

ARNOŠT REISER

A Life in Science
1939–2009

ICT Prague Press, 2010

PERSONALITIES
IN CZECH
SCIENCE



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PREFACE

The life of the author followed a truly unusual path. It was marked by numerous stationary points, minima, descents, saddle points and ascents. His early years were spent happily in Masaryk's democracy, only to be torn apart by the invasion of the Nazis, imprisonment and barely surviving under inhumane conditions. This was followed by defeat of the dictators in Europe and the Far East and the miracle of liberation. The joy of enthusiastic studies was spoiled by the onset of a new dictatorship in Czechoslovakia. Twelve years later, in 1960, it became apparent that the brazenness of the police regime had reached such extremes that there remained little choice but to leave with his family and friends. Departure was a dangerous but unavoidable decision and was painful, not only because it was a departure from home, but also because Arnošt Reiser was leaving promisingly evolving scientific work and truly impressive teaching results. The courses in physical chemistry that the author held together with Eduard Hála were unique. They became an unforgettable part of the lives of participants in these lectures. At the time when A. Reiser left Czechoslovakia, the second volume of the excellent physical chemistry textbook by Eduard Hála and Arnošt Reiser was in press. Thanks to the great efforts exerted by E. Hála, the second volume was also published with the names of both authors (although the emigrant had ceased to exist for the perverse forces in power).

His life continued in England where he worked for the Kodak company for twenty years. The author's knowledge and abilities led to fruitful contributions to work related to the rapid developments in the physics and chemistry of semi-conductors, transistors and integrated circuits, all of which were connected with photophysics and photochemistry. He participated in a unique combination of what is sometimes painstakingly and unwisely differentiated into basic and applied research: from elucidation of the mechanism of apparently inexplicable reactions to processes connected with the fading of colours.

In 1981, the company decided to substantially reduce the size of its English branch. An attractive offer from France was surpassed by an invitation from the Polytechnic Institute in Brooklyn N.Y. Research on the formation of images was becoming a topical subject at advanced institutes of learning: The unique career of A. Reiser soon began to culminate in the creation of an Institute of Imaging Sciences and this institute soon established its place in the sun.

The collapse of "real socialism" ten years before the end of the twentieth century made us all free people. Contacts with the Reisers ceased to be illegal and diverse contacts remain a source of happiness on both sides of the ocean.

We might ask ourselves where the basis lay for the

author's enormous research capabilities and his rare lecturing skills. I am of the opinion that these were a result of superposition of the pronounced features of his personality. I am in a quandary as to which of these features and capabilities to mention first. He always attempted to truly get to the heart of his subjects and tasks and was always determined to understand his subject matter thoroughly. He wanted to completely understand and comprehend. This was connected – amongst other things – with his education as a scientist and also with his general education. This is well illustrated by his language skills and his relationship with music. And, although he was no Hercules, his soul has been highly courageous and determined even in the most difficult situations. His character represents a single crystal of the very best material. In conclusion, I cannot resist the

temptation to cite a few sentences from the conclusion of Arnošt Reiser's text:

One of the things I learned is that a piece of science is not contained entirely in formulas and equations, it also needs to be expressed as a narrative. Language is the medium whereby insight is generated. For the teacher to effectively express the thoughts which lead to insight requires an almost poetic effort.

This conclusion is in accordance with the philosophy of languages of contemporary analytical philosophers.

So simply start reading, you have a great deal to look forward to.

*Rudolf Zahradník
Spring 2010*



ARNOŠT REISER

- HE WAS BORN 1920 IN PRAGUE
 - HE STUDIED INSTITUTE OF CHEMICAL TECHNOLOGY IN PRAGUE
 - IN 1947 HE BECAME AN ASSISTANT (LATER ASSOCIATE PROFESSOR) AT THE DEPARTMENT OF PHYSICAL CHEMISTRY AND, TOGETHER WITH EDUARD HÁLA, HE TAUGHT THE PHYSICAL CHEMISTRY COURSE.
 - IN 1960 HE EMIGRATED WITH HIS FAMILY TO ENGLAND
 - FROM 1960 TO 1982 HE WORKED AT THE RESEARCH LABORATORY OF KODAK LTD, WHERE HE STUDIED MICRO-LITHOGRAPHIC TECHNIQUES AS WELL AS THE LIGHT-STABILITY OF COLORANTS.
 - IN 1982 HE BECAME THE DIRECTOR OF THE INSTITUTE OF IMAGING SCIENCES AT THE POLYTECHNIC UNIVERSITY IN BROOKLYN, NEW YORK.
 - SINCE 1989 HE STUDIED IMAGING TECHNIQUES THAT LEAD EVENTUALLY TO THE “COMPUTER-TO-PLATE” PRINTING TECHNOLOGY.
-

A LIFE IN SCIENCE 1939–2009

Having written an account of the life of our family before and during the war I am now looking back trying to remember how I got into science and what happened in the intervening seventy years. I remember that as a teenager I was mainly interested in literature and music and not in science. That changed in the last year of middle school in Prague when our physics teacher, Dr. Keppl, made a group of us aware of recent exciting developments in Physics. It was clearly possible to understand at least part of modern physics without too extensive preliminaries. Dr. Keppl introduced us also to Newtonian mechanics in an interesting way and that made calculus an absolute necessity. To get me started, father bought me Scheffers' *Einführung in die höhere Mathematik (zum Selbstunterricht)*. This charming book, all 500 pages of it, made a real difference; it contained hundreds of worked examples taken from physics. I did almost all of them and gradually began to feel at home in the subject.

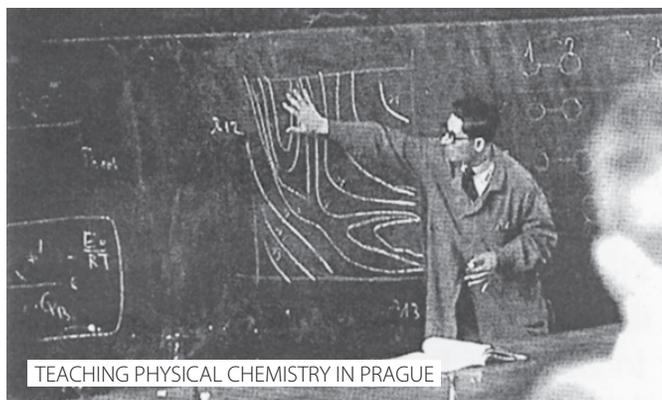
Then, in 1940, I had to teach science to a group of Jewish children that the Germans had excluded from all public schools. They were aged from 8 to 16 and it was not easy to involve all of them simultaneously. To make this nevertheless possible, at some point we constructed a theodolite from an old camera stand. With that, and

with a long knotted string, we were able to determine the height of the local church steeple, measure the width of the Vltava (Moldau) river and eventually make a map of parts of the village of Roztoky near Prague. At first we were making scale drawings to determine distances from viewing angles, but later it was completely natural to introduce sines, cosines and the general ideas of trigonometry. This was exciting to all of us, and in particular to me who began to have a wider view of Euklidian geometry as the quantitative description of space.

If Euklidian geometry describes static reality, Newtonian mechanics is reality in motion. On a more advanced level that is dealt with by vector analysis. In the camp of Theresienstadt an eminent physicist taught a course in vector analysis to a small group of young people. At the time he managed to complete only four or five lessons, but that was enough to convince us of the power of the method.

When the Germans occupied Czechoslovakia they closed all Czech universities, they scattered the libraries, destroyed the laboratories and took many young people into labor camps. It was a very dark time, but it ended in 1945, people returned home, the universities re-opened and slowly normal life re-established itself. I registered as a student of chemistry at the Institute of Chemical Technology in Prague (Vysoká škola chemicko-technologická v Praze, VŠCHT Praha). I managed to pass physical chemistry with good marks and the professor offered me an assistantship. That is where I met Eduard Hala who had been made an assistant a couple of months earlier. At the time no textbooks of any kind were available, and the two of us were put

in charge of the production of the “scriptum”, a written text of the professorial lectures. The mechanics of producing the scripta were primitive; the professor would hand me a rather messy draft of his lecture in his handwriting which I had to clean up and type onto waxed membranes. From those I would make some 400 copies by turning the handle of an old duplicator in the dean’s office. As time went on the professor’s manuscripts became shorter, and soon he indicated only the pages in various English or German textbooks where the sub-



stance of the lecture could be found. That forced Eduard and me to learn physical chemistry from the ground up. I had considerable difficulty with the English texts, but I also found that the English (or American) philosophy of teaching chemistry was very different from the German one. The book by Lewis and Randall was particularly revealing in this respect (Lewis, G. N., Randall, M.: *Thermodynamics*. New York: McGraw Hill Book Co., 1923).

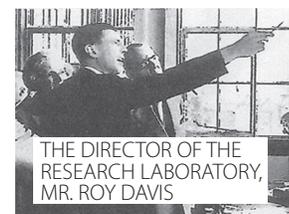
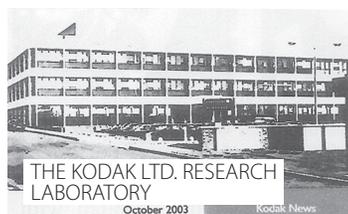
Then, in 1950, something unexpected happened: from one day to the next the professor was transferred to the Academy of Sciences. Right in the middle of the semester the Department of Physical Chemistry found itself without a professor. The rector of the VŠCHT Praha, professor Josef Dyr, called Eduard and me into his office and requested that we take over the professorial lectures for the time being. We were both excited about this, it seemed an unexpected opportunity to do something important. At the same time we were both scared at the prospect of standing up in front of some 400 students. With this new responsibility a period of intense study started for us. We had day-long discussions with our friends and colleagues and once we got below the surface of the textbooks many questions opened up which we tried to answer for ourselves. Starting with Newtonian mechanics we crossed over to thermodynamics via the Carnot cycle and the heat engine. When we thought that we had understood entropy it was a great experience for every one of us and when it turned out, as Boltzmann had shown, that entropy is an expression of molecular statistics, the relief was overwhelming. Although this was never said in so many words, we all believed that the deeper understanding of the world around us and its integration into a consistent “Weltbild” was the true purpose of our lives. Not all students may have agreed with this, but many did and all of them respected our fundamentalist stance. Our lectures were well attended. In fact, to some lectures such as “entropy”, “Eyring theory”, “quantum mechanics” and others people would come two or three years running, and there would be standing room only in the

hall. We were of course very pleased about this, and we considered it the greatest compliment when in the Majales festivities of the Prague universities the chemistry students marched under a banner saying “Entropie je vůl” (entropy is a bitch).

As a fallout of our lectures Eduard and I wrote a Czech textbook of Physical Chemistry. The first volume came out in 1960 and it was well received. In that year my family and I transferred to England. I had finished the text of my contribution to the second volume and had left it on the shelf in our abandoned apartment. One of our friends was able to retrieve it there and hand it to Eduard. When the second volume appeared in 1966 Eduard insisted that my name be on the cover. At the height of Communist rule and in view of my status as an escapee that was an unheard of feat of bravery and friendship.



When we arrived in England I entered Kodak in November 1960. The Kodak Limited Research Laboratory was located at Harrow, a suburb of London. The laboratory had been originally established in the premises of Wratten & Wainright, a dry-plate manufacturer, which George Eastman bought out on impulse in 1912. Since then the buildings had been greatly expanded and in 1960 they housed a collection of first class scientists. The director of the laboratory was a physicist, Mr. Roy Davis a member of the exclusive Atheneum club, very much part of the English scientific establishment. Mr. Sanders was the administrator who received me and who was clearly wondering what to do with me. In the



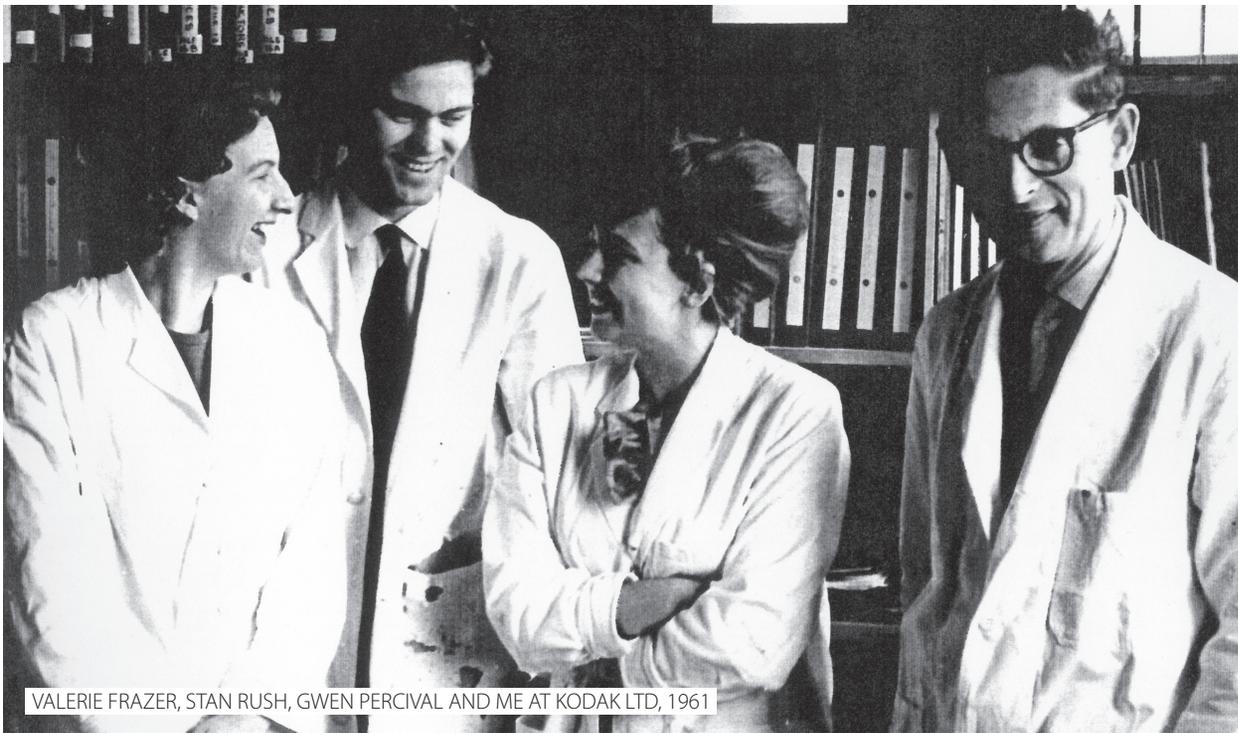
end he made me translate, from the Russian, a book by Alexander Nikolajevich Terenin, *The Photochemistry of Dyes*. Mr. Sanders assumed that, coming from Prague, I would be fluent in Russian. That was not the case, but with the help of a dictionary and very slowly, I found my way through the text and finally produced an English version of its contents.

My next assignment was also quite unexpected. A light-sensitive varnish was being made at Kodak as a favor for Dr. Shockley of Bell Laboratories. William Shockley, Walter Brattain and John Bardeen were awarded the 1956 Nobel prize for the invention of the transistor. Shockley approached Dr. Mees, the head of the Kodak Research Laboratory in Rochester, New York, with the request for a kind of light-sensitive varnish that could be used in the making of the new devices. One of the organic chemists at Kodak, Louis Minsk, came up with the first synthetic radiation-sensitive polymer, polyvinylcinnamate. This worked well in the laboratory but failed when a small production run was attempted. Thus, Kodak had their first customer complaint from Bell Labs. As often happened, the complaint was sent away from Rochester to the London laboratory. There, it landed on the desk of Martin Hepher, the head of the graphic arts



From the left:
LOUIS MINSK,
EASTMAN KODAK

MARTIN HEPHER
AND HANS WAGNER
WHO DEVELOPED
THE KODAK THIN
FILM RESIST (1960)

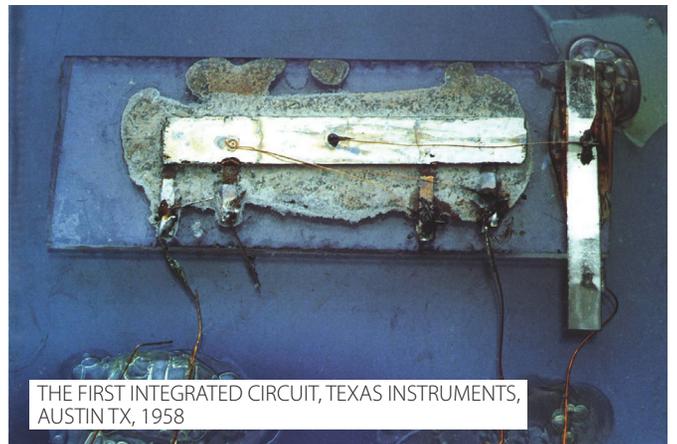
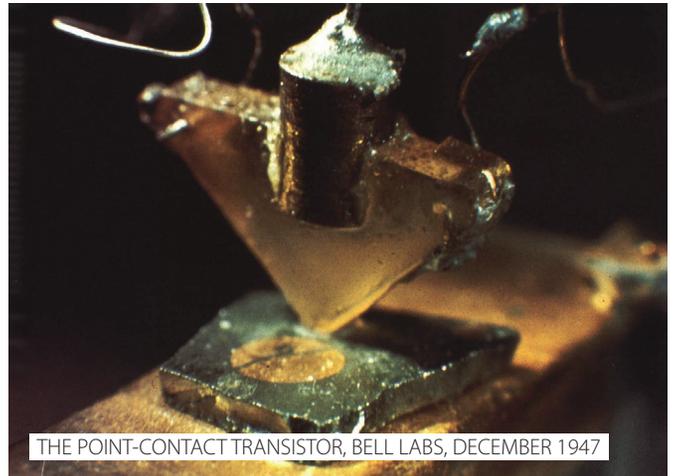


VALERIE FRAZER, STAN RUSH, GWEN PERCIVAL AND ME AT KODAK LTD, 1961

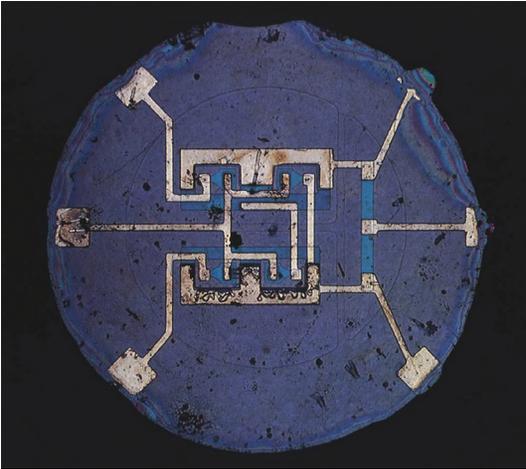
group. Martin was a practical printer, in 1944 during the invasion of Normandy he had produced maps for the troops right at the frontline. He saw immediately that the problem with polyvinylcinnamate was its poor adhesion to glass or to silicon and he thought of making a varnish based on rubber. His friend and lunch-partner Hans Wagner, a German organic chemist, suggested a way to make the rubber radiation-sensitive: add a low concentration of bis-azides which would crosslink the rubber on irradiation and make it insoluble. Hephner and Wagner tried the idea, and it worked. The new varnish was an immediate success. It was called the Kodak Thin Film Resists (KTFR) and was sent out to Bell Labs.

This was in 1960. Martin Hephner had a large agenda in the graphic arts department and he was looking around for somebody to take over the care for KTFR. Nobody in the laboratory was interested. It was not really a photographic product and it clearly had no future at all. Being a newcomer I was assigned this hopeless project and Martin gave me one of his assistants, Valerie Frazer, to show me how to test a light-sensitive varnish, as well as two more young people to help with the other laboratory work, Gwen Percival and Stan Rush. Martin apologized to me obliquely for landing me with this task; he would be looking for a proper project for me as soon as possible. What none of us knew at the time was that we had stumbled into the very beginnings of the semiconductor revolution that, within a few years, was to change life on Earth.

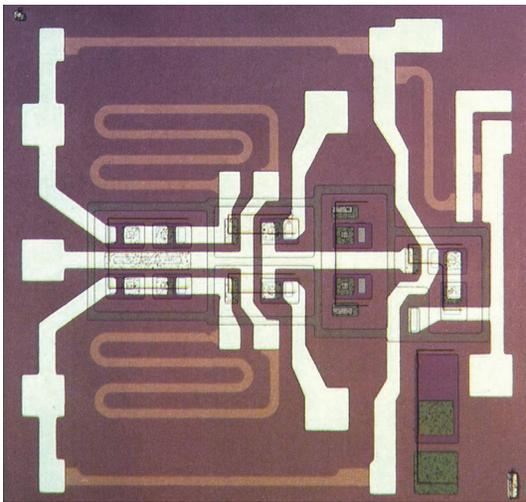
Shockley and his colleagues at Bell Labs discovered the point-contact transistor in December of 1947. It was a rather improbable structure based on a germanium



crystal, but it functioned as an efficient amplifier: a low powered signal (radio wave) went in on one end, and a higher-powered signal would come out the other end.



FIRST PLANAR IC, FAIRCHILD RESISTOR-TRANSISTOR LOGIC, 1961



FAIRCHILD OPERATIONAL AMPLIFIER, 1964

Bell Labs had been looking for such a device to replace the vacuum tube in the radios, which were then the most advanced communication devices in existence. Transistors were soon much improved and streamlined and were introduced into radios, making these more compact and efficient. In those early days the words “solid state” were proudly printed on the cover to indicate that the new devices were inside.

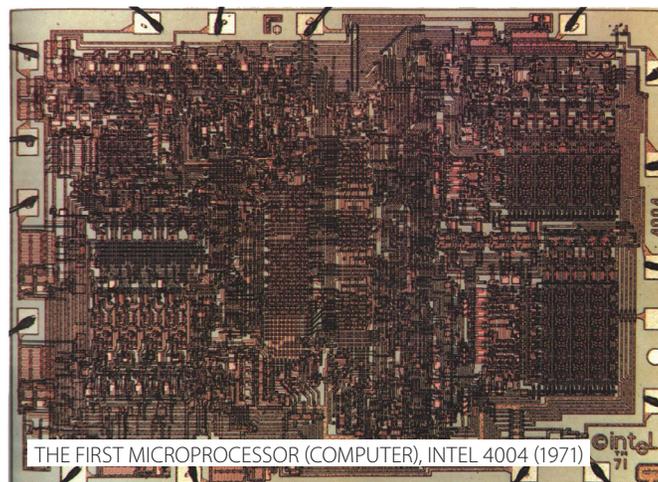
At about the time of the discovery of the transistor an Irish mathematician at Bell Labs, Claude Shannon, published a paper, *A Mathematical Theory of Communication* (Shannon, C. *A Mathematical Theory of Communication*. Bell System Techn. Journal 27, 397–423 and 623–656, 1948), which showed that information consisted of and could be represented by a sequence of binary digits, i.e. yes/no alternatives. A circuit that combined a resistor and a transistor could be either transmitting electrons or shut them out, and would in this way embody the decision making element of information. This made the transistor suddenly a much more important invention as a general information transmitting device. The first circuit which realized this decision-making function was constructed in 1958, rather clumsily, at Texas Instruments in Austin. Shockley and his friends thought that the same function could be built on a silicon (rather than germanium) wafer by doping small adjoining regions of the wafer with electron-donor and electron-acceptor elements (e.g., sulfur and boron) overlaid with a metal electrode. Such a triode was first realized as a “planar integrated circuit” at Fairchild’s on Long Island (1961).

Fairchild made this first integrated circuit (IC) with our KTR resist in a manner which allowed fabrication

of the device on a reasonable scale. They used our resist to define the small doping areas as well as the connectors of the circuit. They coated the KTRF varnish on the wafer and exposed the coated film to radiation behind a mask that protected the area where the first dopant was to be applied. All other areas received radiation and became insoluble (cross-linked). The exposed film was then washed with solvent which revealed the desired area of the silicon surface. After that the wafer was exposed to the vapors of the first dopant for the required time, and finally the polymer film was scrubbed off the wafer and the operation repeated with the second dopant, and then with the connectors, etc. In all these operations KTRF worked perfectly. As more and more firms entered the semiconductor field all of them used KTRF as the imaging material, and our line became actually profitable.

The transformation from an interesting experimental device into an industrial item came within a year or two of the first integrated circuits. Several leading scientist realized the economic opportunities and left the laboratory. Shockley left Bell Labs and formed his own firm in California, and so did Gordon Moore who founded Intel. The explosive growth in the capabilities of the devices is half-jokingly summarized in Moore's law: "Every three years the capacity of the integrated circuits increases by a factor of thousand."

In 1961 when Fairchild made the first planar IC the line-width of the components was 40 μm , and we all thought that that was rather narrow, but three years later the line-width of the ICs had shrunk to 20 μm and at the same time the devices started to change from



planar to three-dimensional structures. Then, in 1971, came a big break. Intel introduced the first fully operational microprocessor, which is in essence a computer. Today computers are ubiquitous and ICs are being used in a host of other devices which permeate our daily life: digital watches, video recorders, cash dispensers, calculators, television, the internet and much more. There is however one application of computers that is more fundamental than the others: the computer has vastly expanded our power of recording information and manipulating data. These capabilities exceed the capacity of the human brain by many orders of magnitude, and systems that contain millions of components become now accessible to logic and to understanding. The immediate applications of this are in molecular biology, in the analysis of genes and similar problems. Large ar-

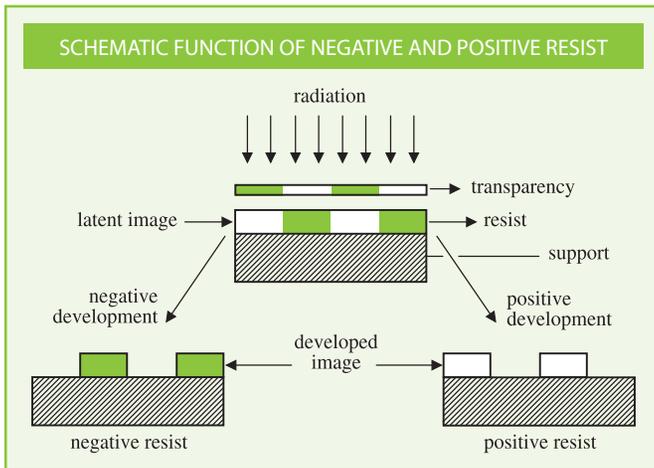
reas of knowledge are now made accessible for the first time. Ours is quite literally a new age. This huge revolution started with a seemingly simple piece of solid state physics, yet I believe that the only other revolutions which surpassed it in significance is the emergence of language some 30,000 years ago and, much later, the invention of writing.



Once or twice a year members of our laboratory were sent to Kodak headquarters in Rochester, New York to get to know their opposite numbers. On my first visit in 1961, I was overwhelmed by the size of the Laboratory (3500 people) and by the sophistication of its scientists. I was also touched by the very friendly and collegial welcome. I met Louis Minsk, the originator of polyvinylcinamate and I was received by Dr. James, the editor of the

Kodak “bible”, *Theory of the Photographic Process* (New York: Macmillan, 4th ed., 1966). At the Rochester lab people were concentrating on silver halide photography, both on the fundamentals and on the practical applications. The practical application of photography were of course all around us; of the fundamentals I remember a sealed Petri dish with crystals of silver bromide sitting on the windowsill of one of the older physicists. It carried a label with the date: July 1945. The crystals were still snow white in 1961, after 15 years of exposure to sunlight: pure silver halide crystals without crystal imperfections are not light-sensitive. In another part of the laboratory a group of chemists were improving the films for instant photography. Edwin Land had conceived and developed the Polaroid process, but for a long time Polaroid films were actually produced at Kodak.

In the early nineteen seventies our resist operation went swimmingly. Then, catastrophe struck. A year after the introduction of the Intel 4004 microprocessor the line-width of the then current devices dropped to 2 μm and that the Kodak resist could no longer resolve. Within a few months everybody in the industry switched to a German resists, the “Kopierlack” of Kalle in Wiesbaden. So, in the middle of 1972 we were out of business. I bought a small bottle of Kopierlack and tried it. It worked perfectly – but HOW did it work? It was hard to imagine. The Kopierlack was a so called “positive” resists, meaning that the resist film became more soluble on irradiation. By then I had met people from the Kalle laboratory and I approached them for an explanation. They told me all kinds of stories, but they did not really know how their system worked. I asked the Kodak manage-



ment for permission to investigate the Kopierlack, but I was turned down. "This is not a Kodak product, don't waste your time on it. Go and do something useful."

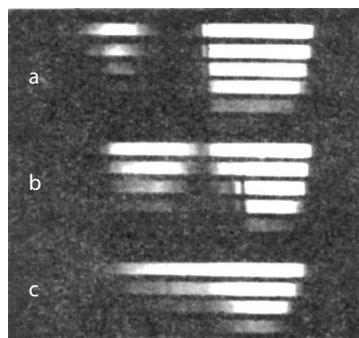
Do something useful! In the preceding years we had worked on maintaining the quality of the rubber-azide resist and had become quite expert in its applications. We were called when people had trouble with KTRF. Most of the time they had not followed instructions and we could put them right over the telephone, but sometimes the problems were more serious and I was sent out to try and help. In this way I met some of the people who were thinking up the new devices and making them with their own hands, and I became infected with the excitement permeating the new industry. I started to feel like a member of the global team.

While working at Kodak, in a suburb of London, we used to join George Porter's Friday colloquia at the Royal Institution. There we got acquainted with the younger members of the group and listened to interesting and sometimes eminent speakers. I remember Ronald Norrish, Linus Pauling, Edwin Land and others. The sixties were a lively time in chemistry and in photochemistry in particular. The old formulaic view à la Terenin which described the final results of a photoreaction had given way to a mechanistic approach with emphasis on the reactive intermediates created in the process. George Porter (later Sir George Porter) had invented the technique of flash photolysis (he was awarded the 1967 Nobel prize), that was able to capture some of these intermediates, and "free radicals" in particular. These had been invoked in a host of processes, but here for the first time their real existence had been demonstrated.

Our little group had been highly stimulated by the sessions at the Royal Institution where many of the discussions spoke directly to us. In the Kodak resist the irradiated bis azides were supposed to crosslink the rubber chains. But how were they doing this? Horner (Horner, L., Christman, A., *Angew. Chem. Internat. Ed.* **2**, 599, 1963) had studied the photochemistry of organic azides and had found that, on irradiation, they released molecular nitrogen, leaving behind a molecular fragment which he termed a nitrene.

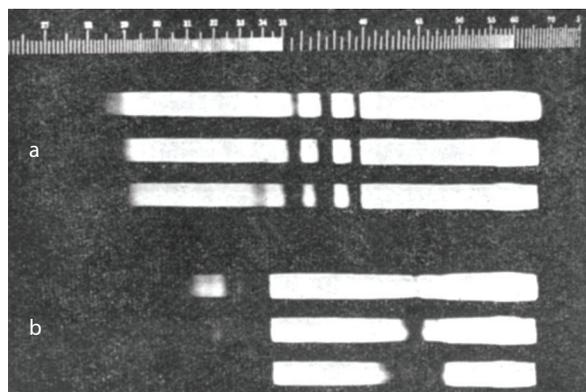


The nitrenes were not radicals but derivatives of monovalent nitrogen; they had only six electrons around the nitrogen nucleus. Two of the six were in exactly equivalent but separate orbitals, they had the same electronic spin, and the ground state of the nitrenes was therefore a triplet state. The nitrenes were thus the equivalents of the carbenes of carbon chemistry, and that made it much more important to prove their real existence. In the Kodak laboratory we had just received a new Beckman spectrophotometer, and we thought that we might just be able to capture the spectra of the nitrenes on that instrument, provided we could do the measurements at sufficiently low temperature, e.g., in liquid nitrogen. Today liquid nitrogen is routinely available in most laboratories. It was not so in 1965. We found that British Oxygen kept liquid nitrogen at their warehouse in the harbor of London. After some negotiations with Kodak management we were allowed to borrow a truck, pack two large glass containers with insulation



SPECTRA OF
NAPHTHYL AZIDE,
ITS NITRENE AND THE
FINAL PRODUCTS
AT 77 K

Bottom:
SPECTRA OF AZIDO-
ANTHRACENE AND
ITS NITRENE, BY FLASH
PHOTOLYSIS AT ROOM
TEMPERATURE



and drive to the docks. When we returned home half of the liquid nitrogen had evaporated, but there was enough left to freeze our solution in the quartz cells and record the spectra of the azides and, after irradiation, the spectra of the nitrenes. When these spectra were published [1] in *Nature* the scientific community was very interested and that interest percolated back to Kodak who decided to create a special Photochemistry

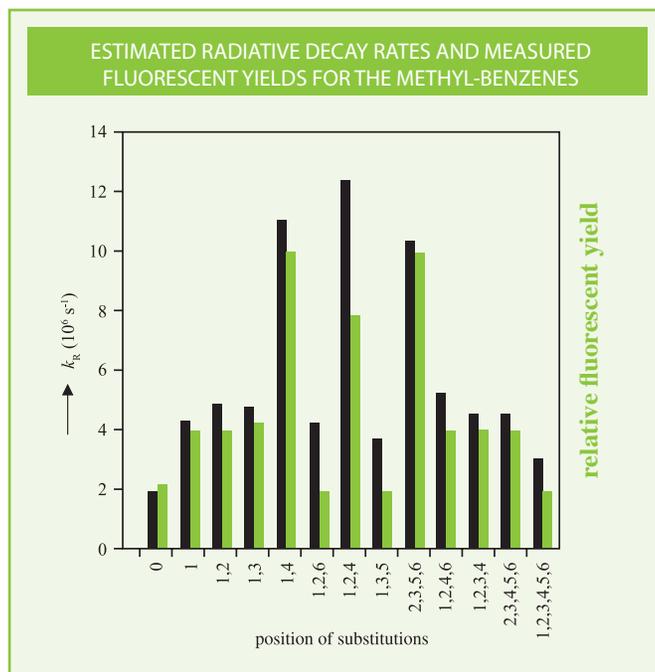
laboratory and put me in charge. After a few months we were able to take beautiful room temperature spectra of anthracene nitrene by flash photolysis [2] (1966). These spectra (left) made it into Porter's 1967 Nobel lecture in Stockholm.

With the establishment of the new laboratory I started to think more broadly about photochemistry in general. Photochemistry is the chemistry of excited states, and to approach that subject rationally we needed two things: a means of describing the molecular and electronic structure of the excited states and a method of estimating their lifetimes. The structure of the excited states can in principle be described by molecular orbital theory. We found a book where the basic molecular orbital calculations were described in some detail, and we set out to follow its instructions. In the end there always comes a point where a fairly large determinant has to be solved. We tried our skill on the smallest possible molecule of interest to us: phenylnitrene. We guessed the roots of the determinant and then refined them by trial and error. We presented these results to John Cadogan when next he came on one of his consultation visits to Kodak. He liked our approach and he understood that we could do much more if we had access to a real computer. John Cadogan (professor of chemistry at St. Andrew's university, UK, who later became the Director General of all Research Councils of Great Britain) arranged for me to be received at the only worthwhile computer in London, the one at the Physical Society. The computer functioned with vacuum tubes; it occupied a large laboratory and it was run like a dental practice. There was a waiting room where several appli-

cants were sitting apprehensively on a wooden bench holding their would-be calculations in a folder on their knees. When a technician in a white coat appeared he would utter a name, and the indicated individual would stand up, hand over his folder and sit down again. When my turn came I did the same, and an hour or so later received a print-out where the roots of our determinants were listed. I thanked the technician and left.

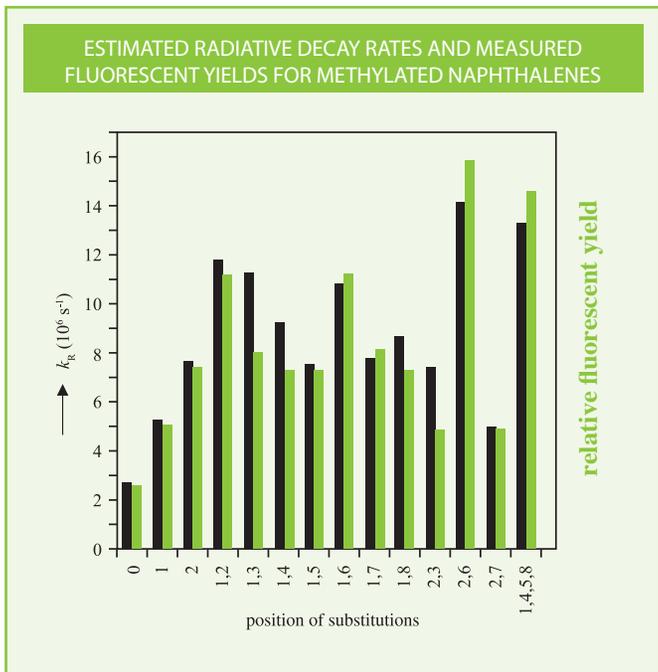
The molecular orbital diagrams of the excited states could now be linked to the absorption spectra of the molecules on the one hand and to the pathways of the photoreactions on the other. The spin states of the molecules and of the reactive intermediates (the primary products of the photoreactions) could be determined from their esr spectra; an esr spectrophotometer was available at the Royal Institution. We were introduced to the estimation of excited state lifetimes by John Murrell at the University of Sussex at Brighton. The Figures below show a comparison of the estimated decay rates with the measured fluorescent yields of methyl-substituted benzenes [3] and methyl-naphthalenes [4]. At least for these molecules the estimates were remarkably accurate (see pages 19 and 20).

Excited state lifetimes are an important aspect of most photoreactions. One very practical example of this is the fading of dyes. That subject interested not only Kodak, but even more the textile industry where the colorants of the various tissues and materials are continually exposed to daylight. There is very little experimental information on that topic because it takes months and years before a measurable change in color occurs. I had some practical experience of this. I had bought



a beautiful tie at Harrods and had worn it almost every day to work. After a couple of years some of the dyes of the pattern had faded and in some places even the underlying fabric had been destroyed. The Figure below shows the colored wool tie after several years of use.

It was known in the industry that the light fastness of dyes can be improved in the presence of metal ions. Different colors in the tie had been stabilized with different metal ions and they had clearly reacted differently. We decided to look into this and we started a research project to that effect with the title "The way Dyes fade".



The fundamentals of the mechanism by which dyes fade were established by Kautsky in the 1930s [5]. The absorption of a light quantum promotes the dye into a singlet excited state which quickly relaxes into a triplet state, and that is the lowest excited state of the dye. Being a triplet, the excited state does not easily return to the singlet ground state and it is therefore comparatively long-lived. The fading of the dye is now triggered by the interaction of the triplet state of the dye with atmospheric oxygen. Atmospheric oxygen happens to be in a triplet ground-state and this interaction produces singlet excited oxygen.



Singlet oxygen has the characteristics of hydrogen peroxide. It oxidizes (destroys) the dye that generated it, and it is the agent that drives the fading process.

We used a technique devised by Kautsky for measuring the rate of singlet oxygen production by various colorants, and this technique (which can be done within an hour or so) was intended to replace the direct observation of dye fading. This in itself was an important advance in assessing the potential light-fastness of dyes. The Kodak management encouraged our dye fading work, but did not like to see it published in black and white. However, word got around and I was invited to give talks in several large firms and at various conferences in the UK and in Europe.

With two very talented young women (Hilary Graves and Linda Johnson) [6] we took the idea of singlet oxygen as the dye fading agent one step further. It had



THE QUANTUM YIELD OF SINGLET OXYGEN FORMATION BY THE PURE (NON-METALLIZED) DYES WERE AS FOLLOWS:

Metal Ion	Relative Quantum Yields of Singlet Oxygen Formation		
	Dye I	Dye II	Dye III
Al(III)	160	–	–
Cr(III)	6.9	6.9	–
Fe(III)	1.1	0.2	–
Co(III)	< 0.03	< 0.003	< 0.000 6
Co(II)	< 0.03	< 0.003	< 0.000 6
Ni(II)	< 0.03	< 0.003	< 0.000 6
Cu(II)	< 0.03	< 0.02	< 0.001 4
Zn(II)	0.36	0.51	0.48
Cd(II)	0.43	–	–

been known for a long time that dyes can be stabilized by complexing them with metal ions and we guessed that this effect functioned by shortening the lifetime of the triplet state of the dye. We tried out the idea on three typical azo-dyes. The quantum yield of singlet oxygen formation by the pure (non-metallized) dyes were as follows:

$$\text{Dye I} = 1,4 \times 10^{-4}$$

$$\text{Dye II} = 1,6 \times 10^{-3}$$

$$\text{Dye III} = 8,7 \times 10^{-3}$$

We then combined each dye with a range of metal ions and measured their rate of singlet oxygen production. The results [6] are shown in the Table above.

What happens when the dye is complexed with a metal ion? In the case of the transition metals Co(II), Co(III), Ni(II) and Cu(II) who have partially filled d-shells, an electron from the excited dye can be temporarily injected into the d-shell of the metal ion. The excited dye loses thereby its triplet character and it can speedily return to its singlet ground-state. As a result, these metal ions suppress the formation of singlet oxygen almost completely. Their quantum yield of singlet oxygen production is reduced by several orders of magnitude. Metal ions such as Cr(III) and Fe(III) have completely filled d-shells and electron transfer from the dye to the metal ion cannot occur. These ions do not change singlet oxygen production substantially.

The ion Al(III) is of particular interest. It has a com-

pletely empty d-shell and it increases singlet oxygen formation by a factor of 160. How can this be? The triplet state of the free, (non-complexed) dye decays to the ground state by a process which is promoted by out-of-plane vibrations of the molecule. In octahedral complexes, such as the one formed with the tri-dentate ligand Al (III) the dye is held in a planar configuration and out-of-plane distortions are inhibited. As a result the triplet state lives for a long time and the singlet oxygen yield is high. These results confirmed the triplet lifetime of the dye as the crucial factor in dye fading. This was regarded as important information by dye makers and by dye users alike.

There was one more aspect of photochemistry that had been neglected, although it is important in many practical applications: the photochemistry of solid systems, in particular the photochemistry in polymeric solid films. These systems can be regarded like a collection of sites of varying reactivity. The reactivity of a group is determined by its environment, and this environment is formed once and for all at the moment of film casting. In systems which require reaction between two or more groups (e.g., in crosslinking systems) there are often comparatively few groups located in close proximity to each other. On irradiation of such films the truly reactive sites are soon exhausted and prolonged irradiation does not substantially increase the success of the operation. We thought that it should be possible to “pre-form” reactive sites. In crosslinking systems that could possibly be done by blending together polymers where the reactive groups carried donor and acceptor substituents (e.g., $-\text{Cl}$ and $-\text{OCH}_3$). It turned out that this intervention increased the probability of pair formation, but most of all it biased the pair distribution in favor of intermolecular pairs (true cross-links) over intramolecular pairings [7].

The Figure on the next page shows the quantum yield of crosslink formation in blends of chloro- and methoxy-substituted polyvinylcinnamates. The lower curve is the quantum yield of crosslink formation in these mixed blends and it shows an efficiency maximum at a composition of 50% (1:1). The upper curve refers to the same system, but this time sensitized with 6% of a bis-coumarin additive. The sensitizer promotes the reactant groups into the triplet state. The triplet

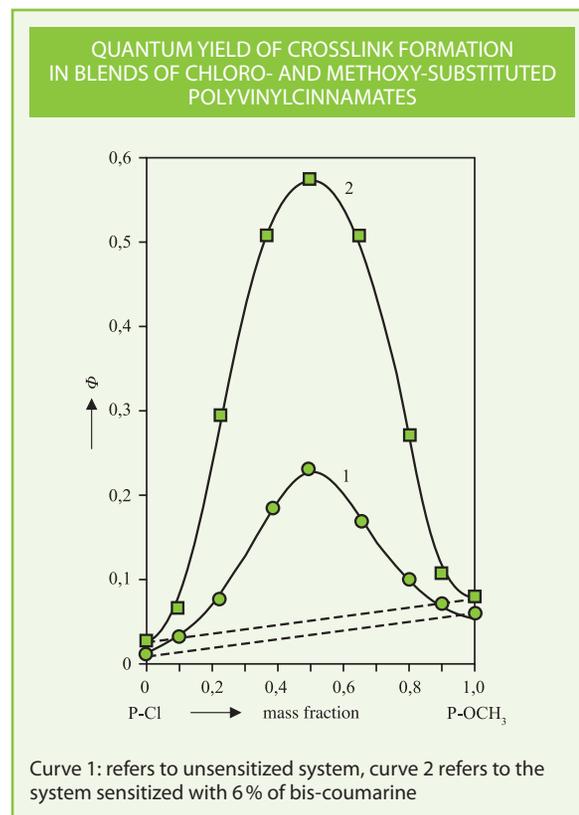


IN 1983 I WAS GRANTED A NATIONAL DEGREE OF D.S.C. WHICH WAS GIVEN TO ME BY PRINCE CHARLES AT EDINBURG UNIVERSITY.

excitation is comparatively long-lived in the solid system and it migrates and scans the matrix for suitable reactive sites. That is why it operates with much higher efficiency. Clearly, a detailed understanding of these systems allows much more efficient structures to be designed.

We had been invited with Hans Wagner to write the chapter on the photochemistry of the azido group in Saul Patai's *Chemistry of the Functional Groups* (the first volume came out at Interscience in 1971), and we were in the middle of establishing a systematic theory of the photochemistry of solid polymers when, unexpectedly, in the fall of 1981, Kodak decided to drastically reduce the personnel of the English research laboratory. The management proceeded with the utmost consideration: only people over 50 years old were affected in the first round. It was a buy-out of the years to go before retirement. I was one of the oldest of the group. Many of us hesitated before accepting the offer, but in the end all of us did. We were given a cordial send-off with a party and dancing, photographs taken, etc. and then, in January 1982, suddenly I was unemployed.

I had to stay at home in the morning and that felt very unfamiliar. At the earliest opportunity I went to the local employment office in Harrow. I arrived there in the morning and took a number. Hundreds of people were already waiting in the large hall. We were all sitting on long benches, people were despondent and there was very little conversation. At noon most of us opened the lunch boxes our wives had given us. If somebody recognized another, he looked away and turned his back. People were ashamed to be seen at the labor ex-



change. Late in the afternoon my number was called and I stepped up to the window. They took my particulars and promised to let me know if there was a suitable opening. And then I went home.

Clearly I had to find employment by myself. I contacted London University and Imperial College as well as several industrial laboratories, but nothing hap-

pened. I was quite prepared to go as a laboratory technician, but for that I was too old, and all the bosses who interviewed me did so only pro forma, out of politeness. Kodak sent me on a farewell visit to Rochester with a view that I might find employment in the U.S. That did not happen, but while I was in Rochester I remembered a contact I had made with professor Fouassier of the University de Mulhouse.

Mulhouse is a town in France at the German border that is almost completely given to a single industry: the dyeing of cloth and fabrics. In the preceding years (1978–1981) I had given a few lectures on dye fading and the role of singlet oxygen. I wrote to Fouassier and he encouraged me to make an application to his university. I remember spending the weekend in New York preparing my presentation in French. I sent the text to Mulhouse and waited. I was back in London when the invitation to Mulhouse came. I gave my talk there in French and the faculty at Mulhouse were really nice about it; they had liked the fact that a non-French person had bothered to prepare his presentation in (even if not perfect) French. It seemed that they would make me an offer and I returned home. Three weeks later a large envelope arrived from Mulhouse; it was an offer, for one year, extendable to a second year. The salary was low and there were many conditions and restrictions. However, that did not deter us, Ruth and I were quite eager to take the offer and live possibly two years in France. We were sitting in our kitchen and I was translating the French contract to Ruth when the phone rang. I took it and somebody at the other end said: "You don't know me, my name is Bernard Bulkin and I am the dean of

Polytechnic University in New York. We are on the point of founding a new Institute of Imaging Sciences at our university and we wonder whether you would like to come to Brooklyn and lead the new Institute. Maybe I could persuade you to come to Brooklyn for a visit and have a look at our university". I was very surprised and somewhat hesitantly said, yes, I would like to visit sometime. "Well," said Dr. Bulkin, "you will have a ticket deposited at American Airlines at Heathrow for the morning flight on Tuesday. I shall be waiting for you at JFK in the afternoon". And so it was. I flew out on Tuesday (May 1982), and that is where the next section of our lives started.

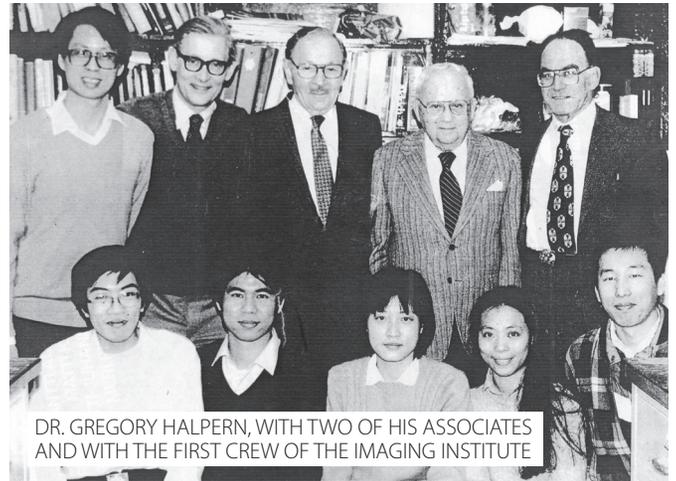


Polytechnic University is an old engineering school in Brooklyn, one of the less glamorous boroughs of New York City. At the time of my arrival it was located on Jay Street in an old razor blades factory. Its physical state was poor, but it had some interesting faculty in electrical engineering and in chemistry. The Imaging Institute had been the idea of Mr. Gregory Halpern, a wartime refugee from Germany who had built a substantial printing business ("Polychrome") on Long Island. In 1981 a Japanese company bought Mr. Halpern's business and he found himself suddenly with a large amount of money and nothing to do. He conceived the idea of a scientific institution dealing with the science involved in image making, and he decided to offer a million dollars to Columbia University if they created such an institution. His good friend Dr. Adler persuaded Mr. Halpern to divert his donation away from Columbia to Polytechnic

University, of which he was an alumnus. Dr. Adler was sure Polytechnic would be more grateful for the donation and would also create a more practical Imaging Institute. Like my old bosses in England Dr. Adler and Mr. Halpern liked to see useful activity unfolding in response to the finances they were offering. They started to look for somebody to put the idea into practice. Herbert Morawetz, who knew me since the chemical congress in Prague, suggested my name, and that is how I came to Brooklyn.

Dr. Bulkin introduced me and showed me around. I found a friendly reception by the faculty, but nothing was prepared for the Imaging Institute, and nobody had any idea what an imaging institute should look like. Yet, no matter how unprepared Polytechnic was for an imaging institute, I was very much attracted to the idea of defining a new branch of science.

I tried to think which parts of science need to enter into imaging. The transmission of images follows optics and images are ultimately detected by our sense of vision. The mathematics and physics of imaging are contained in digital image processing and in image analysis. Finally, images are recorded by physical and by chemical means, and, increasingly more often, electronically. This structure of the fundamentals of imaging was discussed and confirmed in many conversations with colleagues and friends. In addition to the basics we put together a list of applied imaging topics: pattern recognition, medical imaging, microlithography, remote sensing, computer graphics, computer vision, electro-optics, data communication networks, fundamentals of radar, information theory, electron microscopy and oth-



DR. GREGORY HALPERN, WITH TWO OF HIS ASSOCIATES AND WITH THE FIRST CREW OF THE IMAGING INSTITUTE

ers. One Sunday I visited the Halperns at their Connecticut home, made a case for the program and obtained their approval and support.

Dr. Bulkin and I realized our concept of an imaging institute in a Master of Science degree program which we started in the Fall semester of 1983. When we planned this program, the Polytechnic faculty were not enthusiastic. I therefore approached my friends in industry who, subconsciously, had been waiting for years to teach their subjects. In this way we got not only outstanding teachers, but also very interesting personalities.

To bring the imaging program to the notice of a wider audience we supplemented it with a periodic publication, "Imaging Quarterly", which started in 1983 and went on till 1991. We found interesting people to contribute articles, and the graphic looks of the Journal were outstanding (see the next page). A second ven-

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Polytechnic University
Institute of Imaging Sciences
Brooklyn, N.Y. 11201

Q U A R T E R L Y



EARTH OBSERVATIONS FROM LANDSAT SATELLITES

Richard P. Mroczynski
Earth Observation Satellite Company

On October 10, 1957, the U.S.S.R. launched the first artificial satellite to orbit the earth. A year later, the U.S. Congress authorized the creation of the National Aeronautics and Space Administration (NASA) with explicit instructions to expand human knowledge and to establish long-range studies of the potential benefits to be gained from the utilization of space.¹

By the summer of 1960, the U.S. had launched the first orbiting weather satellite and was making use of its data. These early meteorological satellites provided the first spaceborne remote-sensing data of the earth. Although the resolution of these early sensors was rather coarse, 1 to 10 kilometers², the data were useful for tracking cloud movements and improving weather forecasts. In the summer of 1972, NASA launched the Earth Resources Technology Satellite (ERTS). The ERTS satellite (subsequently renamed Landsat) provided the first high resolution (30 meter) multispectral data from an operational altitude of 918 kilometers.³ Over the past 15 years, the U.S. government has

supported five satellites in the Landsat series. These include Landsats 4 and 5, the current generation of U.S. remote sensing satellites.

HISTORY

The idea for making earth observations from spaceborne platforms evolved from early photographic experiments conducted on the manned Mercury and Gemini missions. Results from these early experiments led to the concept, design, construction, and launch of the Landsat 1 satellite.

The first satellite was launched with a two sensor suite. The prime mission instrument was a bank of Return Beam Vidicon cameras (RBVs) capable of collecting reflected energy from the earth's surface in green, red, and near infrared wavelength bands. The RBVs were, in essence, TV cameras having 80 meter ground resolution and the capability of generating black-and-white or color infrared photo imagery similar to the photographs returned by the early manned missions. The principal parameters for this type of data were

established by the U.S. Geological Survey, whose interest was in geologic, cartographic, and environmental mapping applications.

Other potential user agencies, such as the U.S. Department of Agriculture (USDA), had been experimenting with aircraft scanners and computer assisted analysis technology to assess the importance of spectral information for crop identification. These USDA studies led to the requirement for an instrument capable of producing high quality spectral data even if it meant sacrificing the spatial resolution. The second instrument on Landsat 1 was a Multispectral Scanner (MSS) similar in design to a sensor that had been successfully flown on aircraft.

The MSS is a four-channel scanning radiometer designed to return data signals in the visible spectrum and two discrete wavelength bands in the near infrared spectrum. Although it was the secondary mission instrument, the high quality of the MSS data was responsible for the initial and continuing success of the Landsat program.

Both the RBV and MSS instruments were capable of imaging along a continuous swath 185 kilometers wide. During the ground processing of the raw data, the swaths or satellite paths were framed to produce a product with dimensions of 185 kilometers square. The consistent framing of the imagery resulted in the data being made available in a grid network, described by path (north-south) and row (east-west) which allowed the user to identify data by a simple numerical coordinate system. Products from both sensors were offered in a computer compatible (CCT) tape format as well as a film image product in each of the black-and-white bands or combined in a color infrared photograph.

Subsequent Landsat spacecraft have all flown the MSS instrument. The RBV's continued through Landsat 3, and were replaced by a more sophisticated scanner called the Thematic Mapper (TM) on Landsats 4 and 5. The 30 meter ground resolution of the TM, combined with a new spacecraft design for Landsats 4 and 5, provides higher resolution and precision pointing. This has enhanced

the user's ability to generate higher quality cartographic maps and other classification products. The image of a portion of New York City shown in Figure 1 illustrates this achievement.

SPACECRAFT AND GROUND COMMUNICATION

In order to maximize the amount of the land surface available for imaging, most earth observation missions operate from low polar orbiting satellites. Earth remote-sensing resource satellites operate from the 700 to 950 kilometer altitude range, descending from the North Pole southbound with an equatorial crossing time between 9:30 and 10:30 a.m. local time. Early morning equatorial crossing times are selected to optimize sunlight and to minimize cloud cover, which tends to accumulate later in the morning due to the warming of the earth's surface. As these satellites cross the equator at the same local time, they are said to be sun-synchronous.

Since the launch of Landsat 1, there have been two major spacecraft designs used to support the U.S. land remote-sensing mission. Landsats 1, 2, and 3 were based on the General Electric Company Nimbus spacecraft design (Figure 2) which was modified to carry the earth resource sensors. The spacecraft weighed 911 kilograms, and was 5-axis-stabilized, capable of providing 0.7 degree pointing error accuracy. Power was provided by two solar arrays capable of delivering an average of 375 watts which was required to support the experiments. Additionally, each spacecraft was launched with two tape recorders capable of storing sixty minutes of video data or 25.2 million bits of sensor information.

Landsats 4 and 5 (Figure 3) are larger satellites based on Fairchild Space Company's Matmission Module Spacecraft design. In addition to supporting the standard MSS mission, the new Landsat series included the TM sensor, a wideband near infrared system, and a new communications subsystem. On orbit, Landsats 4 and 5 weigh close to 2500 kilograms, are 5-axis-stabilized, and can deliver 2 kilowatts of power from a four panel solar array. Tape recorders were abandoned in favor of a communications link with NASA's geostationary Tracking and Data Relay Satellite (TDRS). Landsat transmits MSS data at 13 Mbps and TM at 85 Mbps to TDRS directly to a ground receiving station, then to the Goddard Space Flight Center (Figure 4).

Raw data from the spacecraft are preprocessed at ground receiving stations and

ture intended to connect us to the imaging community in the New York area were the "Imaging Colloquia" (see the next page) that were held from 1983 to 1993 and these colloquia were well attended.

The imaging program was a success; in 1985 we had 75 students registered, and 20 well-known firms had joined our management corporation and were contributing financially. The photochemistry and the microlithography courses were the most popular and to these people came from the whole tri-state area. Gradually we established a reputation, and we were invited to give specific courses in various localities. Apart from the United States we were occasionally invited abroad, e.g., to the University of Zurich and to the University of Heidelberg.

In the spring of 1985 I got an invitation to Fudan University in Shanghai to teach the microlithography course there. We flew out with Ruth and spent six weeks in China. In 1985 that was still very much Mao's China. We were accommodated in the guest wing of the faculty quarters of the university and every evening we were taken for entertainment. We were also gently kept separated from the Chinese who were keen to make contact with us. In fact Ruth was quite often accosted by people who wanted to practice their English and in some cases she was interviewed about life in America. I taught the course in English to an overflow crowd with almost instantaneous translation. The listeners took notes but did not speak among themselves or respond in any way. Then I made a joke in English and everybody laughed. It was a success situation. Early in our stay we were invited for dinner with the president of the university. The pres-

ident did not speak English, but he entertained us in lively Chinese. Two professors who were also his guests laughed uproariously at his jokes, and so did we. Then the two professors took turns to translate the jokes and we had to laugh a second time. On the first weekend we were taken to a park where we marched slowly, one family after another. The first couple in line was allowed to hire an instant camera and were now taking pictures of their children while all others patiently waited. When the family was finished they handed the camera to the second couple and we could observe that family having a private time in the middle of a crowd. Later, we were taken to other universities in the region and occasionally we were impressed by the personalities and the dignity of some of the professors. In the last few days we traveled to Beijing and, one morning, went to the Great Wall. That was an intense experience. About one mile of the Wall is now reconstructed and kept in good order; the rest of the Wall, thousands of miles, cannot be maintained by the modern state of China. Our stay in China was full of incident, but we did not make any friends, and the whole trip remained curiously without consequences.

Back at Polytechnic University I took part in almost all imaging lectures. Apart from teaching me something it brought me, and Ruth, together with several interesting people who became our friends. That was true in particular of Leonard Shaw and his family and of Israel Abramov, Irving Hirschberg and Michael Bruno. I was teaching Photochemistry and the basics of Micro-lithography. These two courses proved so successful that the publishing house of Wiley asked me to write



Polytechnic *imaging*
C O L L O Q U I A

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333 JAY STREET, BROOKLYN, NY 11201**

**INSTITUTE OF IMAGING SCIENCES
SPRING 1984**

**Refreshments at 4:00 PM
Colloquium at 4:30 PM**

**For Information call
Yulet Clarke at (212) 643-5158**

<p>Tuesday February 7 Room 418 RH</p>	<p>PROFESSOR DAVID CASASANT, Carnegie Mellon University <i>Optical Data Processing</i></p>
<p>Thursday February 23 Room 705 RH</p>	<p>PROFESSOR ROBERT W.G. HUNT, City University, London <i>The Reproduction of Color</i></p>
<p>Tuesday March 6 Room 418 RH</p>	<p>PROFESSOR LEONARD ORNSTEIN, Mount Sinai School of Medicine, CUNY <i>Pattern Recognition in Cytology</i></p>
<p>Tuesday March 13 Room 418 RH</p>	<p>DR. KENNETH MCCARTHY, Polaroid Corporation <i>Additive Color Reproduction by Photographic Means</i></p>
<p>Tuesday March 20 Room 418 RH</p>	<p>MR. DINO A. BRUGIONI, Former Senior Official and Photointerpretation Expert of the CIA <i>The Evolution of Aerial Photography in Intelligence</i></p>
<p>Tuesday March 27 Room 418 RH</p>	<p>PROFESSOR GERALD OSTER, Mount Sinai Medical School, CUNY <i>Moiré Optics</i></p>
<p>Tuesday April 3 Room 418 RH</p>	<p>DR. BELA JULESZ, Bell Laboratories <i>Textons, the Fundamental Elements of Human Vision</i></p>
<p>Tuesday April 10 Room 418 RH</p>	<p>DR. PAUL B. GILMAN JR., Eastman Kodak Company <i>Spectral Sensitization in Photography</i></p>
<p>Tuesday April 24 Room 418 RH</p>	<p>PROFESSOR KING-SUN FU, Purdue University <i>Recent Developments in Image Analysis</i></p>

a textbook. I was busy with this most of 1985 and 1986; it came out in 1986 under the title *Photoreactive Polymers, the Science and Technology of Resists*. While writing this I became again painfully aware of the fact that I did not know anything substantive about the most important resist system, novolak-diazoquinone. In this I was not alone, the chemists at Kalle, later Hoechst and AZ Resists at Sommerville, New Jersey were in the same position. In spite of this, it was a very disagreeable feeling and I welcomed the opportunity to participate in a study of the dissolution of novolak in alkali which was the subject of the Ph. D. thesis of Ms J. P. Huang under the guidance of professor T. K. Kwei.

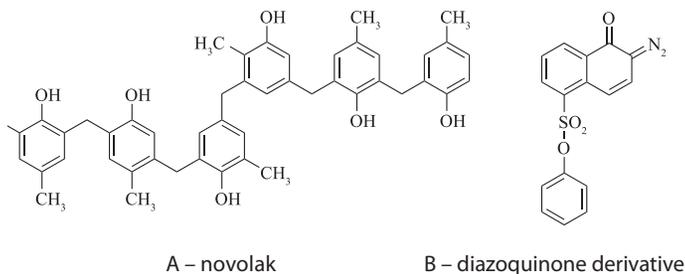
In 1986 Kodak, Xerox and Bell & Howell banded together to finance a Center of Imaging Science at the Rochester Institute of Technology. This Center occupied two new buildings, it had 15 full professors and it was endowed with 35 million dollars. The Rochester Center invited me to give the keynote address at their opening.

I was of course very pleased and I spoke on "*The Archeology of Imaging*". All this was very nice, but of course our small and woefully under-financed Institute could not compete with the Center and within two years our supply of students dried up.¹

The loss of the imaging program at Polytechnic was less damaging than we thought it would be. A lot of the fundamentals of imaging could be preserved in the Physics course, in Electrical Engineering and in Computer Science. Microlithography, in a shortened form, was placed into Chemistry and Macromolecular science. With the new freedom of action we could now address some of the urgent problems of microlithography. The most important of these was an understanding of the mechanism of novolak-diazonaphthoquinone resists.

I mentioned earlier that the resist market had changed profoundly in the ninetenseventies. Crosslinking resists had fallen out of favor and almost all semiconductor devices were now built using the novolak-diazoquinone resist discovered at Kalle in Germany. Novolak (A) is a phenol-formaldehyde condensation polymer of moderate molecular weight.

It dissolves easily in aqueous alkali, but in the presence of some 5% of a diazonaphthoquinone derivative (B) novolak films become almost insoluble. If, however, such films are exposed to ultraviolet radiation they dissolve even more rapidly than pure novolak does. Oskar Sues at Kalle was able to design a highly successful print-



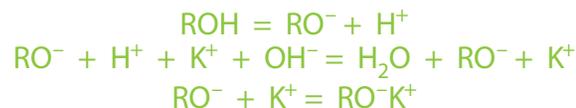
¹ The Center was not the only imaging institution to be founded in our wake. In 1991 Chicago University established a Department of Medical Imaging under Robert Beck.

ing plate on the basis of this observation. He also used the material to formulate a light-sensitive varnish which he called Kopierlack, and which is in fact a photoresist. Novolak-diazoquinone films are so-called positive resists, i.e. they become more soluble in the irradiated areas, in contrast to crosslinking resists where the irradiated areas become insoluble (see page 16). It is not easy to see how positive resists function, and nobody, including the people at Kalle, had a clue how the system works. When I came to Brooklyn in 1982 the computer industry was in full swing and 95% of all integrated circuits (computer chips) were produced using novolak-diazoquinone resists as imaging materials. I found it shocking that an essential ingredient of this life-changing technology had remained a mystery, but I was too busy establishing the Imaging Institute to do anything about it. Then, in 1986 a young Chinese woman, J. P. Huang, came to work with my colleague professor T. K. Kwei, formerly at Bell Laboratories. The title of her thesis was "The dissolution of novolak in aqueous alkali". Professor Kwei invited me to participate in the project and I gladly accepted. And that is how a long term investigation into the molecular mechanism of novolak-diazonaphtoquinone resists got under way.

Our first step with J. P. was to learn how to measure the rate of dissolution of polymer films by laser-interferometry. That magical method had been developed by Grant Willson at IBM and it became the basis of all our subsequent work. J.P. measured the dissolution of a whole list of phenolic resins and found that the rate of dissolution in aqueous alkali was directly proportional to the acidity of the resin [8]. On that basis she wrote

an excellent thesis, but it took a long time before we appreciated the significance of her results.

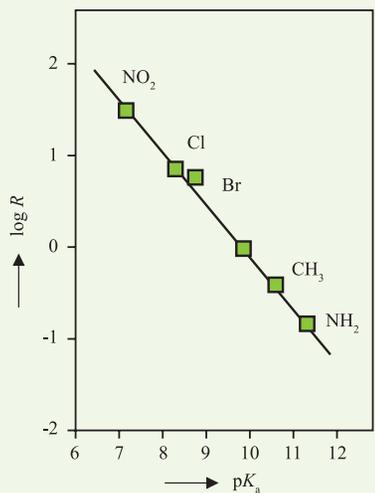
A clue was contained in an observation by Rudolf Arcus at Eastman Kodak. He had suggested (1986) that in the dissolution of novolak films the base (KOH) enters the polymer matrix first, ahead of the solvent, water, and that thereby a penetration zone is formed where a substantial fraction of phenols has been turned into phenolates. This penetration zone is somewhat hydrophilic, water can enter and gradually solvate the resin. Accepting Arcus' suggestion we figured that base ions could enter the matrix only by a kind of "ion pump" mechanism. At sites where a phenol molecule of the resin is actually dissociated; the proton of the dissociated phenol is free to move in the matrix. It combines with a hydroxyl ion of the base and forms a neutral molecule of water.



That second step perturbs the electrostatic field in the neighborhood; the phenolate ion (RO⁻) of the dissociated phenol is thereby "de-shielded", a base cation (K⁺) crosses over and joins it, and with that a matrix site has been permanently ionized. By this electrostatic mechanism the base penetrates into the novolak matrix. This step can occur only at dissociated phenolic sites, and because of this the rate of dissolution depends on the concentration of dissociated sites, i.e. on the acidity of the resin (see the left figure on page 30).

Assuming that we now understand the mechanism

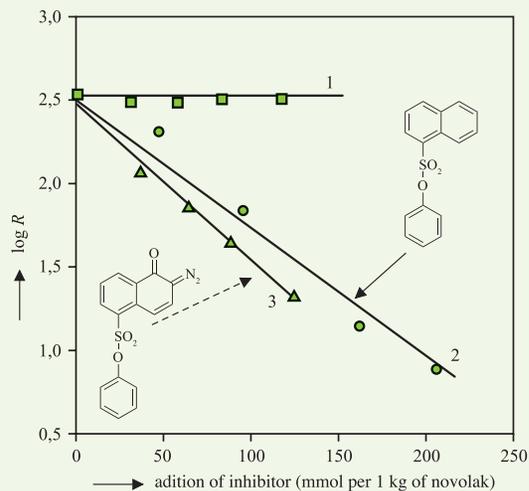
THE EFFECT OF RESIN ACIDITY ON DISSOLUTION RATE



The substituents indicated in the illustration are in the para-position of the phenols and do affect the pK_a of the molecules.

of novolak dissolution, the next question is: how can a diazonaphthoquinone derivative inhibit the dissolution process? We realize that an inhibitor can affect the dissolution if it changes the acidity of the resin; but how can this happen? One of the inhibitors in general use is a diazonaphthoquinone (DNQ) to which a sulfonic acid ester is attached in the 4-position of the quinone ring, (see structure B on page 28). We tried to find out which part of this molecule is actually effective as an inhibitor? When we used the diazoquinone part on its own it had

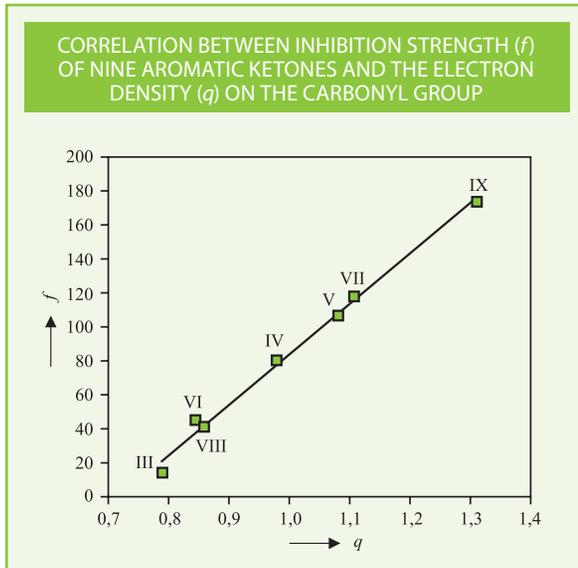
THE EFFECT OF DIFFERENT INHIBITORS ON THE DISSOLUTION RATE OF NOVOLAK



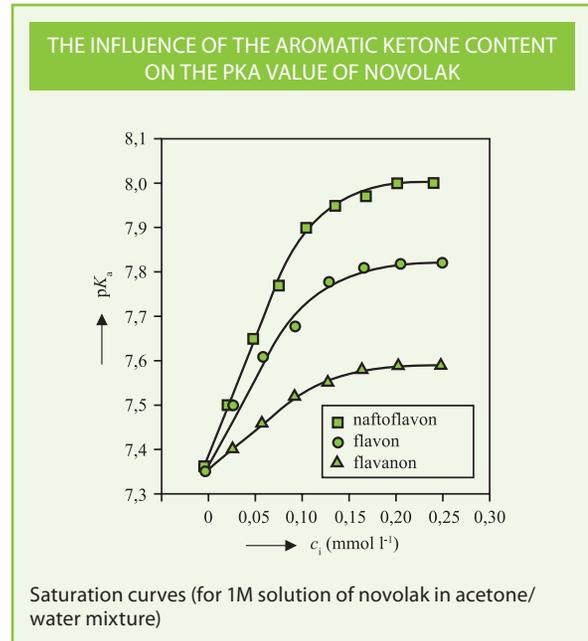
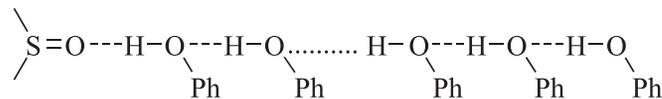
Curve 1: without inhibitor, $f = 0$;
Curve 2: naphtalene sulphonate, $f = 8.5$;
Curve 3: naphtoquinone sulphonate, unlighted, $f = 9$

almost no effect on the dissolution rate, and it turned out that the main inhibitor was the sulfonate group. This is shown on the right figure on this page [9].

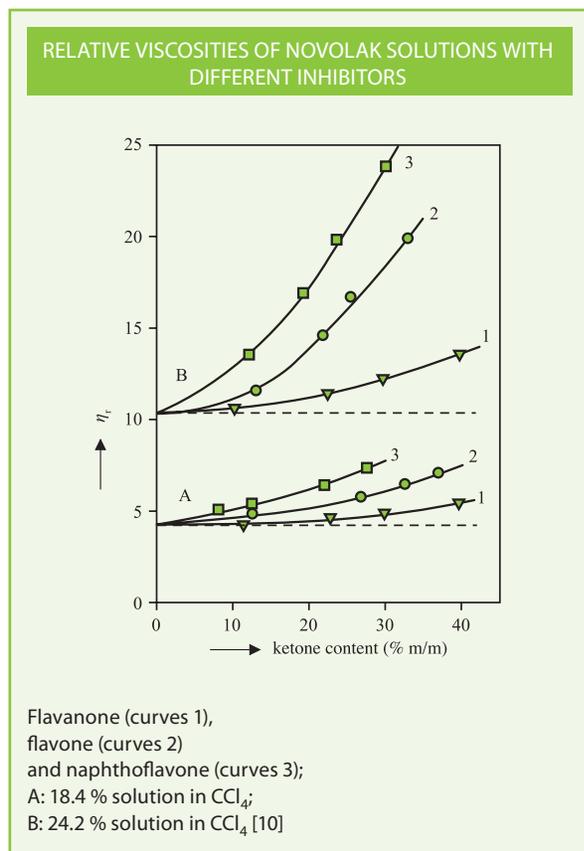
We tried other additives and found that those that did inhibit novolak dissolution contained strongly polar groups, such as sulfones or ketones. The common feature of these groups is that they all can form hydrogen bonds with the hydroxyl groups of phenols. In a group of aromatic ketones we found that the inhibition strength increased linearly with the electron den-



sity on the carbonyl oxygen [10]. Looking more closely at the hydrogen bond between the generating group and phenol one finds that the oxygen of the phenol is more negative than the oxygen of an un-involved phenol. This somewhat more negative oxygen becomes now the acceptor for a second hydrogen bond with the nearest phenol, etc. etc. In this way a whole string of hydrogen-bonded phenols is formed. We use the term "string" to distinguish this structure from the molecular "chains" of the polymer (see below).



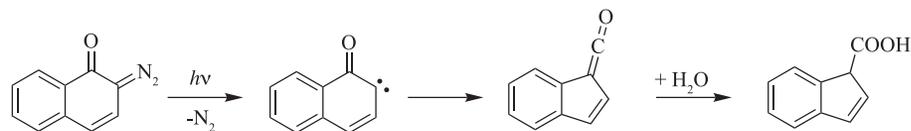
Phenolic strings are the central concept of dissolution inhibition resists. The acidity of the phenols in the strings is considerably lower than that of free phenols, The reason: the hydrogens of the OH groups are now covalently bound to one oxygen, and hydrogen-bonded to another. They are thus held more strongly than the hydrogens of free phenols, and as a result they are less dissociated. We can show this on the acidity (pK_a) of

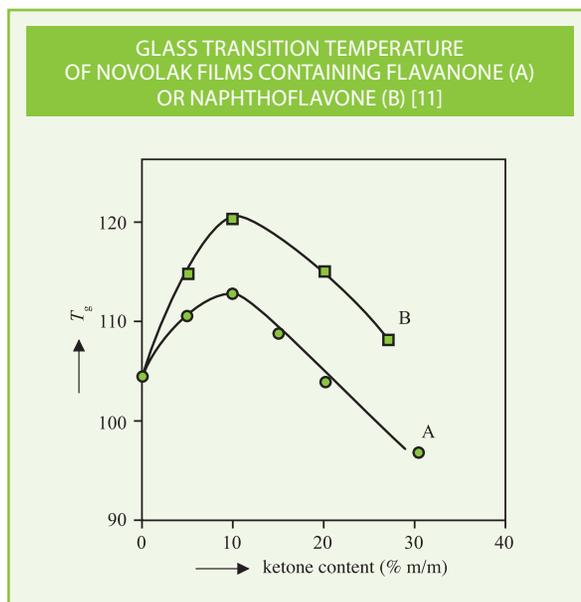


a novolak resin in the presence of increasing quantities of three inhibiting ketones (see on page 31). Because of the lower acidity of the resin, phenolic strings bring about a lowering of the dissolution rate.

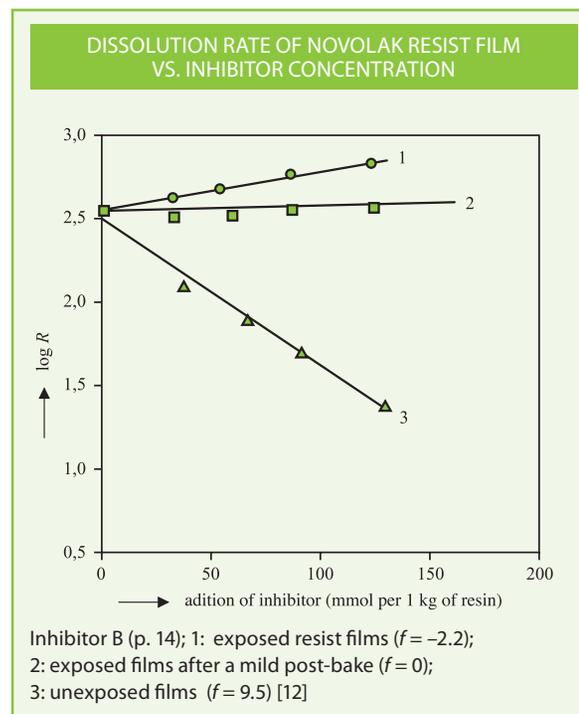
Today, hydrogen-bonded networks are fairly commonplace in biology, but at the time, hydrogen-bonded strings were a novel concept and our model was viewed with skepticism. The question was, are phenolic strings real? To demonstrate their real existence we measured the viscosity of novolak solutions in the presence of inhibitors, (see at left). The inhibitors brought about a strong increase in viscosity. We also observed a corresponding increase in the glass transition temperature of the inhibited dry novolak films (see the next page). Both are convincing indications of filamentary structures.

This brings us now to the last question: what happens when the inhibited novolak film is exposed to radiation? The photosensitive part of the inhibitor is the diazonaphthoquinone function. Its photochemistry is well known since the work of Wolff in 1912 [13]. On absorbing one quantum of radiation the diazonaphthoquinone releases nitrogen and that leads to ring contraction within the molecule and eventually to the formation of a carboxylic acid:





Oskar Sues the inventor of the novolak-diazoquinone technology believed that the dramatic change in the dissolution rate of novolak on irradiation was caused by the appearance of this acid. We were fairly certain that the carboxylic acid is responsible for only a small part of the effect, and we were torturing our minds trying to involve the diazoquinone photoreaction in some other way with the novolak molecule, but it did not make any sense. Then the penny dropped: the Wolff rearrangement is exothermic and it is fast, and it therefore releases a large quantity of heat into the surroundings. By making reasonable assumptions on the reach of the heat wave one finds that the temperature in the vic-



nity of the reacting diazoquinone increases by more than 200 °C, and it is that high temperature which severs the phenolic string from its origin. As soon as this happens, the string disintegrates into a sequence of isolated phenols that are considerably more acidic than they were in the hydrogen-bonded string. Most of the increase in dissolution rate is thus caused by the destruction of the phenolic strings and only a small part is due to the appearance of the carboxylic acid in the Wolff rearrangement.



PRINTING PLATE MADE DIRECTLY FROM A DIGITAL PHOTOGRAPH

We measured the dissolution rate of identical novolak films that contained increasing quantities of the classical inhibitor, repeated these measurements after having irradiated the films to completion, and repeated them a second time after having the films exposed to completion and then post-baked for 30 minutes to 70 °C. Post-baking removed the carboxylic acid and these post-baked films dissolved exactly at the same rate as pure novolak. The meaning of all this is that the destruction of the phenolic strings is a thermal process. The diazonaphthoquinone plays here the role of a local heater that can be switched on by a light beam [14], [15].

■ ■ ■

When we reported our findings at the 1997 SPSE conference in San Jose, most people did not believe us, but a few did and those could see the possibility of replacing the photoreaction of the diazoquinone by an external heat source. Three months after the conference I got a call from my colleagues at the Kodak laboratory in Colorado. When I arrived there they took a digital photograph of the small group in the room and then within a few minutes they produced a printing plate directly from the camera with a computer-controlled infrared laser. A photograph of this printing plate is shown here.

That is when we first realized the great industrial interest in thermal printing plates. Our group at Polytechnic had concentrated on the mechanism of micro-lithography resists. We were aware of the possibility to replace diazoquinone in the standard printing plates by an infrared laser, but we thought, quite wrongly, that the printing industry had all the plates it could wish for. We did not realize that the industry was desperately trying to join the digital age. A Canadian firm, CREO was pioneering this effort. They used a computer-controlled laser to scan the fresh plates and expose them pixel by pixel to a desired pattern. This arrangement is the essence of the “computer-to-plate” printing methodology. It has enormous advantages: it eliminates the necessity of an original optical document and retains the editorial flexibility of the computer right up to the moments of cutting the plate. The advantages of the CtP method are so great that no printing business can ignore them.

All this we did not know. Another piece of information we did not have was the fact that infrared lasers are much cheaper than ultraviolet lasers, and much

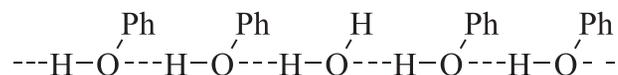
more reliable. That is why Kodak and AGFA tried hard to produce an infrared-sensitive printing plate. Both succeeded in a halfhearted way. Their plates had low image contrast; they were only weakly inhibited. Shortly after the conference Kodak applied for a patent of the basic idea of thermal plates. The legal procedure was well under way when AGFA intervened and challenged the Kodak application in light of our work. There followed a protracted legal battle and in the end the Kodak application was withdrawn. Kodak, AGFA, Fuji and Mitsubishi then filed more modest patents for various inhibitors since the principle of inhibition was now known. These patents were published in 2000 and 2001 and they stand to this day. These inhibitors made the plates into high contrast imaging systems and they allowed the subsequent rapid development of thermal plates into the principal medium of today's printing industry. Thermal printing plates account now for over 80% of all printing plates worldwide. The computer-to-plate method implemented with thermal plates is now a 10 billion dollar business.

With the publication of our 2002 review paper in the *European Polymer Journal* [15] we believed that this chapter was behind us, but something unexpected happened in November 2003. An Englishman, Jonathan Bentley, phoned from Barcelona, Spain, introducing himself as the production manager of IPAGSA, a medium-sized maker of thermal printing plates. He said that

at this point everybody knew that freshly made plates could be stabilized, i. e., made more consistent in their photographic response, by keeping them a day or two at some 60 °C in a controlled atmosphere of 50 to 60% relative humidity. Using this procedure Bentley had the impression that it increased the degree of dissolution-inhibition of the plates. He called to ask whether this rather puzzling observation could possibly be accurate. That day we were on the phone for a long time and at the end of the call we thought that we understood the phenomenon.

The degree of dissolution-inhibition of a plate depends on the average length of the phenolic strings emanating from the inhibitor molecules. Up to this point we had believed that the length of the strings depended on the strength of the inhibitor, but this idea had now to be subtly modified: the lengths of the strings depends exclusively on the positional statistics of the OH groups. In fact, even in the absence of any inhibitor the OH groups of the resin interact and form hydrogen-bonded strings:

The inhibitors don't affect string length but they increase the strength of the hydrogen bond by an electrostatic effect, increasing thereby the acidity of the resin and its degree of dissolution inhibition. When an inhibitor molecule polarizes an OH group its effect extends over all OH groups of the string. The string eventually ends when no other OH group is within reach





making it impossible to form another hydrogen bond. At this point the water treatment intervenes: In the gap between the two afore-mentioned OH groups a water molecule intercalates itself and bridges the gap.

The water molecule can form hydrogen bonds with both OH groups and can thereby increase the length of the phenolic string. As a result the surface layer of the coating which alone contains the intervening water molecules is more strongly inhibited than the bulk of the film, just as Jonathan Bentley had observed. The situation is described in the Journal of Imaging Science and Technology [16].



What remains of all this? It is the realization that I have taken part as a kind of second fiddle in the semiconductor revolution of the twentieth century. The patterning system of the computer chip is an integral part of the technology that has changed our lives. To solve the problems of this system we had to dig deep below the surface of appearances. Trying to understand the cross-linking process of the Kodak Thin Film Resist we discovered the nitrenes, a class of molecules that are now an accepted part of organic chemistry. We clarified the role of metal ions in preventing dye fading. Finally, the molecular mechanism of novolak-diazoquinone resists was cleared up and traced back to the formation of hydrogen-bonded phenolic strings, a thoroughly non-chemical arrangement reminiscent of some recently discovered biological systems. This last observation caused the imaging system of the computer chip to be re-integrated into a rational Weltbild. An unintended

side effect of this was the discovery of highly effective dissolution inhibitors that have made thermal plates what they now are: the most important medium of the printing industry.

One of the things I learned is that a piece of science is not contained entirely in formulas and equations, it also needs to be expressed as a narrative. Language is the medium whereby insight is generated. For the teacher to effectively express the thoughts which lead to insight requires an almost poetic effort. I did not think that our students in Prague were aware of this aspect of our lectures until I received a letter from a former student, now a grandmother, who reminiscing on her university days writes that "...we (the students) listened with bated breath to your presentations taking in the beauty of the language even more than the factual contents..." I take this as a compliment although I should be unhappy about the relegation of contents into second place. I am not unhappy because I know that form and content are inseparably connected and cannot fail to come across together. Looking back I find that teaching physical chemistry to the post-war generation of Czech engineers was probably the most important and the most successful job of my life. Our students were an inspiring audience. The nation was starved of scientific culture and the study of science was taken very seriously. Within a very short time Czech science went through an explosive revival. It was a unique moment in European history.



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Figures 7, 8, 9 and 10 have been reprinted from [17].

