

Thirty-Five Years in Rad Cure: Taking Radiation Curing From Academia to Industry

By Douglas C. Neckers

At a recent RadTech meeting, Alex Mejriski and I were waiting for his talk when he said to me, “This conference is made up almost entirely of end-users of radiation cure. I don’t see what your connection is to it.”

What Alex didn’t see, because he couldn’t, was that more than two dozen former students from my labs

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were at the meeting. His comment meant that I had accomplished my goals in the radiation cure industry—goals that I never imagined when I was first introduced to the notion of photopolymerization in 1974. At that time, Ciba-Geigy scientists were already starting to market the Irgacure photoinitiators; and a division of the UpJohn Company, located in Connecticut, was marketing benzophenone as a photoinitiator. Photo applications used to quick-dry printing inks were entirely new in

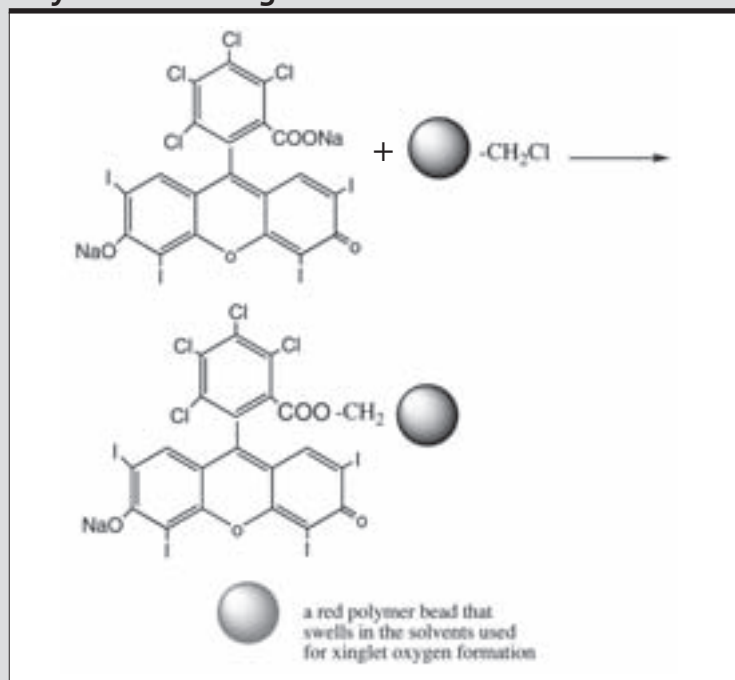
polymer chemistry, and markets were growing by the month. UV cure was “all solids” and environmentally clean compared to solvent-based ink. This was the initial selling point.

In my first National Science Foundation (NSF) grant, “Photopolymers,” I proposed making polymer-immobilized photocatalysts based on Merrifield resins. Bruce Merrifield won the Nobel prize in 1984 for developing Solid Phase Peptide Synthesis (i.e., building a poly(peptide) by immobilizing the first amino acid to a polystyrene bead and building a sequence from there). With my first NSF grant, we managed two rather important contributions—“Polymer Protected Regents”¹—that in the hands of Tokyo University scientists and their industrial colleagues, turned into multibillion-dollar gas purification reagents and “Polymer Rose Bengal”² (Figure 1) which, in Paul Schaap’s hands, gave rise to enzyme sensitive dioxetanes, Lumigen and the entire chemiluminescent diagnostics business.

I thought NSF got their money’s worth, but when my renewal was submitted the reviewers said, “This program has been modestly productive, but not spectacularly so,” and the continuation was not funded. So it goes in the wonderful world of academia. Fortunately, polymer

FIGURE 1

Polymer Rose Bengal



persons at NSF did take notice and in two years I was funded by the NSF's Division of Materials Research.

My first introduction to radiation curing came at an American Institute of Paint Chemists meeting in Columbus, Ohio. I was invited to give a talk because the meeting chairman said that (1) "You know something about photochemistry of ketones" and (2) "You're cheap." So, for a \$50 honorarium and an overnight stay at a Holiday Inn, I gave a two-hour talk on ketone photochemistry. I couldn't help noticing several Nick Turro alumni in the hall. (Turro, a professor at Columbia University, is widely recognized as a leader and pioneer in the area of supramolecular chemistry, organic photochemistry, molecular spectroscopy, host-guest chemistry and magnetic effects on photochemical reactions.) I found out later that Ciba scientists, using technology that had been first outlined by David

Trecker at Union Carbide Corporation in Charleston, W. Va., were already marketing acetophenone derivatives to photopolymerize acrylates.

Bob Bassimer, from Sun Chemical Corporation, spoke after me at the meeting and talked about photocuring printing inks with "Hammond's Initiator." In the question-and-answer session, I asked who Hammond was and Bassimir said "George." Thus, a simple conference on paints connected what I had spent my graduate career studying—aromatic ketone chemistry and the industrial world. Those two days in Columbus changed my life.

I next went to Carlstadt, N.J., to see Bassimer demonstrate benzophenone-initiated curing of printing inks and found that benzophenone (on which I had written my dissertation in 1963³) was being used commercially to quick dry inks! I learned that "cure" meant "dry"; that there was a growing business in photochemical

polymerizations; and that Sun Chemical was already selling \$250,000/year benzophenone containing printing inks to be UV dried!

My 1972 NSF proposal posited that polymer immobilized benzophenones could be useful photosensitizers. That turned out to be wrong for two reasons—photoreactions of chromophores on polymers weren't efficient and nobody needed immobilized UV photosensitizers anyway.⁴ However, an accident in the synthesis and a good observation led to really important results from the program. In trying to immobilize a ketone functional group to a poly(styrene-divinylbenzene) using a Friedel Crafts reaction, I accidentally located the catalyst $AlCl_3$ in the polymer beads. After a first *Journal of the American Chemical Society* paper was published, I was invited to Hercules, Inc., in Wilmington, Del., by Ed Vanden Berg where I gave a talk on my current work. Vanden Berg told me how many dumb things I had done while accidentally discovering that polystyrene beads (later called Bio Beads) trapped (i.e., "protected") anhydrous $AlCl_3$. But I had been observant enough to see what I thought was going on, published the work and this led to numerous commercial opportunities for me, as well as for those who further developed the concept of polymer-protected reagents. Vanden Berg was chair of the Gordon Conference on Polymers that year and invited me to give a poster on polymeric derivatives of benzophenone.

Numerous industrial contacts resulted, but the one that was the most important was with Ray Seltzer at the Ciba-Geigy Corporation in Ardsley, N.Y. Seltzer told me that he was sure that his colleagues in Basel (Rudi Kirchmeyer and Godwin Berner) would benefit from

conversations with me because they were developing a line of UV-sensitive initiators for unsaturated poly(ester) polymerizations. So a meeting was arranged and I went to Basel for the first of many years of consulting with Ciba-Geigy. Kirchmeyer and, subsequently, colleagues in America, Switzerland and England taught me how acetophenone acetals could be used in forming polymers; while Berner showed me some of his practical labs and the tests they were using with photoinitiated acrylate formulations. This brought commercial realities for photoinitiated poly(acrylate) formation plainly into focus.

As a result of my paint chemists' experience at Batelle, I asked a new postdoctoral to find routes to benzophenone containing peresters and, in short order, we had synthesized p-benzoyl tert-butyl perbenzoate.

I quickly pointed out to Kirchmeyer that, "we have a sure-fire new photoinitiator that will solve all of your problems and you have to test our photosensitive peroxides."^{5,6}

The p-benzoyl tert-butyl perbenzoate⁷ provided a first lesson in industrial photochemistry. Kirchmeyer tested it in unsaturated polyester formulations—the biggest commercial use of radiation cure at the time. He found that, in their procedures, my peroxide photoinitiators were certainly no better than Kirchmeyer's acetophenone acetals. Worse, formulations held at 60° for a few days polymerized completely so there was no way to ship a tank car of acrylate monomers containing my initiators from Hoboken to Phoenix. The car contents would have polymerized at least by mid-Kansas (probably exploding)—providing the entire country with evidence that the Trommsdorf effect was for real! Their letter of rejection was kind. "These things are not good for the purposes

intended. Sorry Charley—no big royalty checks for you and your university." (Liberal interpretation mine.)

Their technicians did their job and, of course, formulations containing our peresters did not work as well as the same formulations containing photoreactive ketones for curing unsaturated poly(esters), the compositions of which contained styrene and other ketone triplet state quenchers. But, at the time, neither Kirchmeyer, Berner nor I followed up on other commercial applications of p-benzoyl tert-butyl perbenzoate. They didn't know and should have; I just plain didn't know. In fact these photoreactive peroxides were excellent initiators in alternative formulations and years later Japanese scientists patented a minor modification of our original idea to photo form electronic encapsulants.

Bowling Green State University (BGSU) did not offer the doctoral degree then (we created the Ph.D. in the photosciences in 1988), so only undergraduate students and postdoctorals worked in my labs. Chris Dalton (a BGSU photochemistry professor at the time) and I held joint group meetings at BGSU and Mike McLain was a master's student working for Dalton. McLain had an undergraduate degree from the College of Wooster, in Ohio, and, after he finished his master's degree, he took a job at Mead Paper's central research facility in Chillicothe, Ohio. Almost immediately, McLain was calling me on the phone about once a week wanting some samples of "those peresters we had recently made."

This went on for months and I got more and more frustrated with that pain in the neck McLain's inveterate calls for more samples. I must have satisfied him to a degree because, eventually, he called and said, "We're looking for a Ph.D. organic

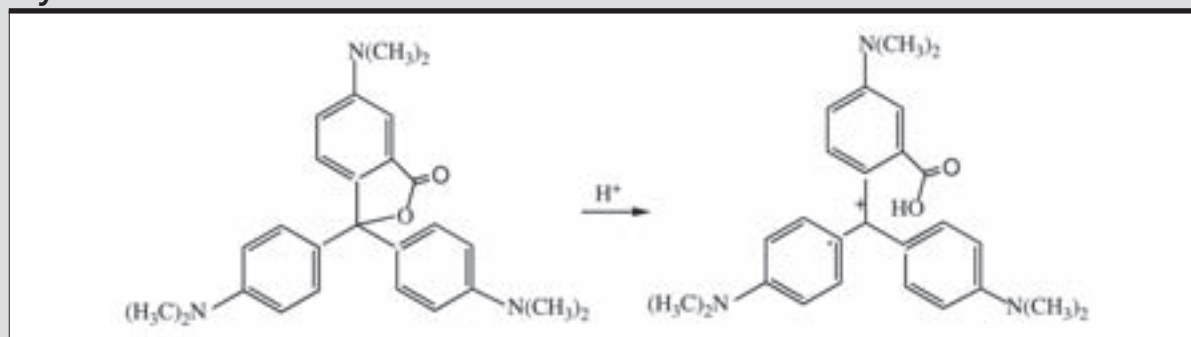
chemist with some experience in photochemistry. Have you anyone?"

Paul Davis, one of my first Ph.D.s, was doing postdoctoral work at Colorado State University, was looking for a job and was interested. Therein began the *Mead Imaging* story.⁸ Paul was looking for a job in Ohio to be near his girlfriend and McLain's bosses took my recommendation, called him, and Paul moved to Chillicothe. A few months after Davis started work, he called me. "We need another organic chemist," said Davis. "We're moving our labs to Dayton and expanding our research force." Peter Gottschalk was just finishing his postdoctoral work in an NIH-funded program to develop long-wavelength sensitizers for singlet oxygen for use in photodynamic therapy.⁹ So, when Mead Imaging labs opened August 1, 1986, Gottschalk was one of its first new employees.

Mead Imaging (a division of the paper company Mead Corporation) was chartered to develop new methods to produce color copy on paper using Mead's proprietary microencapsulation technology. At that time, the technology was used exclusively in carbonless carbon paper systems for which the technology had been developed in the late 1950s. In carbonless paper applications, the capsules contained an indicator dye that changed color when exposed to the acid surface of an accompanying, laminated piece of indicator paper. The indicator dye in carbonless carbon paper was a derivative of crystal violet that turned deep blue at the points where the capsule had been ruptured.¹⁰ A clever invention by Fred Sanders at Mead Corporate research proved that microcapsules filled with photopolymerizable monomers could be polymerized to a greater or lesser degree preventing, or partially preventing, the mechanical capsule rupture essential to produce an image.

FIGURE 2

Crystal Violet Lactone



Microencapsulation was the critical technology for carbonless applications. By encapsulating dyes that could be converted in simple acid-base reactions to colors, breaking the capsule gave an image on the surface of the receiving sheet of paper. In the original carbonless applications, the dyes that were used faded. But, by 1970, various stabilizers incorporated into acidic Novalak resins were used as the developer held the color (formed from the acid-sensitive crystal violet lactone) for years.

Mead Imaging's Cycolor technology employed three different microcapsules filled with polymerizable acrylates; three different photoinitiators sensitive in the yellow, magenta and cyan; and three different pro-dyes (one

producing cyan, another magenta and the third yellow in each of the capsules) assembled together on a sheet of paper. These three dye sets were accompanied in the capsule with three photoinitiators sensitive at 450 nm, 550 nm and 650 nm, and assembled on the surface of the donating sheet. When the capsule assembly was properly constituted, after irradiation with three different light sources and the capsules ruptured, a color image was produced that was near photographic in quality.

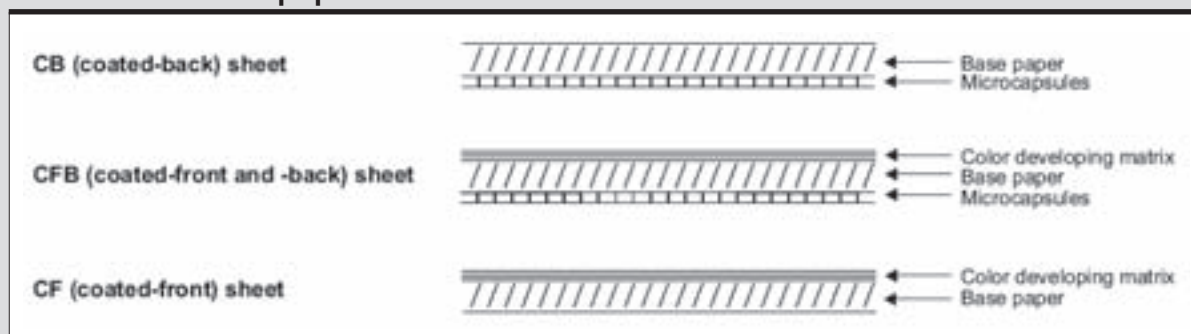
Almost as soon as they moved to Dayton, Mead Imaging leadership assembled a team of scientists and business people to advise them on the next steps in the development of their technology. Gary Schuster and I formed the photochemistry team. Schuster

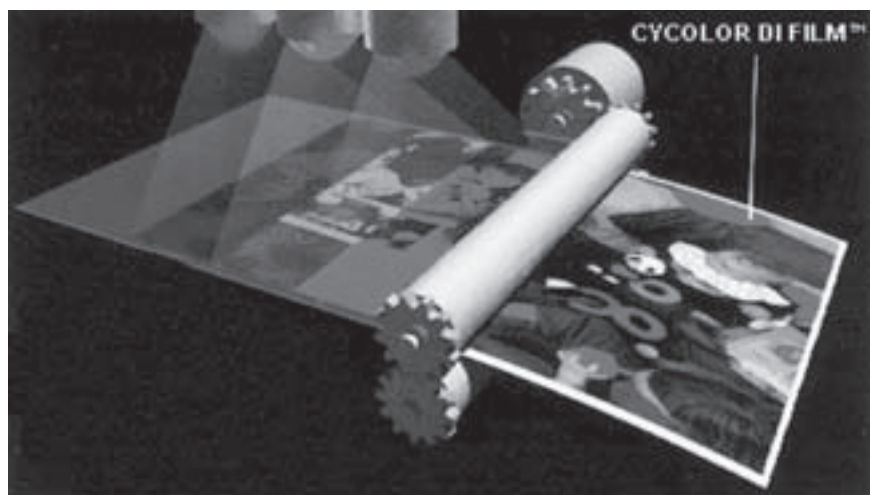
was forever suggesting to Dick Wright, vice president for research, that he try to use "the borates" to photoinitiate the polymerization of acrylates in the microcapsule. Based on his work with model systems, Schuster felt borates would be effective initiators. He also knew initiators that would absorb light at multiple wavelengths could be easily made.

Gottschalk started work on Aug. 1, 1986, and by Oct. 1, 1986, the first of numerous patents for the "cyanine borate initiators" had been filed.¹¹ Gottschalk took cyanine dye expertise from my labs, listened to Schuster's pleadings about using the borates as radical initiators, and built complexes of positive cyanine dyes with negative borates.

FIGURE 3

Carbonless carbon paper





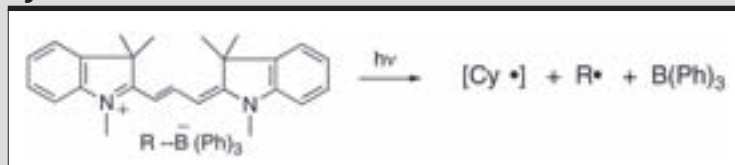
Cycolor Di Film

No single invention in the history of photopolymerizations has generated as much patent intensity as did the cyanine borates. Schuster, Gottschalk and I had many cyanine borate patents,¹² while

technology to produce color copy from color originals, there were few color originals to copy in 1989. By 1990, when this was painfully obvious and there was an economic downturn,

FIGURE 4

Cyanine borates



Japanese scientists made careers out of their patent intensity in the field.

By 1989, Mead Imaging produced near photographic quality images that suggested a real business in which the investments made would turn Mead the paper company into Mead the copy company. What Mead Imaging scientists had invented was quick, high-resolution, hard-copy technology for color imaging and printing.

Advisers urged caution. Nick Negroponete (One Laptop Per Child), Brian Thompson (provost, University of Rochester) and others kept saying, “Careful guys, you don’t have the business plan in place.” And, in the end, they turned out to be right. Though Mead Imaging had excellent

Mead Corporation discontinued the effort. Though Mead Corporation had invested millions in a plant to manufacture Cycolor paper, the business just wasn’t there so Mead Imaging closed, the plants were sold or disassembled, and the technology dispersed.

However, by then Chris Dalton and I had developed a course on organic photopolymerization and managed to occasionally teach courses at

various professional societies on photopolymers and photochemistry. In 1986, we taught one such course at the Society for Photographic Engineers meeting in Cambridge, Mass. While there, a reporter wrote a story about my research in photochemistry, including photopolymers as one of the applications.

Shortly after the paper was published, I received two phone calls. One was from Andy Zucotta (from Ford Design), who said, if “you know how to make a liquid from a solid with light, I know how to make a plastic model of a car door.” The other call was from Chuck Hull (from what was later to become 3D Systems). Hull said, “We are developing photopolymer technology to convert computer-aided designs into three-dimensional models. We’re having trouble with the polymer photochemistry. Can you share your expertise with us?”

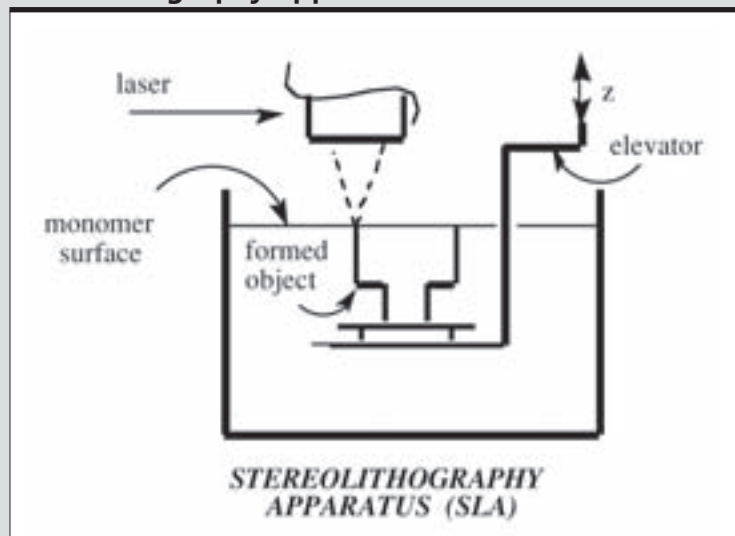
I told Hull about Zucotta and then went to Los Angeles to meet Hull, Ray Freed, Chick Lewis and Stuart Spence—the four people who constituted 3D Systems at the time. They showed me a Petri dish filled with blue liquid in which a platform was slightly under the surface. When the liquid was irradiated by a penlight



Mead copier

FIGURE 5

Stereolithography apparatus



driven over its surface by an x-y recorder, an image of photopolymer was produced on the platform. On top of this a second, third and fourth image could be added as the platform was dropped into the liquid. The drawing in Figure 5 is from the published patent.

Unlike Mead Imaging, 3D had a marketing plan. That marketing plan was Ray Freed. He said, “See that laser over there. We’re going to use a laser instead of a penlight and I’m going to sell six stereolithography systems to the auto companies in the first year for \$200,000 each.”

Hull, Spence and Lewis constituted the 3D scientific team, and the formulation they were using from a nail polish supplier in Los Angeles was originally constituted as a printing ink. Inks had to cure quickly to turn hard, but the coats needed were thin so mechanical properties and the z-dimension weren’t an issue. In the 3D application—even though the individual layers of photopolymer curled and shrunk, and adhesion of one layer to another was hit or miss—the concept was there and a patent

was issued.¹³ Ray Freed was going to turn this into a business, but the photopolymerization processes used in SLA #1 left a lot to be desired.

I knew immediately I didn’t have the personnel at Bowling Green to manage the research Hull needed to pull off his dream, so I introduced him (or confirmed his introductions) to the photopolymer management at DuPont, Mead Imaging and Ciba-Geigy. DuPont’s response was, “we invented that years ago,” and they proceeded to seek a re-examination of Hull’s 1986 patent which, when it was rejected, merely strengthened the original 3D patent. Mead Imaging’s response was, “Our initiators will never work for that and, besides, we’re a copy company.”

Ciba-Geigy, though, could see a serious business opportunity. On my next trip to Basel, I met the senior management of the Plastics and Additives Division and a member of

the *vorstand*. They asked me many questions about 3D Systems and Hull’s stereolithography technology. Two or three months later, Hull called and asked if I knew certain Ciba personnel and he proceeded to list those I had met earlier in Basel. By the end of the year, Ciba-Geigy had purchased 37% of 3D’s stock and Ciba’s management in Marly had assigned a young team of Swiss scientists to work with Hull and his team. Soon it was possible for 3D to invent a field that it called “Rapid Prototyping.”

Back at BGSU, we founded the Center for Photochemical Sciences in 1985—with gifts from Harold and Helen McMaster and Mead Corporation forming the backbone of two endowments. State funding for new hires and later for an eminent scholar allowed us to hire young faculty. When Mike Rodgers arrived as the eminent scholar, we successfully sought approval for a Ph.D. program in the photosciences. By 1991, we were admitting approximately 10 new Ph.D. students a year (most of them from Russia). We were soon graduating young people with degrees that were formed, as much as anything, by the experiences I already had with the energy cure industry.

Mead Imaging and the eminent scholar were responsible for the next



Chuck Hull and Ray Freed at 3D in 1987.



Sandra Knutsen, curator of antiquities (Toledo Museum of Art/TMA), Ohio Governor Bob Taft IV and D. C. Neckers on the occasion of a Taft visit to the Center for Photochemical Sciences. The subjects of attention of stereolithographic images on TMA mummies on display during a museum show.

turn of my world. Mead management was all over the world (including Columbus, Ohio) trying to get their Cylcolor technology off the ground. My name came up in these discussions. Therefore, when the Ohio Department of Development (ODOD) was looking for new business ideas, it called on its eminent scholars. Mike Rodgers, a BGSU eminent scholar, met Chris Coburn (then director of ODOD) and came back to me with the idea that, “Neckers should start a company.”

So armed with the potential for a \$250,000 loan from the state (if I could find investors), I approached Harold McMaster about an idea that came to me the first time I met Hull in San Gabriel, Calif., in January 1987. Why not use stereolithography to make medical models from CT and MRI scan input? The latter were already in tomographic form and should be easily transported to a stereolithography apparatus for model making. 3D had provided BGSU with a 5W argon/ion laser for our use, so I began collaborating with a small group of image analysts at the Medical College of Ohio in Toledo to

see if we could turn my idea of medical stereolithography into reality.

It took a couple of months, but in mid-1987 we produced a small model of a heart from MRI information. I took the model to my neighbor who was a family physician. She found an old anatomy book and we both were amazed at how closely my little model resembled the drawing of a heart in a physician’s first-year anatomy book. We had managed, for the first time in history, to print a three-dimensional model of an anatomical feature using stereolithography.

I met with Harold McMaster to talk about the idea and he said, “Let’s start a company.” So, armed with an investment by Harold and several of his colleagues, we wrote a proposal to the state of Ohio to get funding to start what is now Spectra Group Limited. Awards to Bowling Green from the state and from Spectra Group in September 1990 started us down the path of turning medical imaging stereolithography into a business.

Spectra’s birth was modest. Our one paid employee was a part-time

secretary. Later, a technician was hired to work with image analysts and radiologists. When we had made several models from odiferous formulations containing stinky acrylates and methacrylates, I called physician friends John Bergfeld (head of sports medicine at the Cleveland Clinic) and George Zuidema (vice president for medicine at Michigan) to ask them if I could bring by several anatomical models as “show and tells.” My idea appealed to orthopedic surgeons at the Cleveland Clinic and for several years we produced medical models for them on a weekly basis for orthopedic surgical planning.

But it soon became obvious that because of the way insurance reimbursements were handled here, a long road for medical models lay ahead before we could sustain a profitable business. Without more investor funds or doing other things to pay the bills, we would not be able to stay in business. The latter was, of necessity, chosen and by 1999 we were on our way to becoming the Spectra of today.

As Spectra emerged, I was graduating three or more new Ph.D. students from my lab every year. In time, I transferred most of the radiation cure work to my colleagues in the private sector. Though we published photopolymerization work¹⁴ and occasionally sought patents,¹⁵ my main efforts at Bowling Green were to push the envelop in the photosciences using the creative input of the then current crop of graduate students¹⁶ and postdoctoral fellows.^{17,18} Spectra took over more and more of the applied work with photopolymers, becoming experts for the field in the process. It was, therefore, clear why Alex Mejiritski would say to me, “So just what is it you know about this field anyway?”

In retrospect, what has happened is that through the brilliant efforts of

many students who graduated from our Ph.D. program and found work in the energy cure industry, the field has grown and thrived. I am more removed from the day-to-day advances in the original field than I was in 1970 and that is the way it should be.

On Oct. 11, 2008, 150-plus colleagues, former students, postdoctorals and friends gathered to celebrate my 70th birthday. The incredible joy I have had working with students from 37 foreign countries from every continent, save the Antarctic, is indescribable. As the day went on, I remembered that, as chair of chemistry at Bowling Green, I watched the various iron and bamboo curtains fall as students from the world's formerly closed countries came to study.

Our world has changed significantly since those early days of studying polymer-assisted photochemical reactions. For me, it has been a fun ride so far, and I hope it is not over. ▀

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ODE TO UV (PART 2)

These days, the planet needs to get "cleaner".
And lucky for Mother Earth, UV is "greener".
What makes the technology thoroughly sustainable
is that by using UV curing, quality is truly attainable.
Every dollar counts when times and cash are really tight.
Customers want products that are well-designed and made right.
In order to survive in today's competitive economy,
Get lean, go green, and use instruments from EIT.
With EIT you get sales, service, support and more!
And that's a real stimulus package you just can't ignore.

**EIT radiometers help you keep some "green" in your pocket.
We have the products, the experience and staff - both in the
field and in-house - to help you understand, document,
achieve and maintain control of your UV process.**



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