to sieve out certain proteins, or even viruses. "The possibilities are almost endless, because, by manufacturing different films made of different zeolites, we could create membranes that would separate almost anything," Tsapatsis concludes. "If we are successful, anything you didn't want included in the end could be excluded up front by the engineering of the right molecular gatekeepers."

NETI Project Profile # 12

Pop Goes the Polymer

Carbon Dioxide Found to "Swell" Polymers, Minimizing the Need for Toxic Solvents

By Deborah Parker

The same gas that makes carbonated beverages "pop" may someday replace toxic solvents used to manufacture some of the polymer-based products used both in industry and homes. Dr. James J. Watkins of the Chemical Engineering Department at the University of Massachusetts Amherst has discovered that compressing CO_2 gas, carbon dioxide, into a mass of polymer molecules allows the plastic to behave exactly as if manufacturers had added solvents to the mix instead. On an industrial scale, the discovery could result in the manufacture of new and improved products and significantly reduce emissions of objectionable organic solvents.

Watkins says the original discovery was somewhat accidental. "Our initial goals were rather modest. We were experimenting with different ways of running chemical reactions at the surfaces of solid polymers, ones that are resistant to wetting by most solvents. Since compressed gases such as CO_2 do not exhibit any surface tension, they will wet all surfaces. We thought they would make good candidates for our purposes." When the surface experiments began, however, Watkins found not only that the CO_2 successfully wet the surface, but that it also dissolved rapidly into the polymer solid, exactly the way a liquid solvent might have. As a result, the intended reaction occurred within the solid, as well as at its surface. "That's when the light bulb went off, that this could have an enormous impact on the industry as a whole," Watkins recalls. With funding from NETI and the corporate support of Alza Corporation and the Procter and Gamble Company, Watkins and his colleagues went to work to see if reactions that might typically be carried out in volatile organic solvents could be conducted in polymer melts swollen with compressed CO_2 instead.

Why was this important? The use of organic solvents has long been tied to many reactions in the plastics industry, and removing these solvents at the end of the line has always been very energy intense, Watkins explains. "Picture, if you will, trying to dry out a very wet sponge. Not only did the drying process require a lot of energy, but the solvent emissions posed a threat to the environment. Removing them safely, and capturing fugitive vapors, has always been challenging and expensive," he continues. The new found potential to create liquefied polymer melts by using carbon dioxide gas - which is not toxic and is obtained directly from the air around us - thus has obvious and multiple benefits. "What's more, this approach appears to work just fine in existing processing equipment; the pressure demands are no different than those in polymer extruders," Watkins concludes. "If the research continues to pan out, this means the use of CO_2 gas may well replace the use of liquid solvents for many a chemical reaction in the future."

NETI Project Profile # 13

Controlling NO_x at the Source

UMass Scientists Are Unlocking the Mysteries of Nitrogen Oxide Formation … and Giving Designers the Tools to Prevent It

By Deborah Parker

Nitrogen oxides or NO_x - the name scientists give to the many ways nitrogen and oxygen can come together - play a crucial role in the human body. Without trace amounts of the compound, vital nerve signal transmission will cease. Up the parts-per-million, however, and the substance becomes a bio-irritant; long-term exposure to NO_x is associated with a series of lung ailments and diseases. When smog warnings are issued, alerting those with breathing problems to stay inside on a hot summer day, it's often because high concentrations of NO_x have been measured in the air. Preventing those high concentrations from forming at the source is the focus of some new research at the University of Massachusetts Amherst. We're surrounded by nitrogen and oxygen every day; they are in the air all around us. "But we don't have nitrogen oxides just forming in the air around us, "Phillip R. Westmoreland begins. "Nitrogen is a loner. In the air, it prefers to stay that way unless disturbed by high temperatures. It takes very high temperatures to create nitrogen oxides, and we have those conditions in combustion every day."

Westmoreland is a specialist in the chemistry of combustion and a professor in the Department of Chemical Engineering at UMass Amherst. Armed with funding from NETI and the corporate support of General Electric and United Technologies, Westmoreland and his students have used computational molecular modeling to identify exactly where in the process noxious NO_x is created in power plants and jet engines. Earlier research by Westmoreland and others - using a molecular beam mass spectrometer housed at UMass - allowed them to see the reacting fragments of molecules and measure rates of reactions. However, one of the great problems facing researchers is that the experiments they can run are limited by the pressures that can be used, while new engines, applying the known data, will be running at 60 to 100 times the air pressure normally around us.

Westmoreland's group used their expertise and computational modeling to create calculations and flowing diagrams of the NO_x chemical reactions occurring in the more extreme conditions. With this information, research and development specialists planning the engines and turbines of tomorrow are working on new designs for staged combustion chambers that circumvent the conditions required for the NO_x to form in the first place. According to scientists at United Technologies Research Center, it's this expertise in computational quantum chemistry, and Westmoreland's ability to theorize what is happening at far higher temperatures, and at pressures higher than can be created safely in a laboratory, that has the industry poised to finally make major strides in NO_x reduction.

"Engineering correlations of combustion processes are usually based upon observed phenomena and often lead to significant errors when extrapolated to new or advanced engine designs," notes Meredith Colket III, a researcher for United Technologies Research Center. "Professor Westmoreland's research is helping to unravel such details of combustion; it's assisting in developing tools that can reliably be used in real-life engine conditions. The bottom-line? This fundamental research is helping with the development of cleaner engines, at lower cost to the industry. And that should eventually translate to cheaper fares for the consumer."

Westmoreland and his students, Sree Rao and Karin Rotem, are just delighted to see their theories and applications well on their way to becoming the cleaner engines of tomorrow. "We're very excited that United Technologies is actually using these projections in their computational models. Because we were able to model the different reactions under different design conditions, right down to the behavior of individual atoms, they are able to design new engines that should be able to reduce NO_x to fewer than ten parts-per-million," Westmoreland says. "In the past General Electric and United Technologies Research Center have had to make test engines - to cut metal - in an educated trial and error fashion. Our work makes it much more efficient to make these new engines, engines that will change the environment for the better."

NETI Project Profile # 14

Turning Up the Heat

"Supercritical Fluids" Offer Promise of Replacing Solvents in the Manufacture of Many Polymer Products

By Deborah Parker

For most people, using the words propane gas and high temperatures in the same sentence brings to mind sizzling burgers on a backyard grill. But to scientists at the Conte Polymer Research Center at the University of Massachusetts Amherst, combining the two may hold the answer to one of the most pressing environmental problems facing the plastics industry today. According to polymer scientist H. Henning Winter, experiments at UMass suggest that propane, as well as a number of other common gases, can be carefully managed into a supercritical state by the simultaneous application of heat and pressure, a state that renders them into highly effective solvents required for the production of many polymer products. If this non-toxic technology can be effectively transferred to an industrial scale, the discovery could virtually eliminate the need for the toxic solvents currently required to produce many of the plastic products consumers use every day.

The "gas-as-solvent" procedure was originally discovered by Paul Ehrich, an adjunct professor at UMass Amherst. Winter, an internationally recognized specialist in rheology - the study of the flow and deformation of matter - is now using the technology to create new forms of porous polymer materials. "Our goal has been to use commodity polymers to make advanced sponge-like materials in which the pores - some 100,000 of them in a single inch - will retain their shape and structure," Winter explains. The current technology used to turn powdered polymer components into these highly complex materials is based on the use of aggressive solvents to dissolve the polymers into a liquid that can be molded, and then returned to a non-liquid state. "During the reaction, the formulations undergo a process called crystallization, a process that connects the molecular chains in a stable way," Winter explains. "Without this crystallization, the final product would instead look and behave like 'Silly Putty™'."

The existing technology then requires cleaning or separating the solvents from the desired plastic, "and sometimes, yet another solvent has to be used to clean up the first one," Winter notes. "In almost every case, the final product is almost always contaminated with trace amounts of some kind of solvent molecules still adhering to, still bonded to, the polymer molecules." Since polymer-aggressive solvents are just as aggressive about mixing with water, soil, and air as they are with polymers, they have long posed an environmental challenge and in some cases, a health threat. In 1998, Winter received funding from the National Environmental Technology Institute to research the possibility of using supercritical fluids instead.

"A supercritical fluid is really just a gas that has been forced into a state it cant normally assume under ambient conditions," Winter explains. "Take propane. Under normal conditions, if one applies very high pressure to propane, it becomes a liquid, like the liquid in the tank that runs a cooking grill. When the valve is turned, that pressure is gradually released, the liquid turns back into a gas or vapor, and that vapor burns to cook your food." But, if one heats propane above 94 degrees Celsius - roughly the boiling temperature of water - scientists discovered that even at very high pressures it will remain a gas, rather than turning to a liquid," Winter continues. "This is what we call its supercritical state. In this state, the combination of heat and pressure makes the propane molecules move about at very high speeds, thus creating even higher pressures."

Winter and his colleagues have discovered that if enough heat and pressure are applied to a mixing chamber filled with propane and polymer powder, the now highly mobile supercritical propane molecules will actually homogenize the polymer into a liquid, acting exactly like a solvent. "The resulting polymer solution is then solidified into the desired foam structure by crystallizing the molecules, effectively locking them into place," Winter explains. The one critical difference, Winter says, is that when the heat is reduced in the mixing chamber once again, the propane "settles down" and can be removed in its entirety from the tank. The crystallized polymers that remain have no residual traces of the solvent in the end product, while all of the propane can be reclaimed for reuse.

The environmental benefits are several fold, Winter notes. "Not only does no toxic residue leave the plant as part of the product, but none has to come into the plant in the first place. Propane is totally non-toxic and non-aggressive under ambient conditions - at room temperature it doesn’t combine with polymer, air, water, or soil," Winter concludes. "We are now also conducting experiments using CO_2 and are developing some new polymers that CO_2 can dissolve in the same way." The resulting 100 percent clean polymer product will be of special interest to companies that specialize in bio-medical applications, since only residue-free devices can be used to make devices for the human body. "It turns out that this new product can also be used to build scaffolding to grow tissues, for applications like skin grafts," Winter continues. "We’ve also discovered that while most clean polymer product is made in membrane form, ours can be produced in monoliths, in solid, durable pieces that can be forged into shapes for things like artificial joints. The porous polymers, in column form, could also make excellent vertical filtering systems."

One of the major Massachusetts industries that has stepped forward to help sponsor the research is Millipore Corporation in Bedford, a firm that produces membrane filters for critical purification applications. "Professor Winter's work has the potential to produce novel porous materials and, at the same time, reduce the use of solvents required," notes Millipore spokesperson Anthony Allegrezza. "We are glad to help sponsor this work, as it will put less strain on the environment if it does lead to new products."

Computer engineering firms are also expected to take a close look, as the new highly porous product appears to have the dielectric properties necessary for improving data transfer. "In fact, the only disadvantage we can identify is that propane is extremely flammable, and the mixing apparatus would have to be able to withstand high heat and high pressures. But much of the polymer manufacturing equipment already in use today, such as the current technology used to produce polyethylene, already meets the required specifications," Winter notes.

Winter and his students are now working on designing the equipment and manufacturing protocols that will be required for industries to make the switch. "Once we have the details worked out, I believe almost every manufacturer in the country will want to consider applications for this new technology, as they are all under the gun of the Clean Air Act and other environmental statutes to reduce their use of solvents and solvent-made products," Winter concludes. "The savings will also far outweigh the cost of making any required changes. There will be reduced cost in purchasing traditional solvents, reduced costs in having to clean and separate them, and finally, the totally clean nature of the final product is certain to open up numerous new markets for these manufacturers. This promises to be one of those rare win-win-win situations for manufacturers, for consumers in the medical, pharmaceutical, and communications industries, and for the environment."

NETI Project Profile # 15

Spinning with Gold

UMass Microreactor Allows for Selective Oxygenation

By Deborah Parker

In a well-known fairytale, a miller's daughter once earned the attentions of a king by spinning hay into gold. In a modern-day twist, scientists at the University of Massachusetts Amherst have been attracting international attention by using gold to better utilize oxygen in a variety of manufacturing applications. What's more, their new discovery may also help prevent household carbon monoxide poisonings someday. Dr. Dionisios Vlachos and Dr. Michael Tsapatsis, faculty in the Chemical Engineering Department at the University of Massachusetts Amherst, have designed a thin film, wheel microreactor that, using small particles of gold as a catalyst, helps control the amount of oxygen used in the production of certain chemically-engineered compounds. The experimental system appears capable of selectively interrupting normal chain reactions in gases and does so at room temperature. Both capabilities show promise of having a major impact on industry and environmental safety.

"Take the manufacture of propylene oxide, used to make resins for industry," Tsapatsis explains. "To make this substance, you mix or react propylene with oxygen. The problem is that once you begin adding more than one molecule of oxygen to any hydrocarbon, it wants to become carbon dioxide. And you need to stop it somehow, because that's not the hydrocarbon you were after." Up until now Vlachos notes, chemical manufacturing plants have used complex equipment and extreme temperatures to react the two types of molecules as best they could, using catalysts to intervene in ongoing reactions, removing the desired product such as propylene oxide, and then dealing with all the product that was produced accidentally as waste, "those carbon dioxide molecules among them."

Based on research completed in Japan that demonstrated the interesting catalytic properties of small amounts of gold, Vlachos and Tsapatsis went to work to address one of the major problems associated with attempts at using the metal. You must have only very small particles of the gold for this to work, so small that they're really just a few atoms put together, Vlachos explains. "Up until now, it's been impossible to keep them that small; the particles have always clumped together." The good news is that the UMass researchers discovered that titunia - an oxide of the element titanium - can be used as a substrate to stabilize the minute particles of gold, keeping them in the desired form. "What we have determined is that gold particles, laid on a foundation of titunia, can be used as a catalyst to react oxygen with hydrocarbons selectively," Tsapatsis explains. "And the microreactor we have designed allows the oxygen to flow through in only the amounts required to react with the exact amount of hydrocarbon available. Because there is no excess, the formation of carbon dioxide is interrupted. There is no second molecule available. If the researchers can demonstrate that what works in the lab can work on an industrial scale and might work on other types of gases as well, the impact on industry would be enormous, says Vasillis Papavassaliou, a research and development scientist with Praxair, a manufacturer of a variety of gases used by industry.

Papavassaliou says this is why Praxair teamed up as an industry partner on the research project funded by the National Environmental Technology Institute, noting "the long-term practical applications for the industry as a whole could be staggering." "Any technology that would increase the production of a substance that you do want, while wasting less of a valuable raw material, would be of great economic importance to our customers," Papavassaliou explains. "The fact that the procedure would also decrease, or even eliminate emissions, the production of substances you do not want, would have great environmental significance as well." Since the UMass researchers believe that the reaction can be conducted on gases in their gaseous form - sidestepping the current need to cool them into a liquid state - there would also be a large reduction in the energy consumption required by traditional reaction and separation models. "All of this is what has caught the attention of the manufacturing and scientific world," Papavassaliou concludes. "If this can work on an industrial scale, its a win-win-win situation."

Last but not least, Vlachos says it may be possible to add yet one more "win" to the string of benefits noted above. Using the same system in reverse, the scientists have also been able to use selective oxygenation to purposely turn carbon monoxide - a byproduct of incomplete combustion in furnaces and engines, and one that can prove lethal as it attempts to rob oxygen from the bloodstream, into harmless carbon dioxide instead. "Because this reactor can function at room temperature, its possible we could someday make these normally industrial reactions available in the workplace or the home," Vlachos concludes. "It's conceivable that garages or basements could have filters that would use this technology to eliminate carbon monoxide fatalities."

NETI Project Profile # 16

Seeking a 'Solution' Solution

UMass Researchers Seek to Revolutionize the Science of Homogeneous Catalysis

By Deborah Parker

Chemical engineers use all kinds of reactions to turn oil into polymers, the building blocks of plastics used in making everything from milk jugs to vehicle fenders. To get certain specialty, "long-chained" polymers, however - the kinds that are strong enough to stop a bullet hitting a bulletproof vest - they depend on a reaction called homogeneous catalysis. "In many reactions, chemicals are brought together and reacted inside the pores of a catalyst pellet," UMass Amherst Chemical Engineering Professor Phillip Westmoreland explains. "But in homogeneous catalysis, the catalyst molecules are actually dissolved in a solvent." In recent years, chemical manufacturers have used these soluble catalysts to complete the reactions required to create specialty polymer products. At the end of the process, however, they have faced difficult economic and environmental choices. Going through the steps necessary to reclaim the catalysts exacts enormous expense, "so most of the time, they just leave the catalysts in the end product," Westmoreland explains. "If the catalysts don’t affect the product or its users, it has simply been the easiest thing to do."

Unfortunately, some of the catalysts are very expensive to be sending out the door, hidden in a product that doesn’t require them. "Platinum, for one," Westmoreland explains. "Other catalysts, like chromium, would be perfect for some reactions, but are too dangerous to send out trapped in a product. Chromium oxides are toxic, so the catalyst cannot be released into the environment." Because the different mechanisms and chemistries involved are so complex, little progress has been made in trying to find alternatives to the current catalysis systems until recently. With funding from the National Environmental Technology Institute (NETI) and corporate sponsors, five scientists from the University of Massachusetts Amherst have joined forces to conduct a multi-year research study on homogeneous catalysis from the molecular level on up. Their goal is to develop environmentally benign "solution" solutions. Each prominent in their fields and winners of national recognition, the collaborators on the joint project include

Chemical Engineers Phillip Westmoreland, Ka Ng, Michael Tsapatsis, and Dionisios Vlachos and Chemist Vincent Rotello.

Ka Ng, a specialist in systemic assessment and computer use to create optimum chemical plant designs, is charged with looking at the big picture. "My job is to bring the parts together into a whole, to help apply the findings of each individual researcher to ultimate plant design," Ng explains. "I am asking the 'what if' questions, such as how can we retrofit an existing plant to perform this new task? With the new information we discover, how can we tinker with the recipe to make homogeneous catalysis more productive and safer? As the other investigators evaluate every aspect of this chemical process, my task is to weave the computational designs, the materials science, into reactor and process designs." Ng is also using newly developed computer software and an exhaustive database to help examine and compare technologies and equipment currently in use. Using the new software, Ng can project the efficiency of customized retrofits for physical components of chemical engineering plants, or project what a slight change to the chemical recipe may mean for cost savings or safety.

Meanwhile, Dionisios Vlachos, a specialist in the dynamics and modeling of crystal surfaces, chemical synthesis, and materials growth and processing, is researching new approaches to reaction dynamics and reactor safety. "My particular research specialty is reactor modeling from the molecular to the macroscopic reactor design scale," Vlachos explains. "I hope to develop a rational approach on bridging the length and time scales and design issues related to catalyst immobilization." Dr. Vlachos will be passing on what he learns to be figured into Ng's optimum plant equations.

Phillip Westmoreland is using his expertise in computational reaction chemistry, the ability to predict where and when a certain change might take place. A specialist in combustion at the sub-molecular level, Westmoreland's team is using computational chemistry to perform calculations of molecule structures, "and also of their properties, like how fast they react. Homogeneous catalysts are quite big molecules for this type of calculations, each result taking days to weeks on the fastest computers," Westmoreland explains. "However, using these calculations, we can now compare how different catalyst molecules perform in free solution and in confined spaces."

Vincent Rotello, a specialist in the structure and dynamics of peptides, mechanisms and modulation of redox cofactors, and materials science, is exploring new possibilities in catalytic chemistry and catalyst entrapment. His principal research interests include the architecture, conformational energetics, and reactivity in macromolecular systems. "For the homogeneous catalysis project, I am investigating the mechanical and chemical stability of the silicate matrix toward providing a durable support for catalytic functionality," he notes. "If we can confine the otherwise soluble homogeneous catalyst in a wall, or in dispersed particles, then separation from the solvent would become moot. Difficulty in separation, and catalyst loss, are the two things that have always prevented wider use of this powerful tool."

Michael Tsapatsis, a specialist in the development and application of advanced inorganic composite structures, is experimenting with entirely new means of catalyst immobilization. He is attempting to perform homogeneous catalysis in the laboratory using new materials; including the molecular sieves he has designed using zeolites. These members of the silica family form around pores of such precise shape and size, they can be used like a "chemical colander," Tsapatsis explains. "Using sieves in homogeneous catalysis can circumvent several of the current disadvantages, including the need to separate the product, the use of solvents, and the limited flexibility in process conditions, he notes. Our goal will be to explore the possibilities for sieve selectivity and activity, to see if the new technology might be performed in an economically feasible manner."

When they are done, the team hopes to have answers for dozens of questions including: What is really happening on a quantum level, a molecular one? How can manufacturers use catalysts more effectively? Can the catalysts be trapped mid-process, rather than abandoned in the product? Can the product or catalyst be removed in a gaseous form? Can the catalysts be trapped inside a particle of something else entirely, which in turn might be easily separated? "We were looking for a joint project that would require the best of what we do here, and this research area fit the bill," Westmoreland concludes. "It poses a number of challenges, it interests each of us for different reasons, and, if we're successful, it could have enormous implications for the industry and for the environment. We anticipate that additional corporate sponsors are going to want to participate, because of the potential for an industry-wide payoff, a development with far-reaching impact."