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On the cover
A Dylux® 503 proof created from a 34-year-old negative that was used to demonstrate the Dylux® imaging system in the field. The proof illustrates that a two-sided proof can be made. It also shows how either negative-working or positive-working proofs can be made. Negative-working is a proof in which the transparent areas of a lithographic negative allow UV-light to pass through to form a colored pattern. In a positive-working proof, the passage of visible light through the lithographic negative deactivates the exposed areas and a subsequent flooding ultraviolet exposure forms color in the unexposed areas. Courtesy of Rolf Dessauer.
This issue of The Spectrum includes the juxtaposition of three disparate technologies that have a common theme. First, is Rolf Dessauer’s lifelong work at DuPont which led to the development of printing plates and color proofing materials. Second, is Arnost Reiser’s numerous contributions, particularly at Kodak, in the development of both negative (cinnamate) and positive (diazo ketone) photoresists. Third, is my paper with Bipin Shah on the history and photochemistry of benzophenone. All represent areas where the creative contributions of industrial scientists to their respective companies generated huge businesses.

Photoscience in industry moved beyond silver halide photography shortly after World War II. Plambeck’s patents from DuPont are widely credited as providing the first steps in the development of polyol(acrylate) photochemistry. Subsequently, this led to the development of printing materials, coatings, adhesives, lithography, and stereolithography. Lou Minsk’s patents from Kodak are widely recognized for begetting the photoresist business. Minsk, who knew about cinnamate dimerization in the solid, postulated that cinnamate esters of various polymeric alcohols might crosslink (insolubilize) when exposed to light. Out of this simple observation came negative resist systems which entered the market in the mid 1960s. Benzophenone is used as a cheap photoinitiator for acrylate polymerizations. Sales per year are in the thousands of tons world-wide. Its hard to say where benzophenone as a photoinitiator first appeared, but the DuPont group had some role in this development too. Classic papers and patents coauthored by Catherine Chang were certainly important in this development.

Scientists sometimes forget, in the rush for new nanos and recombinants, that what fuels their work is the research and development breakthroughs of their predecessors. One has a hard time getting an accurate number on just how much of DuPont’s current sales come from the ingenuity of Rolf Dessauer and his colleagues, but millions of dollars are mentioned by everyone concerned. Rolf Dessauer may not be considered a Hewlett, Packard, Varian, Noyce, or Gates entrepreneur in the classic sense of the word, but an entrepreneur he most surely is. Same thing with Arnost Reiser. His work and the work of a number of his scientific colleagues, collaborators, and successors on both sides of the Atlantic at Kodak began to build an entire business. As Reiser points out, it could be postulated that without Otto Süs’ observations, the computer on which I’m writing this viewpoint might not have been possible.

Today research and development in industry is in a huge state of flux. Companies are constantly closing research labs, or moving R&D projects off-shore where overhead and costs are less. In this region of the Midwest, pharmaceutical facilities of long standing in Kalamazoo, Michigan; Holland, Michigan; and Skokie, Illinois have been closed or their missions drastically altered. It is only a matter of time before the work of these facilities shows up somewhere else in the world.

One wonders then where the next generations of industrial scientists will come from. Will the changes in the where and the what affect the emergence of a future generation of scientists like Rolf Dessauer and Arnost Reiser who have contributed so much not only to their respective industries but to the body of science at large?

Those of us in academe are betting the future will have to come from somewhere or we will become obsolete. Nurturing the creative, inventive mind is our most important responsibility.
So you've discovered some new photochemistry with all the makings of a blockbuster commercial success. How do you move it out of the laboratory and onto the store shelves? As one promising potential commercial application after another fizzles, how do you keep supervisors interested in funding and staffing further research on the project? In an industry setting, basic research findings are important, but managers ultimately want to turn chemistry into cash. If a discovery doesn’t lead to a product quickly, it may wind up as a footnote in corporate research history, rather than the cover story in the next annual report.

Rolf Dessauer’s pioneering work on biimidazole chemistry, which ultimately led to DuPont’s amazingly successful Dylux® line of photo-proofing products, is a case study in the dilemmas that confront bench side researchers and corporate managers every day. Dylux® 503 is a photo-imaging paper used in the printing industry to produce dry instant proofs of lithographic negatives for editing pages, customer approval, and quality control. The printing industry makes millions of proof pages each year and Dylux®, introduced in 1969, was a huge improvement over existing proofing technology.

In many ways, Dylux® was one of photochemistry’s commercial debuts, concrete evidence that interactions between light and matter alone could yield profit—and plenty of it. Dylux® products are still a commercial success, with few major competitors and cumulative sales exceeding $200 million.

But Dylux® is just part of the legacy of Dessauer’s contribution to industrial photochemistry. Biimidazoles are a preferred class of photoinitiators for a variety of photopolymer products and by one estimate, have been responsible for more than $2 billion in earnings. And Dessauer has had a hand in other projects, including optimization of technology for producing color TV tubes, new products for the photodecoration of wood and leather, and development of novel imaging materials and cholesteric crystals in graphic arts, decorative, and information-handling fields.

Few other individuals would have as strong a claim to being a major contributor to industrial organic photochemistry. Rolf Dessauer was born in Nuremberg, Germany, in 1926. He emigrated to the United States with his parents in 1939, attended schools in New York City, and served in the U.S. Army in World War II. Following the war, he got a B.S. and M.S. from the University of Chicago, and a Ph.D. in organic chemistry from the University of Wisconsin-Madison. He joined DuPont in 1952 and began a new career as a consultant for several Fortune 500 companies after leaving DuPont in 1991. Rolf and his wife, Angela, live in Greenville, Delaware, when not engaged in frequent travels. He has become an authority on watermarks on stamps and documents, a field where Dylux® paper finds extensive use. Dessauer also is writing an autobiography.

In this interview with The Spectrum, Dessauer discusses the technical difficulties and management intransigence that almost left the biimidazoles gathering dust on a shelf. Their rocky road from lab to marketplace is a lesson in the importance of persistence for any inventor today. He also discusses the road that took him from a childhood in Nazi Germany, where he narrowly escaped the concentration camps, to DuPont.

The Spectrum: You were a child in Germany just before World War II, and must have some vivid memories of that tragic period. We’ve heard about one episode involving a portrait of Paul Ehrlich, the 1908 Nobel Laureate in Physiology or Medicine.

Dessauer: My father was a physician in Nuremberg, and had earlier worked in a hospital in Frankfurt under Ehrlich, who was the founder of chemotherapy. We had an oil portrait of Ehrlich hanging in our apartment. Kristallnacht was truly a memorable event. The Storm Troopers came to the door of our apartment around 3 a.m., and I heard my mother tell them that my father had served as an officer in the German army in WWI, had been a physician in this neighborhood.
for almost 30 years, and had never done anything wrong. They devastated the apartment, smashed furniture, overturned cabinets, glass was broken and foodstuffs scattered around everywhere.

A young man appeared at the door the next day, and said that he had heard that the storm troopers damaged an oil painting, and he would like to restore it. We had no idea who he was, how he heard about the Ehrlich painting, or what motivated him. Two days later the same man returned with the Ehrlich painting nicely restored, wrapped in newspapers, and told my father that he and many of his friends were so sorry about what had happened, and wanted us to know that there were many Germans who were not in sympathy with these events.

That picture was among the few belongings that we brought to a new life in the United States, when we finally were able to leave Germany. We landed in New York City on June 2, 1939. The Ehrlich portrait is hanging in my living room today.

The Spectrum: What would have happened if you were unable to leave?

Dessauer: Oh, I suppose I would have wound up as a bar of soap.

The Spectrum: Was it your father’s career in medicine that got you interested in science?

Dessauer: No, it was the 1939-40 World’s Fair, one of the most exciting experiences of my childhood. It was an exhibit of the future of the world, and DuPont had an exhibit describing the achievements of industrial chemistry that fascinated me. I had been collecting toy trains. But that changed after seeing the DuPont exhibit. I sold my trains so I could buy a chemistry set and embark on a career as a chemist.

The Spectrum: How did you find your way to DuPont?

Dessauer: DuPont was one of the companies that sent recruiters to the University of Wisconsin in late 1951, and I remembered the World’s Fair. They offered a job in dye chemistry and I accepted it enthusiastically. The job met one of my principal criteria, some proximity to New York City, where my parents were living, but getting older.

The Spectrum: Did you start on biimidazole chemistry right after joining DuPont?

Dessauer: Oh, no. I worked on a number of other projects in the Jackson Lab—dyes and UV absorbers—which was about 10 miles from Wilmington, and had around 500 Ph.D.s and engineers there including Charles Pedersen, a Korean-born chemist, who years later became the only DuPont chemist to win a Nobel Prize. I worked on macrocyclic compounds. That project was terminated, and I was assigned to investigate a new low-cost route to butanediol, which DuPont needed to produce a synthetic rubber product. That was a dead end, and in 1954 I was transferred to the Anthraquinone Division to develop color-forming reactions for a novel dying process.

The Spectrum: A lot of zigs and zags. Is there any lesson there for young chemists today who are just starting an industry career?

Dessauer: I found that it was essential to commit oneself totally to learning all aspects of the area that one was working in, and that included a thorough understanding of the patents and literature, and of course the markets for which these products were being developed. That is a lot easier today than it was 30 years ago. And of course, one has to be willing to stick one’s neck out!

The Spectrum: And your start in biimidazole chemistry—had there been much activity in the past?

Dessauer: A number of publications preceded our work, but it was DuPont research that elucidated and commercialized products based on these unique compounds.

The Spectrum: Getting back to biimidazole chemistry. When did you get into that field?

Dessauer: It all began in 1958, when the DuPont Organic Chemicals Department assigned me to examine chemistry that would lead to new products that could use the facilities in the Chambers Works, which had been used in the manufacture of dyes and related aromatic chemicals. At that time, automobiles were being designed with larger glass areas, and one possible application was to design glass that could automatically darken when sunlight became more intense.

DuPont produced Bitacite®, a plastic material used to provide stability and protection to automotive window glass, and it was hoped that incorporation of a photochromic material in the automotive interliners would provide a ready market. I had earlier found that certain classes of
metalized hydroxyazo dyes could be dissolved in Butacite, and when surrounded by glass, had extraordinary stability.

L. A. Cescon, a very meticulous chemist, was assigned to this program at this point, and we would work together for years. He saw a reference (Hayashi, T.; Maeda, K. Bull. Chem. Soc. Jpn. 1960, 33, 565-566), which required lophine, or triarylimidazole, as a starting material for a photochromic compound. Cescon repeated this work and concluded that the compound synthesized by the Japanese workers, though not identified, was probably the dimer of the triphenylimidazolyl radical. The radical formed by irradiation of the dimer was purple, and we decided that we should make related triarylimidazoles, and before long we had biimidazoles which gave rise to a wide range of colored radicals, including blues and greens, and more important, different levels of stability. I was assigned to study applications of these hexaarylbimidazoles, which we nicknamed HABIs (hexaarylbimidazoles), and in general provide guidance to the group. My days as a dye chemist were just about over. Our division head, George Coraor, provided enthusiastic and capable leadership and we made a great deal of progress, drawing on many resources in the DuPont Company, including the excellent Radiation Physics Laboratory.

The Spectrum: Was the lab equipped to do photochemistry in those days?

Dessauer: We really had no equipment initially to do any photochemistry. We obtained a Cary recording spectrophotometer after a long wait, and our light sources inevitably were photographic flashguns. I had some photographic equipment at home, which I brought to work, and so we could use flashes of light to produce photochromic colors.

Our initial attempts at making photochromic windows were not successful. In general, the radicals may have recombined, but they also underwent fatigue, giving rise to compounds which no longer were photochromic. The DuPont business unit that marketed Butacite assigned more scientists to the program and they tried to provide us with media in which the biimidazoles were to be incorporated.

The Spectrum: Did DuPont use outside consultants?

Dessauer: George Hammond, who then consulted for DuPont, heard about our work and agreed to consult for us too. He was the first photochemist of stature whom we sought as an advisor. In time, Ron Breslow and Nick Turro of Columbia University were also brought in. Hammond was then starting the series of books Advances in Photochemistry, and asked me to write a literature survey of photochromism for the first volume. I did a thorough literature survey and after about six months of this, my co-author Jean Paris and I began to question whether photochromism would ever lead to useful products.

The Spectrum: What discouraged you?

Dessauer: The fatigue of the HABIs, the weak colors that were formed, and the likelihood that these colors would fade, rather than reverse themselves. I also suspected that nobody had ever effectively commercialized photochromic materials in a major way because the fatigue reaction could not be overcome. I told my friends that the academic scientists who reported in this field were content with a few dozen reversals, which might be achieved by low quantum yields of formation, and so there was an ample reservoir of dimers, provided one did not push too hard. People in the 1960s era might remember photochromic sunglasses that sold for a lot of money in department stores but did not work especially well or long.

It became obvious that the development of automotive or architectural photochromic windows would be a lengthy task. Although we were a research group, we knew that sooner, rather than later, someone would ask the question—how soon can we make some money from all that? And we would need to be testing materials for years to establish satisfactory performance!

The Spectrum: Did you look at any other product applications?

Dessauer: Print advertising with photochromic inks was one. We could spread solutions of HABIs onto paper, and with flashes of light, or even outdoor sunlight, produce blue or green coloration. We added HABIs to some ink vehicles, painted them onto paper, and did produce photochromic images. These worked quite well in sunlight, but we realized that people would not likely read magazines outdoors, and we either had to generate color rapidly with indoor light, or forget this application.

Cescon and I tried to make polymeric HABIs from terephthaldehyde. When oxidized, an intense bright blue color resulted. But it could not be reversed. Cescon said perhaps we should make color photochemically, and not bother with reversibility. I told him that perhaps we could oxidize leucodyes instead, remembering an old DuPont project in which novel leucodyes had been made.
The Spectrum: If only they saved samples.

Dessauer: They actually did, and that proved to be very important. One was leucodye TLA-454, a triarylmethane derivative. To our great pleasure, a solution containing HABI, TLA-454, and p-toluenesulfonic acid in an acetone solvent turned an intense cyan. We made a fresh solution as above, dipped a piece of filter paper in it, let it dry, and again produced intense color with a flash of light. The system could be stabilized by immersing the paper in an ether solution containing hydroquinone.

Cescon and I repeated the experiment for George Coraor, who was duly impressed, as were others in our group. At that time, George’s boss was Alfred C. Haven, who was somewhat slower in sharing our enthusiasm for photo-oxidation—as we called our process. He had sold his management on the fact that we were making photochromic materials that were to be reversible.

The Spectrum: And this was leading in a different direction. Was it just this particular manager, or was there a general uneasiness with research results that didn’t fit into a program’s predetermined goals?

Dessauer: This was one of many instances in my career with DuPont where I found that new applications, derived from programs, which were expected to deliver another specified application, were not enthusiastically received by management. It was simply that to get a program started it had to be sold to too many people, who would then object to deviations from a selected path—thus slowing the road to the market.

The Spectrum: Did he realize that you might have something more marketable than photochromic compounds?

Dessauer: Oh, yes. A few weeks later we had a research review, which was a session at which scientists presented the results of their work to the entire research management of the department. Just before the review, Tim Chilton, of DuPont’s Development Department, asked if he could come to the research review to learn more. He said he could probably sell this chemistry to our management.

When the review began, our research director asked Tim who he was and what he was doing there. Tim very positively presented himself, his background and said we might be on the verge of a great discovery, if it was properly pursued. He said that he knew of nothing like it. Enthusiasm really ran high, and this was my only review in my career where management people stayed around after a review, well after quitting time, suggesting what we should do.

The next step was to show what we had to the Photo Products Department, who were in charge of the company’s photographic business. At that time, different DuPont departments sold products to different industries, and we realized that a department that sold dyes was in a poor position to market a novel imaging material. They were not very impressed, because the color-forming process was slow, and we didn’t have good black and white images.

The Spectrum: What tweaking did the process need?

Dessauer: Our immediate need was to develop a more elegant way of stabilizing the images that were made by photo-oxidation of leucodyes. One obvious way was to truncate the absorption spectrum of HABIs, so that the activation occurred only in the ultraviolet region—at wavelengths below 380 nm. Despite a significant synthetic effort, this was not accomplished.

Another route was to consider thermal generation of inhibitors. Phil Manos prepared several ether derivatives of 2,5-Di-tert-butylhydroquinone, which thermally gave rise to reducing agents. By this time, Cescon had decided that to make good images we needed to dissolve the imaging chemistry in binders, and we went to Eastman’s cellulosic esters as vehicles for our chemistry. With Manos’ chemicals we could now make coatings on paper, expose with ultraviolet light, and stabilize the image by heating. Cescon discovered that the reaction could be speeded up when we included plasticizers in the formulations, and we soon were making attractive coatings on small pieces of paper.

Catherine Looney, a spectroscopist, who had retired from DuPont to raise a family, joined us as a consultant. Kay suggested that we stabilize our images by embedding the imaging chemistry in a thermoplastic binder, which could be thermally softened to permit migration of leucodyes and radicals, but when cold, locked the chemicals in place. Cescon did it, and we were able to perform a remarkable trick—image a coating with light, but form no color change until heat was applied subsequently. The stability of imidazolyl radicals made all this possible.

The Spectrum: You still had a system which involved thermal development or activation.

Dessauer: And that’s not what we wanted. The Organic Chemicals Department then supported basic research in this field at the Company’s Radiation Physics Laboratory
under the direction of Al Maclachlan, later to become DuPont Science VP. One day Al called me and said he had an idea, which he had demonstrated, but he did not know how stable the solution he had prepared was—so hurry. I rushed to his lab, and he showed me that he had dipped a filter paper in a solution that contained a HABI, TLA-454, phenanthrenequinone, and a Carbowax™ polyethylene glycol exposed it with a flashgun through a UV-blocking filter and a stencil, and was able to bleach out the yellow color, to give a near white pattern.

When he then exposed the paper through a cobalt blue glass, the previously unexposed areas turned blue. It looked like he had a "photofix" reaction! We repeated the experiment for Coraor, who immediately saw its importance. We had found a way of incorporating the entire imaging/fixing chemistry into a single solution, which obviated the need for a chemical after-treatment, or thermal fixing. We definitely had something new!

Maclachlan continued optimizing his invention, and Chuck Yembrick, who had joined our group recently, was assigned to optimize Maclachlan’s system. He did a superb job and before long we had developed coatings, which functioned reliably.

The Spectrum: Was there much concern about patent protection at this point?

Dessauer: We filed an extensive application, which sought to cover all HABIs that we had made and showed improvements over the oxidation product of lophine, which was not claimed, but suggested in the literature. We sought to get composition of matter claims. The examiner told us that similar imidazoles had been reported to give off light when heated, and that what we had showed was novelty over the prior art. I replied that the phenomenon, which we had invented, was photochromism, a color change induced by light, as in certain organisms like salamanders, while what he cited was chemiluminescence, a phenomenon attributed to fireflies. Since fireflies are different from salamanders, we knew nothing then about photopolymerization. Our deactivation, or fixing speed, was purposely low, so that the materials could be handled in ambient light. Could we speed it up? I suggested that as we needed plasticizer to permit color-formation to occur at all, perhaps we needed to consider the rapid photochemical removal of the plasticizer as a route toward a higher speed. All of a sudden, an obvious approach appeared—use a monomer as plasticizer, and polymerize it to "fix" the system.

We formulated our preferred leucodye and HABI in a binder/monomer system, and added an anthraquinone photoinitiator to effect polymerization in the visible portion of the spectrum. It worked! Over the next weeks we optimized the system, showing that visible light initiated polymerization and UV-exposure would yield color. Cescon and Cohen demonstrated that the system was intensity sensitive and to our great surprise, worked well even without the anthraquinone initiators. The HABI had acted as photoinitiator! At high intensity of light, polymerization and color formation ensued, but at low intensity irradiation, only polymerization occurred. The postulated mechanism was one in which the ion-radical formed on photooxidation of the triphenylmethane leucodye could, at high concentrations, disproportionate to form dye, but at low concentrations, initiate only polymerization. In time we learned that HABIs themselves were poor photoinitiators, but in combination with certain co-initiators were extremely effective in triggering acrylate photopolymerization.

The Spectrum: So HABIs were acting as photopolymerization initiators?

Dessauer: We had asked that question for years. Of course, we knew nothing then about photopolymerization, and asked people in the Photo Products Department for help. V. C. Chambers, who headed a group which worked on a photopolymer based copying system, wanted to make black images using our chemistry, and he got a patent describing the improvement in photopolymerization due to HABIs. That was the first patent identifying HABIs as
photopolymerization initiators. Cescon, Cohen and Dessauer’s patent, in true Orchem-style, was issued much later, because we never were in a hurry to see our patents issued.

The Spectrum: So it’s the early 1960s. You have a very successful research program that needs to shift gears into product development. How did that happen?

Dessauer: There was a false start that created a crisis situation for the technology’s future. We spent years working on an idea to use it in an optical printer. Printing then was done either via IBM’s Selectric typewriters or on teletype machines. There were no UV lasers or computers, and the need for high speed, quiet printing was obvious. We envisioned an optical printer, which could expose a beam of light via lenticular plate optics, to print silently maybe 20 characters per second. By the mid-1960s, the Organic Chemicals Department decided that they would not want to market a printer, and instead sought partners such as AT&T, Western Union, and Litton Industries. With the unresolved patent situation, we were very limited in what information they could disclose to our would-be partners. The result was that no one was very interested in working with DuPont.

Things had come to a crisis, and Robert Terss, who then directed our UV imaging program, felt that his bosses were determined to produce a salable commodity, whatever that could be. Larry Friar, of DuPont’s Rochester Photo Products plant, had suggested using our technology for proofing. Friar gave me a negative of a girl sitting in a bathtub, and we made a nice print on UVI-paper, but it was blue and yellow. Friar said, “Tell your bosses you have the ideal proofing medium!” I went back with that message, but it did not persuade anyone at Photo Products management. There were other ideas to use the technology in holography, as a self-contained imaging system, to create hard-copy images of news and other text delivered via television or other cathode-ray tubes. Capturing images from cathode ray tubes seemed like an exciting idea as a way for handling electronically generated images, but our materials lacked the requisite speed. I kept on plugging away at using it in microfilm and proofing. We even thought of toys, but that seemed too frivolous for a company like DuPont.

The Spectrum: When did you think of using the technology in photoproofing?

Dessauer: In the early 1960s, after I had an opportunity to partake in a very interesting visit to Meredith Publishing Company in Des Moines, Iowa. Their idea was that researchers in industry probably knew little about the printing industry and might actually have materials that could impact on their business. So, a group of us were invited for a strenuous week of learning all about printing. It was fascinating and provided me with some comprehension of the opportunities in that field. I saw them making proofs of pages for magazines and books. So it occurred to me that we might be able to adapt our blue-and-white images to make proofs.

The Spectrum: Do today’s chemists and students get enough of this real-world contact?

Dessauer: As modern companies have fewer layers of management, chemists have a better opportunity to visit potential customers. There is much more awareness of interaction between scientists and the market. The Internet is a broad source of information for those who want to dig a little.

The Spectrum: Did DuPont accept the proofing idea?

Dessauer: No. They felt that the quality of our images was not adequate; their permanence had not been established. Clearly, Photo Products, which was primarily in the silver-photographic business, was not interested in getting into an application that would compete with low-cost diazopaper. We could not convince the Photo Products management that they should market this product at a premium, and the Organic Chemicals Department simply lacked a distribution system to get a photosensitive product onto the market. With our technology we could do unique things: We obtained good continuous tone images without processing. We could add images on to the photosensitive coating before it was photofixed. We could thus make color breaks. We could make two-sided coatings, which later turned out to be a very important factor. Our paper could be readily folded. The blue color was attractive, but we could also make coatings, which yielded other colors.

The Spectrum: What did it take to break down those barriers?

Dessauer: A better understanding of imaging sources and the market: A chemist, an electrician and a Harvard MBA were important in this. Peter Strilko began to study available light sources, and found that certain backlight fluorescent lamps emitted the pure ultraviolet light required to image our photosensitive coatings. He also identified
a low cost cobalt blue glass used in church windows that could be employed to modulate existing light sources, so that the visible light components were blocked. In 1967, Harold Wilbur, an electrician, was assigned to our group. He modified small commercially available contact printers to expose 8 x 10 inch negatives onto our photosensitive paper. With the printer, we could make contact prints of continuous tone and lithographic negatives in about 20 seconds. In time, DuPont sales personnel were equipped with these printers and could effectively persuade potential customers of the advantages of using Dylux® proofpaper. Help came from some enthusiastic supporters in marketing groups. Larry Friar and Philip Botsolas were two experienced Photo Products people who helped immeasurably at various stages in this development.

The Spectrum: The MBA?

Dessauer: That was John de Campi, who joined our group in 1968. He too felt that the use of our technology in the printing industry represented a great opportunity, and did a superb job of demonstrating the advantages of a dry instant access material. John and I traveled around to see printers and in 1969, I received very positive responses from printers in St. Louis.

At one company, the plant manager apologized that he had no time for me. I asked if he could spare one minute, and show me an electrical outlet. I made a 20-second proof for him, packed up, and said he could call me when he was interested. His response was: "Sonny, I suddenly have all afternoon for you!" As a matter of fact, he borrowed my printer and some paper, so that he could give a demonstration at a printer’s club meeting that night. The next morning, he said that it would be nice if DuPont sold this product only in St. Louis—so that the local printers would have some advantages over the rest of the country. He was ready to buy.

I called my then boss, Bill Wartell, and told him that what we had was ready to sell, and while some improvements might be needed, these could be made once we had established a business. Wartell believed me and said "let us go commercial". But we still had to convince Photo Products Department to put Dylux® into their product line. Also, we had yet to produce significant quantities of coated paper in commercial equipment!

Thanks to the Society of Photographic Scientists and Engineers meetings, I met a chemist who held a high position at Agfa-Gevaert in the United States. He had followed my attempts to get this technology to the market, ever since I presented a technical paper at an SPSE meeting. He asked whether Agfa-Gevaert could market this material, if DuPont had no interest. I urged him to send me a letter to this effect. When the letter finally came, we passed it on to Photo Products management. They then decided that perhaps they should consider marketing Dylux® after all. In September 1969 we introduced Dylux® to the world at the National Printers and Lithographers show.

In time, the industry realized that we had developed a negative-working proofing product, which fit the customer’s needs, and dedicated exposure equipment became available and sales of single and double-side coated Dylux® 503 increased every quarter for years.

In 1981 and 1982 I received patents on unsymmetrically substituted HABIs, which were more effective, and reduced the manufacturing cost. Two very dedicated engineers, Thomas M. Sheets and later David Logrando, kept on improving the manufacturing process and effected further cost reductions.

The Spectrum: What else did DuPont do with this technology?

Dessauer: A. B. Cohen at Parlin directed a group of chemists who developed a film resist, Riston, which revolutionized the printed circuit industry, and the Cromalin Proofing system. These products, photopolymer films with excellent shelf life and performance characteristics, employed HABIs as photoinitiators. These and several other HABI based photopolymer products established DuPont as a leader in non-silver imaging technology, and were responsible for significant growth of the Photo Products Department. Our composition of matter patents, issued in 1974 and 1981, prevented competitors from entering the field.

A number of very talented chemists, including Tom Dueber, Dennis Donald and Jon Caspar, made significant contributions to the understanding of sensitizers, inhibitors and the physical chemistry of hexaarylbiimidazoles. And there were many other DuPont scientists who contributed to our understanding of HABI chemistry. (These guys are still at DuPont.)

The Spectrum: And HABI use took off, with hundreds of millions in sales of HABI based-technology. How did DuPont reward you?

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how to minimize photobleaching during image acquisition

David Kessel
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In the acquisition of images for fluorescence microscopy, two separate shutter systems are used. One regulates the CCD camera exposure, and the other is placed between the light source and the excitation filter. To minimize photobleaching of the sample, it is necessary to limit the exposure of the microscope stage to exciting light. This is especially important when acquiring multiple images involving different filter combinations, or when a Z-series of exposures is to be obtained, varying in the focal plane.

A system in use in our laboratory involves a SenSys CCD camera, a Roper Scientific capture card, a Uniblitz shutter with a D122 driver, and MetaMorph software from Universal Imaging. The AIA image transfer cable from the camera is connected to the Roper card in a computer, and a second cable from a parallel port on the computer is connected to the pulse-input BNC port on the D122.

The software can control the position of the Uniblitz shutter, to facilitate examining fluorescence images before exposure, but there is no procedure for closing the Uniblitz shutter and the camera shutter simultaneously. Regardless of the actual time of exposure, the Uniblitz always remains open until the image is transferred to memory, requiring 5-6 seconds.

An examination of the SenSys and Uniblitz driver circuits suggested a solution. There are three ports on the camera: a 68-pin AIA cable for image transfer, a 9-pin D-subminiature port for power input, and an unused 9-pin input/output port. The latter port can send a 4.7 volt signal (from pin 3) when the camera is exposing. If this signal is sent to the pulse input port on the D122, the Uniblitz shutter will open and close with the camera shutter. A connecting cable can be fabricated from a male BNC connector and a male S-subminiature 9-pin connector. The simplest procedure is to purchase a 9-pin cable, remove one plug and install the BNC, remembering that pin 3 connects to the red wire and ground to the green. The only drawback is that the position of the Uniblitz shutter can no longer be independently controlled by the MetaMorph software. Since the D122 and similar driver units have switches for controlling the shutter position, this poses no significant problem, and photobleaching is minimized.

About the Author
Dr. Kessel was trained at MIT (S.B., Chemistry), University of Michigan (Ph.D., Biochemistry) and Harvard Medical School (Postdoc). He has been Professor of Pharmacology & Medicine at Wayne State University School of Medicine since 1974 and began studies on photodynamic therapy a few years later. He organized a conference on this subject at the annual January meeting of the SPIE. His e-mail is dhkessel@med.wayne.edu.

Bowling Green Graduate Receives Harvard Fellowship
Anna Kornilova, Postdoctoral Fellow in the Center for Neurologic Diseases at Harvard Medical School, has received The Edward R. and Anne G. Lefler Fellowship. It was awarded for her research entitled “Probing g-secretase with photoactivatable inhibitors”. g-secretase plays a crucial role in the pathogenesis of Alzheimer's disease, and she studies its biochemistry using the catalytic-site directed photoprobes.

The Edward R. and Anne G. Lefler Fellowship Fund supports the training of pre-doctoral students and postdoctoral fellows. The fund seeks to support three or four individuals per year, including the most promising postdoctoral fellows working on projects relevant to neurodegeneration and neurodevelopment. This program ensures the continuation of the recipients’ education and training, while also ensuring the dissemination of the Lefler legacy throughout the world as these exceptional scientists move on from Harvard and into their careers.

Anna completed her Ph.D. under Professor Michael Ogawa in the Center for Photochemical Sciences at Bowling Green State University.
designing esters which release alcohols upon exposure to light

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Photoremovable protecting groups are of interest since their use has been demonstrated in photolithography, synthetic organic chemistry and biochemistry. Fragrant alcohols are used in applications such as body care and household cleaning goods. One of the drawbacks of using volatile alcohols in fragrances is that the desired aroma is perceived for a relatively short time in applications. We are interested in designing photoprotecting groups that will release alcohols slowly in applications upon exposure to light, independent of the reaction media and thus make the photorelease of alcohols feasible in film-type applications. Recently, Porter et al. reported that photolysis of esters of 2-benzoyl benzoic acid, 1, in 2-propanol yielded the corresponding alcohol and lactone 2. This reaction takes place by intermolecular photoreduction of 1 to form radical 3 which then undergoes dimerization and intramolecular lactonization to form 2 with consequent release of the alcohol (see Figure 1). By forming an ester of a volatile alcohol with 2-benzoyl benzoic acid, it is possible to release the fragrance in a controlled manner over an extended time period by exposure to light. The limitation of this method is that release of the alcohol takes place only in solvents that have abstractable H-atoms. In addition, the triplet excited state of 1 is long lived enough to be quenched by molecular oxygen. To address these problems, we prepared benzoyl benzoic acid ester derivatives with alkyl substituents in the ortho positions making it possible for the corresponding triplet excited ketones to undergo intramolecular H-atom abstraction to form 1,4 biradicals. These biradicals are expected to decay into E and Z photoenols which can undergo intramolecular lactonization to release the alcohol moiety. For example, irradiation of ortho methyl benzophenone and ortho methyl acetophenone yields Z and E photoenols (Z-4 and E-4, see Figure 2). Z-4 is short lived since it reketonizes via an intramolecular 1,5 H-atom shift, whereas the E-4 enol is much longer lived because it reketonizes via the solvent. Interestingly, E-4 is long lived enough to be trapped with dieneophiles. Furthermore, the triplet excited state of ortho methyl benzophenone is short lived since it decays very efficiently by intramolecular H-atom abstraction and is therefore not quenched by molecular oxygen. We prepared esters of benzoyl benzoic acids that have methyl (5), ethyl (6) and 2-propyl (7) substituents in the ortho position (see Figure 3). For synthetic reasons esters 6 and 7 have an additional alkyl group in the para position.

We examined whether irradiation of geranyl esters 5-G, 6-G and 7-G in argon-saturated benzene solutions released the alcohol moiety. We specifically chose benzene since esters 5, 6 and 7 cannot abstract H-atoms from this solvent. Photolysis of 5 in argon-saturated benzene did not yield any photoproducts, whereas 6-G and 7-G both released the geranyl alcohol. Since 7-G released geraniol more efficiently than 6-G, we decided to focus our research on ester 7 and...
determine the effects of the environment on its ability to release an alcohol moiety. Quantitative analysis of the photolysis of 7-G in argon-saturated toluene showed that the photoproducts, geraniol and 8, are formed with similar yields (see Figures 4 and 5). The depletion of 7-G is quantitative within experimental error and corresponds to the formation of the photoproducts. The photoreactivity of ester 7-G was not affected strongly by the reaction solvent and it can be seen from Figure 6 that the rates of release were similar in toluene, 2-propanol, chloroform and benzene.1 We studied the effect of oxygen on the photochemistry of 7-G by irradiating oxygen-saturated benzene, methanol and 2-propanol solutions of the ester and all yielded geraniol and peroxide 9 (see Figure 4). Photolysis of 7 in solutions open to atmospheric air also yielded geraniol and 9.

We were curious about the mechanism of photorelease by esters 6 and 7 and, conversely, why 5 did not release any alcohol. The product studies suggest that the ketone moiety in 7 abstracts an \( \gamma \) H-atom to form biradical 10 (see Figure 7). This biradical must decay into photoenols 11 which release the alcohol and undergo intramolecular conrotatory electrocyclicization to form cyclobutene 8,9 in the absence of oxygen. In the presence of oxygen, photoenols 11 and the biradical 10 must be trapped to form peroxide 12 which releases the alcohol moiety to form 9. In order to verify this reaction mechanism, we performed laser flash photolysis studies of ester 7. We also compared the phosphorescence spectra and molecular models of esters 5, 6, and 7.

Molecular modeling of esters 5-M, 6-M and 7-M shows that the minimal energy conformers of these compounds are similar.10 These conformers are all oriented in such a manner that intramolecular H-atom abstraction is feasible since the distance between the oxygen of the ketone moiety and the

Thin films of 7-G were prepared in volumetric flasks which were sealed and exposed to daylight. Afterwards the contents of the flask were diluted with solvent and analyzed by GC-FID and GC-MS which showed that geraniol was released. This verifies that esters of 7 can be used to slowly deliver alcohols in applications.5

![Figure 4. Photoproducts from photolysis of ester 7.](image)

![Figure 5. Quantitative measurement of formation of geraniol and 8 from photolysis of 7-G (from reference 3).](image)

![Figure 6. Conversion of 7-G in various solvents (from reference 3).](image)
The H-atom on the ortho alkyl substituent is less than 2.6 Å. We calculated the conformations of esters 5-M, 6-M and 7-M in the instance that the alkyl substituent is facing away from the carbonyl group and found that these conformers were 2-5 kcal/mol higher in energy than the minimal energy conformers. We also calculated the minimal energy conformations of the E and Z photoenols from esters 5-M, 6-M and 7-M, which demonstrated that the photoenols all have intramolecular H-atom bonding between the hydroxyl groups that result from photoreduction of the carbonyl moiety and the carbonyl ester group.

The phosphorescence spectra of esters 5, 6 and 7 in ethanol at 77K are very similar, except that the intensities varied for each compound with 6 having the highest intensity and 7 the lowest (see Figure 7). For comparison, we included the phosphorescence spectrum of benzophenone in Figure 8. At 77K the intensity of the phosphorescence from benzophenone was greater than that of esters 5-7. Since the intensities of the phosphorescence spectra of esters 5-7 are lower than for benzophenone, we can conclude that these esters decay by intramolecular H-atom abstraction as well as phosphorescence. Presumably at 77K only the conformers that have an H-atom on a carbon atom γ to the carbonyl group and situated close enough for abstraction decay by intramolecular H-atom abstraction whereas other conformers must return to the ground state via phosphorescence. Thus
we hypothesize that the divergence in the phosphorescence intensities of esters 5, 6 and 7 is a reflection of the populations of conformers in the frozen glass that are reactive versus those that are not. This is supported by molecular modeling since the conformer of 7 where the ortho alkyl group is facing away from the carbonyl group is 5 kcal/mol higher in energy than the ground state conformer. Consequently, less of the unreactive conformer should be present, whereas for 5 the energy differences between the corresponding conformers, 2 kcal/mol, is smaller. Ester 6 decays more efficiently by phosphorescence than both esters 5 and 7. Thus, ester 6 must be intrinsically less reactive towards intramolecular H-atom abstraction, which correlates with it releasing geraniol less efficiently than 7.

We performed a laser flash photolysis study of 7-M and it gave a broad transient absorption with a λ<sub>max</sub> at 390 nm due to the absorption of photoenols Z-11 and E-11 (see Figure 9). In the kinetic mode we followed the decay of the shorter-lived Z-11 enol and found that it had a lifetime of ~1300 ns in dichloromethane and accounted for approximately 75% of the total absorption while in ethanol the lifetime was prolonged to ~ 3000 ns. This was comparable to the lifetime of Z-4 in protic solvents.5,12 The main difference between Z-11 and the Z-4 was that the latter was much shorter lived in non-protic solvents where the lack of hydrogen-bonding between the solvent and the hydroxyl group facilitated reketonization. According to our calculations, Z-11 had intramolecular H-atom bonding between the hydroxyl group and the ester carbonyl group which must delay reverse H-atom transfer to the isopropenyl substituent in non-protic solvents. The involvement of the hydroxyl group in the intramolecular hydrogen bond was, nonetheless, not sufficient to impede the reverse H-atom transfer long enough to allow release of the alcohol moiety of Z-11. By comparison, E-11 is much longer lived than Z-11 because it cannot revert to 7 through intramolecular 1,5 hydrogen transfer and it did not decay significantly over a 100 μs time scale.

We did not detect the absorption of the triplet excited state of ketone 7; however, we did succeed in quenching the triplet excited ketone with isoprene. Stern-Volmer treatment of the quenching of the absorbance at 390 nm with isoprene in dichloromethane allowed us to estimate the lifetime of the triplet ketone to be between 0.08 and 0.8 ns.

The yields of photoenols Z-11 and E-11 were reduced in an oxygen-containing environment without shortening the lifetime of Z-11, presumably because we trapped biradical 10 with molecular oxygen. The triplet excited state of 7 is too short-lived to be quenched by molecular oxygen whereas biradicals are known to react with oxygen with a rate constant in excess of 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup>.7 The trapping of E-10 with oxygen is too slow to observe under our experimental conditions.

We photolyzed ester 7-M in argon-saturated benzene solutions in the presence of maleic anhydride. GC-MS analysis of the reaction mixture showed formation of lactone 8 and a new compound, lactone 13, which can be attributed to trapping the E-10 enol via a Diels-Alder reaction (see Figure 10). In contrast photolysis of esters 5 with maleic anhydride in argon-saturated benzene solution did not yield any photoproducts. The rate of trapping of the E-photoenol of 2,4-dimethylbenzophenone with dimethyl...
acetylenedicarboxylate has been measured to be $10^2 \text{M}^{-1}\text{s}^{-1}$ and we can expect trapping of E-10 with dienophiles to be of a similar magnitude. Thus, we conclude that the photoenol formed by intramolecular H-atom abstraction in 5 must be too short lived to be trapped with dienophiles such as maleic anhydride. Similarly, we propose that their lack of reactivity in argon-saturated benzene solutions comes from the resulting photoenols being too short lived to undergo intramolecular lactonization.

In conclusion, we have made protective groups 6 and 7 that release alcohols upon exposure to UV light independent of the reaction media and are therefore ideal for slow fragrance release in applications. The release takes place through intramolecular H-atom abstraction and formation of 1,4 biradicals that intersystem cross to form Z and E photoenols. The shorter-lived Z photoenol did not result in product formation but reverted back to the starting material through 1,5 H-atom transfer. In contrast, the E-photoenol released the alcohol through intramolecular lactonization. The 1,4 biradical is trapped with molecular oxygen. The trapped biradical released the alcohol and thus the photorelease was not decreased in atmospheric air. In contrast, ester 5 is not photoreactive in argon-saturated benzene, presumably because the photoenols formed upon intramolecular H-atom abstraction are too short lived to undergo intramolecular lactonization. This is supported by the observation that photolysis of 5 in the presence of maleic anhydride does not lead to formation of a Diels-Alder adduct as is observed for 7 under the same conditions.

References


About the Authors

Anna D. Gudmundsdottir received her undergraduate degree from the University of Iceland. She received her Ph.D. at the University of British Columbia for studying asymmetric induction in solid state photo reactions with Professor John R. Scheffer. She was a visiting scientist with Professor Peter J. Wagner at Michigan State University and then became a NATO postdoctoral fellow in Professor Matt Platz's research group at The Ohio State University. She is currently an assistant professor in the Chemistry Department, University of Cincinnati. She received a National Science Foundation CAREER Award for her research on triplet alkyl nitrenes. Her e-mail address is anna.gudmundsdottir@uc.edu.

Armands Konosonoks got his B.S. in chemistry from the University of Latvia, Riga. He is a third year graduate student at the University of Cincinnati, pursuing a Ph.D. degree in chemistry with Professor Anna Gudmundsdottir.

Jana Pika obtained a B.S. degree in chemistry from Concordia University in Montreal. She went on to earn a Ph.D. in Marine Natural Products Chemistry from the University of British Columbia, under the supervision of Professor R. J. Andersen. Following two years of postdoctoral fellowship at Scripps Institution of Oceanography under the guidance of Professor D. John Faulkner, Dr. Pika joined Firmenich Inc. as a senior scientist in 1995. In 2002 she was promoted to the position of Director of Analytical Research and Development, North America.

Pradeep N. D. Singh got his undergraduate degree at the University of Chennai in India. He received his doctoral degree from the same university for his research on photochemical studies on azadirachtins and related bioactive limonoids with Professor Geetha Gopalakrishnan. Currently, he is a postdoctoral fellow in Professor Anna Gudmundsdottir’s research group at the University of Cincinnati, engaged in designing stable triplet nitrenes along with photoremovable protecting groups.

Dessauer Continued from Page 10

Dessauer: I did receive several prestigious career awards from DuPont in 2001, and significant special incentive bonuses in 1973 and 1986. After my retirement, I continued to consult for DuPont and remained technically active for many more years.

The Spectrum: And what has happened to HABI technology recently?

Dessauer: After the DuPont composition-of-matter patents on HABIs expired, many other companies began to employ HABI technology in their products. There are altogether over 800 Chemical Abstracts references in which hexaaryl-biimidazoles are cited, and over 300 U.S. patents, with DuPont, of course, having the most. In 2003 over 50 U.S. patents were filed in which HABIs were cited in a variety of applications, including some involving silver photographic systems. So one might say, we invented materials that have found widespread utility in the imaging field, and I believe that it all goes back to the discovery that hexaarylbiimidazoless can oxidize leucodyes very efficiently. So, persistence has paid off!
The photochemistry of benzophenone has occupied so much attention in the literature that one would think there was nothing left to do. Benzophenone was first synthesized in 1834 by the distillation of calcium benzoate. Its photoreduction with alcohols was first reported by French workers in 1900. Though their combustion analysis was wrong and they missed the structure of the product, benzopinacole, this error was corrected by Ciamician and Silber. Paterno and Chieffi first showed that active hydrogens were required in the reducing agent.

The photoreduction is a simple reaction. One dissolves readily soluble benzophenone in an alcohol like isopropyl alcohol in an Erlenmeyer flask, places the flask in the sun (say on the roof) and waits. In a few days hard, crystalline benzopinacole precipitates. The latter is insoluble and drops out of solution in analytically pure form (1). The oxidation product of the alcohol, in the case of isopropyl alcohol, is acetone, is easily identified.

The first mechanistic study of the reaction is probably attributed to Cohen who studied alcohols other than isopropyl alcohol as reducing agents. In 1920, he followed the disappearance of benzophenone using a rudimentary version of ultraviolet absorption spectroscopy. Bachmann in 1933 reported comparisons of photoreductions in neutral media versus basic media, the latter producing benzhydrol. Weissmann, Bergmann and Hirshberg proposed the initial chemical mechanism. Their suggestion required that each of two benzophenones absorb a quantum of light, be excited to an undefined state, and each react by hydrogen abstraction at the carbonyl oxygen from the alpha position of the reducing alcohol thus producing two pairs of identical free radicals (2).

According to Weissmann, the coupling of alpha-hydroxydiphenylmethyl radicals yielded benzopinacole while the disproportionation of the alpha-hydroxydimethylmethyl radicals yielded acetone and returned a molecule of isopropyl alcohol. Although the reaction is essentially clean, with certain alcohols the diphenylhydroxymethyl radicals couple at the para position producing a yellow product (3), reminiscent of that eventually identified as forming from the coupling of two triphenylmethyl radicals. Fieser, who first used the photoreduction of benzophenone in an undergraduate laboratory text in a section on polyarylmethanes, claimed that adding a drop of acetic acid prevented the para coupling (the yellow color).

The Weissmann mechanism was eventually shown to be incorrect. Pitts, Letsinger and their students recognized that it would require the starting alcohol be partially racemized during the course of the reaction, so they carried out the reduction in optically active 2-butyl alcohol and found the alcohol recovered without racemization. They measured the quantum yield of photoreduction to be almost 2.0. This necessitated that two molecules of benzophenone be reduced as a consequence of the absorption of a single photon. Pitts and Letsinger thus proposed the chemical reduction of ground state benzophenone by the alpha-hydroxydimethylmethyl radical (4).

The latter was confirmed in non-photochemical reductions of aryl ketones by the alpha-hydroxydialkylmethyl radicals.

Essentially the mechanism of the photoreduction of benzophenone (5) was fully established, save for direct observation of the radical intermediates postulated, by the mid 1960s.
Excited State Intermediates

Characterizing the excited states of benzophenone posed a different set of problems. The Pitts/Letinger study ruled out alcohol as the light absorbing species because they used filtered 350 nm light and only benzophenone absorbs in that region of the spectrum, but they only described the excited state of benzophenone with an asterisk (6).

Hammond's first studies in mechanistic organic photochemistry tackled the identity of the photochemically produced reactive intermediate. He chose benzhydrol as the reducing agent because it had the appeal of yielding two identical reaction intermediates from the first reduction step. His treatment of the reaction intermediates as though they were maintained at a steady state concentration 19 seemed to establish that the excited state was the triplet state of benzophenone. Hammond reasoned that given a predictable rate of diffusion of the two reagents, benzophenone excited state and benzhydrol in solvent benzene (≈10⁹ 1 m⁻¹ s⁻¹), the excited state could not react with a rate constant larger than 10⁷ s⁻¹. Since fluorescence was already known to be faster and because benzophenone solutions showed no detectable fluorescence, Hammond said "... this compels the conclusion that the triplet state is responsible for chemical reaction." Bäckstrom and Sandros20 had previously reported that benzophenone “excited state” transferred its energy to biacetyl in fluid solution with concomitant triplet emission (phosphorescence) from the latter in what was one of the earliest reports of triplet energy transfer in fluid solution. The Hammond result did not directly confirm the earlier ideas21 which included that the triplet state should approximate a biradical state, but he submitted in the papers that he agreed with this picture.22 Hammond further estimated that the mean lifetime of the benzophenone singlet(s) could not be longer than 200 picoseconds.

Spectroscopic details involving benzophenone’s excited states began to fill in after transient absorption spectroscopy was developed. In a 1963 paper Porter exhibits a detailed Jablonski diagram for benzophenone and first suggests the energies and rate constants for unimolecular decay of several of the excited states.23 The first absorption spectrum of the triplet state of benzophenone was reported at 77° in EPA glass by McClure and Hans.24,25 The triplet absorption spectrum of benzophenone in solution first appeared in another Porter paper26 while Rentzepis, in 1970, reported the first spectroscopic estimate of the time of intersystem crossing (~ 5 × 10⁻¹² s, a measure that was limited by the duration of the pulse in his apparatus).27

Spectroscopic reports of the absorption spectra of singlet states of benzophenone have been rare. In the first place, the triplet is the reactive state in most instances and that seemed of the greatest interest. In the second place, benzophenone singlet states, we now know, are very short-lived. Until recently, methods for their observation have been non-existent.28

We, working with Michael A. J. Rodgers, have recently clarified this situation. In the case of substituted benzophenones such as tert-butyl 4-(4'-bromomethylbenzoyl)perbenz oate the kinetics of decay of the S, have been clearly shown to be within experimental error of the kinetics of appearance of the T.29 while the case of the parent benzophenone is even clearer. We report the S state of benzophenone absorbs at ~570 nm30 at a higher wavelength than at which the T state absorbs, Figure 1 (Note: the shorter lived singlet absorption at 570 nm and the longer lived triplet absorption at 530 nm).

When benzophenone is excited at 335 nm, the rise of the S state takes place within the instrument response function (~150 fs). The situation changes when the pumping wavelength is 267 nm. Although the spectra of the primary transients were similar at both excitation wavelengths, formation of the S state is not instantaneous after 267 nm.

Figure 1. Transient absorption spectra obtained from ultrafast pump-probe experiments of benzophenone (5.52 × 10⁻² M) in acetonitrile, recorded (-) 1.26 ps, (-) 5.59 ps and (-) 34.2 ps after the laser pulse (excitation at 335 nm).
excitation. At this wavelength, a second singlet state ($S_2$) is formed first and it collapses to the $S_1$. The evolution of the $S_1$ from the $S_2$ is shown kinetically in Figure 2.

The absorption spectrum of the $S_1$ state overlaps with that of the $T_1$ state. The time profiles shown in Figure 3 show interesting dynamic differences. The early rise time measured after 267 nm excitation which is within experimental error to the rise time monitored at 580 nm, reflects $S_2 \rightarrow S_1$ internal conversion. p-Iodobenzophenone shows a similar transient pattern. The lifetimes of the two singlet states of benzophenone and of p-iiodobenzophenone are shown in Table 1.

**Table 1.** The Lifetimes of the $S_2 (\tau_{S_2})$ and $S_1 (\tau_{S_1})$ States of Benzophenone and p-Iodobenzophenone in Acetonitrile

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>Benzophenone</th>
<th>p-Iodobenzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_{S_2}$ (ps)</td>
<td>$\tau_{S_1}$ (ps)</td>
</tr>
<tr>
<td>267 nm</td>
<td>0.53±0.05</td>
<td>9.82±0.24</td>
</tr>
<tr>
<td>335 nm</td>
<td>-</td>
<td>11.01±0.18</td>
</tr>
</tbody>
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**Conclusion**

Though one hesitates to say the last chapter has been written, photoscientists are getting closer to solving the riddles of the benzophenone photochemistry and spectroscopy. It has taken 104 years from the starting point and 40+ years to get beyond George Hammond’s aggressive attempt to connect the spectroscopy of the excited state, via steady
state kinetic methodology, to the organic reaction intermediates whose reactivity were then being categorized in solution. In acetonitrile at least, the energy diagram (with a few embellishments and in the absence of any external quencher) for benzophenone now looks like this.

References
1. Hundreds of tons of benzophenone are sold each year. It is used as a photoinitiator in the photopolymerization of polyol(acrylates).
4. Benzopinacole was first reported in a paper by Linnemann, E. Ann. 1864, CXXXIII, 1. He dissolved benzophenone in ethanol and added it to a solution of “English” sulfuric acid, ethanol and water. Then he added zinc dust. Benzopinacole precipitated after a few days.
6. Ciamcian’s initial studies appeared 12 years before G. N. Lewis’ paper on the nature of the covalent and ionic bond; so they were, in some senses, naïve. However, Ciamcian became a vigorous spokesperson for the value of light initiated chemical reactions. In a lecture to the New York Academy of Sciences in 1912 recognized as prophetic today “The Photochemistry of the Future”, he judged all sources of “natural” energy (including the tides which he said could never be harnessed and atomic energy the potential for which was so huge as to surpass all currently known limits) inferior to the sun. This lecture was reprinted in Science 1912, 36, 385. Among other things this lecture generated was the first book on photochemistry; Ellis, C. P.; Wells, A. A. The Chemical Action of Ultraviolet Rays; Reinhold, 1920. Ellis, a prolific inventor in his own right, attended the lecture, and wrote the book several years later with his then technician, Alfred Wells. Some of us are familiar with the second edition rewritten by Francis P. Heyroth, Chemical Action of Ultraviolet Rays, 2nd ed; Reinhold Publishing: NYC, 1941.
8. Erlenmeyer flasks were chosen selectively; Ciamcian’s long-standing colleague, Paul Silber, was an Erlenmeyer assistant for a short time in Freiburg. See Heindel, N. D.; Pfau, M. A. A Profitable Partnership; Giacomo Ciamcian and Paul Silber. J. Chem. Ed. 1965, 42, 383.
9. In Hammond’s hands (Moore, W. M.; Hammond, G. S.; Foss, R. P. J. Amer. Chem. Soc. 1961, 83, 2789) this meant late Ames summer sunshine. Hammond’s first experiments were done by Bill Moore when a student in Hammond’s labs at Iowa State University).

Continued on page 31
When I recently completed a review of novolak-diazonaphthoquinone resists, several colleagues asked me about the origins of these systems. Here then is a brief history.

The material was discovered in the 1940s at the Kalle Chemical Works in Wiesbaden, Germany. The firm was well known for its blueprint papers used in the reproduction of engineering drawings. The active parts of the blueprints were various diazonium salts. In the presence of ammonia, diazonium salts react with phenolic couplers to form a blue dye, yet under irradiation diazonium salts lose nitrogen and are turned into inactive phenolic derivatives. Thus, when a diazo-paper is irradiated through a translucent line drawing, the black lines of the drawing protect the diazonium salt, while the diazo groups in the unprotected areas are destroyed. On subsequent “development” with ammonium vapor only the protected lines form the blue dye on the copy, hence the name “blueprint”.

Kalle tried to improve their product. They made the blue dye more brilliant by introducing sulfonic acid groups into the diazo. They also found that the keeping properties of the materials improved when the diazonium salts were replaced by diazonaphthoquinones (DNQs) such as the one shown in Structure 1. The diazoquinones were coated on paper using a variety of binders such as gelatin, casein, and among others, a phenolic resin manufactured by the Albert Chemical Works, just across the road from Kalle. This resin sold under the name of Novolak. It usually has a branched structure (see Structure 2). Novolak turned out to be an excellent binder for all kinds of applications. While it was being tested, one of the technicians at Kalle observed that mixtures of novolak and DNQ were hard to remove from their support, but became easily soluble in aqueous alkali when exposed to sunlight. When Dr. Oskar Sues, a leading chemist at Kalle, became aware of this, he thought that novolak-DNQ mixtures might be useful in making printing plates. He developed the Ozatek plates (ca. 1950), which were in essence novolak-diazonaphthoquinone films coated on anodized aluminum. The Ozatek plates were a great success because they were “positive-working”, that is they could be exposed directly behind a translucent original without the need for a costly intermediate negative. Even today, novolak-diazoquinone is the only viable positive-working material on the market.

One of the properties of the novolak-diazoquinone system is its high resolving power, and that makes it attractive for microlithography. In 1972, when the lines on the integrated circuits of the new computer industry shrank to two microns, the Kodak Thin Film Resist, then in general use, could no longer resolve these features. The whole industry, such as it then was, switched to the Kalle novolak-diazoquinone “Kopierlack”. At the time I was working at Kodak in London and I bought a bottle of Kopierlack. It worked perfectly, but I simply could not understand how it worked.

Only 16 years later, at Polytechnic University in Brooklyn, could I return to the novolak-diazoquinone problem. At the time, a young Chinese student, Ms. J. P. Huang, worked on the mechanism of novolak dissolution with Professor T. K. Kwei (formerly of Bell Laboratories). I became a consultant on this project, and that is how the investigation into the mechanism of novolak resists got under way at Polytechnic. Through the work of a group of outstanding postdoctoral fellows we eventually found how novolak-diazoquinone resists really work. Here is what we learned.

The dissolution of novolak in alkali is controlled by the diffusion of base into the solid polymer. Base penetrates into the novolak matrix ahead of the solvent (water) and in so doing forms a penetration zone where some of the phenols of the resin are ionized. The ionized sites are eventually hydrated, and the hydrated polymer chains float off into the solution. In the penetration zone the only mobile particles are the free protons of dissociated phenols. The rate of progress of the zone depends, therefore, on the concentration of dissociated phenol groups, that is, on the acidity (pKa) of the resin. When the acidity of the resin is altered, that changes also the dissolution rate of the resin films.

Early in our investigation we found that it was the sulfone group attached to the DNQ that caused the lowering of the dissolution rate. A hydrogen bond is formed between the sulfone and an OH group of the resin, but the process does not stop there. The oxygen of a hydrogen-bonded phenol carries a larger negative charge than the oxygen of an isolated phenol; it acts as a hydrogen acceptor and forms a second hydrogen bond with another phenol; that in turn is polarized and forms a hydrogen bond with another phenol, and so forth. In this way a phenolic string is formed in which the protons are linked to their oxygen atoms by covalent bonds, and are at the same time hydrogen bonded to a second oxygen. As a result, the protons in the string are
Reiser

held more strongly than the protons of isolated phenols, and they are therefore less acidic. This manifests itself in a lower dissolution rate of the resin film. Dissolution of the films is inhibited by the formation of phenolic strings. Phenolic strings are the central concept of dissolution inhibition.

We discovered further that the photoreaction of the diazoquinone (the so called Wolff rearrangement) does not directly intervene in the exposure of novolak resists. Instead, the heat evolved in the photoreaction increases the temperature in the vicinity of the DNQ by some 200°. That severs the connection between the hydrogen acceptor (the SO₂ group) and the phenolic string. When the connection to the polarizing origin of the phenolic string is severed, the string disintegrates, and inhibition ceases. The photoreaction plays here the role of a local heater that can be switched on by a light beam. Exposure of DNQ-novolak films is a thermal process.

When we reported our findings in 1997 at the SPIE conference in San Jose, several people in the audience saw the possibility of replacing the DNQ photoreaction with an external heat source.

My former colleagues at the Kodak laboratory in Colorado were able to do this by scanning an unexposed inhibited novolak plate, pixel by pixel, with a computer-controlled infrared laser. The system has many advantages: it does not need a darkroom, there is no “optical” original, the exposure beam is controlled by a digital signal, it allows editing and so forth. Four companies (Kodak Polychrome Graphics, Agfa, Fuji and Mitsubishi) have taken out patents on that idea, and these patents were published in 2000 and 2001. In the three years of its existence half of the European printing industry has switched to this new Computer-to-Plate (CtP) technology. This is now a multi-billion dollar business. Kodak Polychrome Graphics has opened a new factory in Leeds, England which produces exclusively the new thermal Electra Excel Plates.

Novolak-diazonaphthoquinone resists are still the most important imaging systems of the semiconductor industry. Even in today’s complex integrated circuits, only the last three or four levels of a chip are made with deep UV resists, the underlying 30 or more levels are still based on novolak-diazonaphthoquinone.

About the Author

Arnost Reiser was a reader of physical chemistry at the Technical University of Prague, Czech Republic. He became involved with microlithography and resists in 1960 when he started as a research chemist at Kodak, Ltd. in London. In 1982 he was invited to join Polytechnic University in Brooklyn where he is now professor of chemistry and director of the Institute of Imaging Sciences. His e-mail address is areiser@duke.poly.edu.
The Ohio Laboratory for Kinetic Spectrometry is a new scientific venture within the Department of Chemistry and the Center for Photochemical Sciences at Bowling Green State University. It was established with a grant of $1.3 million from the Hayes Investment Fund for equipment purchase and matching funds from BGSU for scientific staff.

The laboratory plans to be the premiere laboratory of its type in the nation and is designed and operated for the free and open use of those in the Ohio scientific community having needs for access to the instrumentation and services it provides. The community of users and collaborators are drawn from Ohio's universities and colleges and from a number of Ohio-based industries. The laboratory expects to become an integral part of the present and future basic/applied research programs of many of the scientific community in the state of Ohio, and in doing so it significantly enhances research, scholarship, and education in the state.

At its most basic level, the laboratory provides the scientific community in the state with a readily accessible locale for acquiring new information at the cutting edge of science. Important additional benefits accrue. For example, it serves to stimulate collaborative ventures among individual members of its user group and new research partnerships will be spawned between scientists from different universities, and between university scientists and those in an industrial setting. Furthermore, through mutual interactions at regular meetings, arranged to foster such connections, or through chance on-site encounters, members of the user group come to the realization that alternative instrumental approaches to a particular problem could bring unanticipated fruit. Not least in the anticipated outcomes of the laboratory is the fact that it will form a training ground for graduate students of all disciplines who make up the next generation of leaders in science and technology.

The array of instrumentation in the laboratory is designed to study of the earliest of events, that is, those occurring in the time window $10^{-3}$ to $10^{-14}$ s, wherein a rich harvest of new knowledge is being revealed. Instruments that can measure events on such time scales are expensive, not commercially available and must be constructed and operated by persons trained in their intricacies. As a result, many scientists whose research programs would clearly benefit from dynamic information on such time scales cannot achieve their full research potential. The laboratory provides a state-of-the-art experimental facility manned by experts that is open and accessible to the scientific community.

Currently, the laboratory comprises six advanced workstations. All use pulsed lasers to initiate chemical and physical processes the courses of which are followed in time. These workstations are:

1. An ultrafast pump-probe spectrometer with excitation in the ultraviolet and visible spectral regions and interrogation in the visible and near infrared spectral regions. The maximum time window is 1.5 nanoseconds (ns) and the time resolution is near 150 femtoseconds (fs).

2. An ultrafast pump-probe spectrometer with excitation in the ultraviolet and visible spectral regions and interrogation in the mid infrared spectral region. The maximum time window is 1.5 ns and the time resolution is about 150 fs.

3. A super-ultrafast pump-probe spectrometer with excitation in the ultraviolet and visible spectral regions and interrogation in the visible and near infrared spectral regions. The maximum time window is 1.5 ns and the time resolution is nearly 10 fs (currently being developed).

4. An ultrafast fluorescence up-conversion spectrometer with excitation in the ultraviolet spectral region and sensitivity in the visible and near infrared spectral regions. The maximum time window is 1.5 ns and the time resolution is about 150 fs.
5. A suprananosecond kinetic absorption spectrophotometer with excitation in the ultraviolet and visible spectral regions and interrogation in the ultraviolet, visible and near infrared spectral regions with time resolution near 5 ns.

6. A suprananosecond kinetic absorption spectrophotometer with excitation in the ultraviolet and visible spectral regions and interrogation in the mid-infrared spectral region with time resolution near 20 ns.

Currently, some 30 principal researchers and more than 50 graduate students and postdoctoral associates are participating, or planning to participate. Areas of science that are addressable at the Laboratory include photosciences, optoelectronics, materials, nanoscale systems, tumor therapy, and alternative energy research. The common thread connecting the user community is an interest in the fundamental knowledge that can be gained about many of today’s pressing scientific and technological questions through the employment of instruments that generate information about the dynamics of transient chemical/biological entities.

**About the Author**

Michael Rodgers was born and raised in Chesterfield, England. He was awarded a Ph.D. in chemistry from the University of Manchester, having done research in the laboratory of J. H. (Bax) Baxendale. This was followed by postdoctoral research at the Lawrence Berkeley Laboratory with Warren Garrison. He was appointed lecturer in chemistry at the University of Manchester in 1969 and became Research Coordinator and eventually Director of the Center for Fast Kinetics Research at the University of Texas at Austin (1976). In 1988 he was appointed the Ohio Board of Regents Eminent Scholar in Photochemical Sciences and Professor of Chemistry at Bowling Green State University. His e-mail address is rodgers@bgnet.bgsu.edu.

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Deep Ultraviolet LEDs

Scientists at Sandia National Laboratories in Albuquerque, NM, have developed two deep UV semiconductor optical devices that set records for wavelength/power output. One ultraviolet (UV) light-emitting diode (LED) emits at a wavelength of 290 nanometers (nm) and outputs 1.3 milliwatts of power, and the other emits at 275 nm and produces 0.4 milliwatts of power.

“Emission wavelengths of 275 to 290 nm with such high power outputs is a major breakthrough in UV LEDs development,” said Bob Biefeld, manager of Sandia’s Chemical Processing Science Department. “Only a handful of research groups around the world have come anywhere close.”

Access to the shorter UV wavelengths makes it possible to build miniaturized devices that can be used in photochemical processes such as curing polymers and other chemicals, and UV fluorescence. Other applications include purifying water, detecting biological agents, and performing non-line-of-sight covert communications.

They are small, about one square millimeter in size, and resist damage from vibrations and shock. Biefeld and associates did the work as part of a Defense Advanced Research Projects Agency (DARPA) project to develop compact deep-UV semiconductor optical sources, which have a wavelength less than around 300 nm.

Sandia’s device consists of a sapphire substrate with conductive layers of aluminum gallium nitride, a semiconductor which can be pushed toward shorter output wavelengths by increasing its aluminum content. Increased aluminum content, however, makes the material harder to grow and hinders flow of electrical current through it. One key step in their research was getting high-quality material to grow at the high aluminum levels—about 50%—needed to reach the 275 nm point.

Another was packing the device in what researchers termed a “flip-chip” geometry, which departs from the standard top-emitting LED design. The LED die is flipped upside down and bonded onto a thermally conducting submount, producing a bottom-emitting device with a transparent buffer layer and substrate. Bottom-emission results in light twice as bright because the light is not physically blocked by the opaque metal contacts on the top of the LED. It also results in less energy being converted to heat and more to light.

Biefeld noted that the device’s high power output of 1.3 milliwatts at 290 nm occurs in a continuous wave mode during direct current operation, not a pulsed current measurement like other research groups have used because of inability to dissipate enough heat.

New Student Engagement Study

Chemistry students spend the most time interacting with faculty members in the learning process and business students have the least faculty contact, according to the latest National Survey of Student Engagement (NSSE). The study (www.iub.edu/~nsse), done in the spring of 2003, included about 147,000 freshmen and seniors at 437 four-year colleges.

George D. Kuh, a professor of higher education at Indiana University in Bloomington who directs the survey, said “engagement” is a measure of how involved students are in the material they study and the rest of the learning process. Kuh envisions the survey, now in its fourth year, as becoming a more accurate measure of institutional quality than better-known rankings, such as the “best colleges” lists published by the magazine, U.S. News & World Report.

The survey, however, does not publicize results or rankings on individual colleges. Participating schools get detailed reports about their faculties and students and how they compare with other colleges nationally. The results are used internally to improve student engagement. Most colleges, however, do not release their rankings or other information.

Kuh said the new survey found relatively few major changes in student engagement.

Students at women’s colleges, for instance, are substantially more engaged than are students at other institutions. They report more interaction with professors and more active and collaborative learning than students elsewhere. Women attending other institutions also report higher levels of engagement than men.

The results also puncture a popular myth about flunk-prone freshmen. More than 80% of freshmen said their grades were mostly As and Bs, with only 3% saying that they got Cs or below.
Kuh cited indications that the Internet is improving student engagement, with more than 60% of students reporting that they frequently use email to contact professors to discuss and clarify assignments.

**New WORM Material**

The discovery of a new property in a commonly-used polymer material is leading researchers from Princeton University and Hewlett-Packard toward development of new write-once-read-many-times memory (WORM) devices that could be deposited onto flexible substrates.

Based on the hybrid integration of an electrochromic polymer with a thin-film silicon diode, it is potentially cheaper than conventional compact disc technology.

Single-use memory cards using the technology could be inexpensive and supercompact, requiring only one square millimeter of paper-thin material to store each megabit of data—ideal for archiving digital images or other data. Their memory device combines the polymer, which is inexpensive and easy to produce, with very thin-film, silicon-based electronics technology.

“We are hybridizing,” said Princeton’s Stephen Forrest, who led the research group. “We are making a device that is organic (the plastic polymer) and inorganic (the thin-film silicon) at the same time.”

The device would work like a writable compact disc (CD), with the data writing process making permanent physical changes in the plastic. But it also would be like a conventional electronic memory chip, plugging directly into an electronic circuit and having no moving parts. “The device could probably be made cheaply enough that one-time use would be the best way to go,” Forrest said.

Sven Möller, who is now at HP in Corvallis, OR, made the discovery while a postdoctoral researcher in Forrest’s lab. He was experimenting with a clear, electrically conductive polymer material called PEDOT. It has been used for years as an antistatic coating on photographic film, and as an electrical contact on video displays that require light to pass through the circuitry. Möller found that PEDOT conducts electricity at low voltages, but permanently loses its conductivity at higher voltages and currents, making it act like a fuse or circuit breaker.

They realized that PEDOT could be used for digital data storage in memory devices with a grid of circuits. All the connections have a PEDOT fuse. A high voltage applied to a contact point would blow that particular fuse and leave a mix of working and non-working circuits. These open or closed connections would represent zeros and ones and would become permanently encoded in the device. A blown fuse would block current and be read as a zero, while an unblown one would let current pass and act as a one.

Based on test junctions already made, Forrest said a grid of memory circuits could be so small that one million bits of information could fit in a square millimeter of paper-thin material. If formed as a block, the device could store more than one gigabyte of information, or about 1,000 high-quality images, in one cubic centimeter, which is about the size of a fingertip.

**Photomedicine at NASA**

Medical researchers are expanding clinical trials of a device using specialized light emitting diodes (LEDs), based on NASA technology for plant growth in space, in the treatment of bone marrow transplant patients. Preliminary tests at Medical College of Wisconsin and Children’s Hospital of Wisconsin in Milwaukee, were so encouraging that doctors have expanded the trials to several U.S. and foreign hospitals.

“We've already seen how using LEDs can improve a bone marrow
focus on

transplant patient’s quality of life,” said Dr. Harry Whelan, of the Medical College of Wisconsin. “These trials will hopefully help us take the next steps to provide this as a standard of care for this ailment.”

The trials are part of the process required to seek approval from the U.S. Food and Drug Administration and its foreign counterparts, for general use of the technology.

In the first stage of the study, exposure to light from special LED arrays resulted in significant relief to pediatric bone marrow transplant patients suffering the ravages of oral mucositis, a common side effect of drug and radiation treatment for cancer.

Many young bone marrow transplant recipients contract this condition that produces ulcerations in the mouth and throat, severe pain, and in some cases, inflammation of the entire gastro-intestinal tract. Swelling and bleeding occur, and chewing and swallowing become difficult, if not impossible—ffecting a child’s overall health because of reduced drinking and eating.

“Our first study was very encouraging, and using the LED device greatly reduced or prevented the mucositis problem, which is so painful and devastating to these children,” said Whelan.

They used LEDs developed to provide light for plants grown on the International Space Station as part of commercial experiments sponsored by industry. Researchers discovered that the diodes also had promising medical applications. Cells exposed to near-infrared light from LEDs, for instance, grow 150% to 200% faster, speeding the healing process.

The treatment device is a portable 3-by-5-inch flat array of light-emitting diodes, held on the outside of a patient’s cheek for about a minute each day. Researchers compared the percentage of patients with ulcerative oral mucositis to historical epidemiological controls. Just 53% of the treated patients in the bone marrow transplant group developed mucositis, compared to the 70-90%. Patients also reported pain reduction in their mouths when compared to untreated pain seven days following bone marrow transplant.

The wound-healing device made by Quantum Devices Inc. in Barneveld, WI, is a 3.5-inch by 4.5-inch portable, flat array of LEDs that promotes cell growth. A nurse practitioner places the LED array on the outside of a patient’s cheek where it promotes wound healing and preventing mouth sores caused by radiation and chemotherapy.

Many young bone marrow transplant recipients contract this condition that produces ulcerations in the mouth and throat, severe pain, and in some cases, inflammation of the entire gastro-intestinal tract. Swelling and bleeding occur, and chewing and swallowing become difficult, if not impossible—ffecting a child’s overall health because of reduced drinking and eating.

“This technology will give security or customs authorities the confidence that documents are not fake,” said UT chemistry professor Eugenia Kumacheva, who holds the Canada Research Chair in Advanced Polymer Materials. “It gives a very high level of data encryption and is relatively cheap to produce.”

It involves production of a thin film of polymer material from tiny three-layer capsules with three different dyes. Each layer is sensitive to light at a particular wavelength—ultraviolet, visible, or infrared. High-intensity irradiation of different wavelengths is used to encrypt desired patterns into a passport, smartcard, or other security document. To the unaided eye, the ID might appear to display just a photograph and text. But detection devices using UV or infrared light could reveal signatures, fingerprints, or other identification or authentication information.

The Spectrum Briefing: Stretching the Lithography’s Limits

Moore’s Law shows no sign of strangling the traditional lithography process used in making photomasks for computer chips—even though feature size already is smaller than the wavelength of light.

Intel, the world’s biggest maker of computer chips, announced that it has achieved a feature size of 65 nanometers (nm) for its next generation chip, scheduled for introduction in 2005. That means the number of transistors crammed onto a chip will continue to double about every two years.

That’s the heart of Moore’s Law, named after Intel co-founder Gordon Moore, and it has held true for 30 years. Experts, however, have been concerned that the law would break as chip builders strained lithography
ability to etch ever-smaller features and contended with problems like heat build-up and current leakage.

“This accomplishment puts Intel’s 65 nm technology on a fast track to extend our 15 year record of ramping production on a new process generation every two years,” said Sunlin Chou, general manager of Intel’s Technology and Manufacturing Group.

Only 20 months have passed since Intel announced development of the 90 nm process used on current chips.

The 65 nm process will mean transistors measuring only 35 nm in gate length, which will be the smallest and highest performing CMOS transistors in high-volume production. The most advanced transistors now in production, found in Intel Pentium 4 processors, measure 50 nm.

Lithography is one of the key technologies that enabled Intel to continue following Moore’s Law by allowing a 30% decrease in the size of printed dimensions every two years. Intel has pioneered advanced lithography, including introduction of 248 nm and 193 nm lithography into high volume manufacturing. The firm is investing heavily in extreme ultraviolet research for making masks with still-smaller features.

Masks are intricate stencils used to focus light onto a silicon wafer so transistor and other patterns for microscopic electron pathways can be etched onto its surface. A chip may need two dozen such diagrams to make the various layers of electronic components on a chip, and interconnections between each.

The complexity strains understanding. A 90 nm microprocessor requires 200 gigabytes of data to describe its 22 to 25 masks. Then there’s inspecting and repairing defects in the masks. Intel compares finding and repairing a significant defect to searching for a basketball in an area the size of California. Even after making repairs, only 50% to 70% of masks are production grade.

Intel has already pushed lithography to the point where the minimum feature size of the circuits are smaller than the wavelength of light that can be projected through the mask to create them.

Although designs can be built on the masks, the lines created by the light blur together when reduced onto the silicon wafer. Even with the most advanced lithography equipment, the individual feature sizes are so small and close together, that they no longer resolve.

Bigger lenses are one solution. However, to keep abnormalities to a minimum, lenses can only get so large, and they become prohibitively expensive. Intel is taking a different approach, pushing lithography tools beyond their limits no matter how blurry the image gets, and then finding ways to correct the image.

The firm is using optical proximity correction to correct the image. It involves adding extra rectangles to the mask image so the final exposure on the wafer looks more like the intended image despite the haziness of the light. Other solutions include special masks called phase-shift masks. These masks use a material put selectively onto the mask to overcome the fuzzy images caused by diffraction.

The approach allows the new chip to be made with 193 nm and 248 nm lithography equipment that was used for its current generation of chips. That means huge financial savings.

Global Chemists’ Strike

What if all the world’s chemists went on strike?


Armand Lattes, University of Toulouse, conjured the scenario in which chemists decide not to take any more criticism about unintended consequences of their science. It emphasizes chemistry’s central role in modern society.

IUPAC has launched a feasibility study for a web site that chronicles chemistry’s contributions to society. It would serve as a source of information and education, enhancing public appreciation of the chemistry and a resource for students, teachers, policymakers, and others.

The task group welcomes suggestions on the project. Contact any task group member.

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Synthesis and photophysics


Shah & Neckers Continued from Page 21


16. Kharasch had shown years previously that radicals were essentially planar and radical sites generated at a chiral carbon produced a racemic product.


18. The α-hydroxydimethylmethyl radicals are identified in blue indicating they may be the same radical.

19. George Hammond, in reading a draft of this paper, pointed out that “steady state approximation” is really an inaccurate term. The assumption is that if an intermediate never accumulates to concentrations significant in comparison to the reactants or the products used to monitor the reaction, one can equate the rates of its appearance with the rates of its disappearance. Professor Hammond says that the first time he read about the approximation was in Louis Hammett’s book Physical Organic Chemistry; McGraw Hill: New York, 1940.


About the Authors
Bipin K. Shah received his M.S. degree in organic chemistry from Tribhuvan University, Nepal. Working with Dr. D. C. Neckers, he received his Ph.D. degree from Bowling Green State University in 2003, where he is currently a research assistant professor. His e-mail address is bipin@bgnet.bgsu.edu.

D. C. Neckers received his Ph.D. in organic chemistry at the University of Kansas with Earl Huyser. His teaching career spans nearly 40 years (Hope College, 1964-71; University of New Mexico, 1971-73; and Bowling Green State University, 1973-present). His early research was done with only undergraduate students. Neckers was named chair of the Chemistry Department at Bowling Green State University in 1973, a position he held for 23 years. During this time he started the Center for Photochemical Sciences (1985) where he currently serves as Executive Director and McMaster Distinguished Research Professor. During his tenure at Bowling Green the Ph.D. in Photochemical Sciences degree, the only one of its kind in the country, was begun and currently enrolls fifty full-time students.