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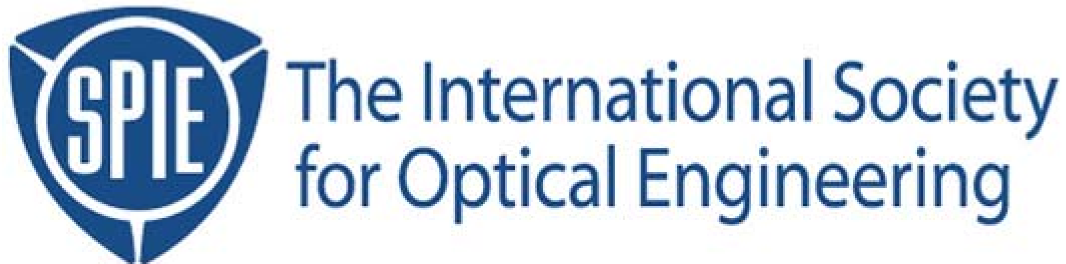

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Photoresist Materials: A Historical Perspective

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Abstract

This paper provides a short history of the development of resist materials. We trace the development of resists from the very beginnings of photography in the early 1800's to today's efforts to develop 193nm resist materials.
keywords: History, photoresist, deep UV, diazoquinone, novolac, bisazide, chemical amplification

Photoresist materials have their earliest origins in the history of photography but most of photoresist development has occurred during the lifetime of our contemporaries. Many of the dinosaurs are still among us! It is appropriate then to discuss these discoveries and some of the clever people who were responsible for them or were involved in the discoveries while they are still here to be interviewed, or at least have the opportunity to review and correct these descriptions of their contributions and those of their colleagues. We have chosen a small subset of the important contributions to this field of materials science for discussion. The specific topics are in some cases clearly "historic" and on the main path of the evolution of resist materials. Others we have chosen because they either had a great influence on our own thinking or they are wonderful examples of ingenuity, and in some cases just because they make a good story! There are several excellent reviews that include aspects of what is discussed in this paper. If the reader is interested in more detail about a particular issue or episode, they are directed to these references

This science started with the work of Joseph Nicéphore Niépce [1a, 1b, 2] who, in about 1826, at the ripe old age of 61 years, managed to make the first "permanent image from nature". This first photograph[1a, 1b, 2] was a sort of projection printed lithographic image. Niépce coated a plate of polished pewter with a thin coating of a tar called bitumen of Judea. Bitumen of Judea is a petroleum residue that has been recovered in chunks from the Dead Sea since the beginnings of recorded history. It is a residue of petroleum after evaporation of most of the volatile fractions. It was used by the Egyptians to embalm mummies. Niépce discovered that this tar is soluble in lavender oil and that high quality coatings could be made from the solution. He used the material to coat a variety of substrates but his best work was done on polished pewter. He coated one such plate and then exposed it to an image of his courtyard that was focused onto the plate with a simple camera (obscura). It was obviously a very fine day in Chalon-sur-Saône, France where Niépce lived since the photograph or "heliograph" as he called it shows both sides of the courtyard to be illuminated. This is because the exposure took 8 hours! Of course, during this time the sun moved. Niépce developed his image with a mixture of oil of lavender and white petroleum. The bitumen of Judea is rendered less soluble upon exposure to sunlight and so development revealed, to a varying degree, the surface of the pewter. It created a relief structure in the remaining organic media.

This first permanent recording of a scene from nature was presented to the Royal Society in 1827 and sent on tour. It disappeared in 1898 and was missing until 1950, when it was discovered in a trunk as a result of the efforts of Helmut and Alison Gernsheim who have worked so hard to chronicle the history of photography[1a,2] The picture is among the Gernsheim collection and now resides at the University of Texas at Austin. It shows a view from Niépce's window. A loft in the Niépce family house is visible on the left. To the right of that structure is a pear tree and in the foreground is the slanting roof of the barn to the right of which is the chimney of the bake house.

You may not be terribly impressed with the fidelity of the first photograph or the resist technology of Niépce, but remember it was the archival nature of the recording that was historic. He managed to record a sort of gray tone image in a digital medium. Besides, he was "projection printing"! If you want to see how well his resist works, please examine a contact print. A particularly fine example is the contact photogravure of Cardinal d'Ambroise, which is also in the Gernsheim Collection at the University of Texas. This beautiful plate was made by contact printing in bitumen of Judea using a vellum drawing of the Cardinal as the mask. The contact print was made by long exposure to the sun, the bitumen was developed and the tin substrate was etched with acid. You can see that Niépce's process worked quite well and that the problem with the photograph was really one of gray scale, lack of resist sensitivity, and the usual problems associated with projection printing. The photogravure or photoengraving of the Cardinal was made by a process that is an exact analogy to the processes used to make semiconductor devices today. So, Niépce was not only the inventor of photography, he was also the inventor of photolithography.

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The image on the left is the famous "Point de vue du Gras", Niépce's first permanent photograph. The image on the right is a photograph of a contact photogravure that Niépce made from a vellum drawing of le Cardinal d'Amboise (The images are reproduced here with the permission of The Gernsheim Collection, Harry Ransom Humanities Research Center, The University of Texas, Austin, Texas.).

The bitumen of Judea resist material favored by Niépce soon gave way to more light sensitive formulations, the most important of which was "dichromated gelatin." The history of dichromated gelatin is complex. It appears that Mungo Ponton, a Scott, was the first to recognize the potential of the dichromate chemistry when, in 1839, he demonstrated the photosensitivity of a system that consisted of paper soaked in ammonium dichromate solution[3]. He did not generate relief images. The following year, Becquerel used this chemistry to produce relief images in a formulation based on starch and dichromate.[3] He is actually credited with coining the term "resist' which he used to describe his formulation. The first really practical resist system was invented by William Henry Fox Talbot, an English gentleman. Fox Talbot used ammonium dichromate in gelatin as his "resist." A solution of gelatin and ammonium dichromate is quite sensitive to light, casts fine films from water and after exposure, can be developed with water.

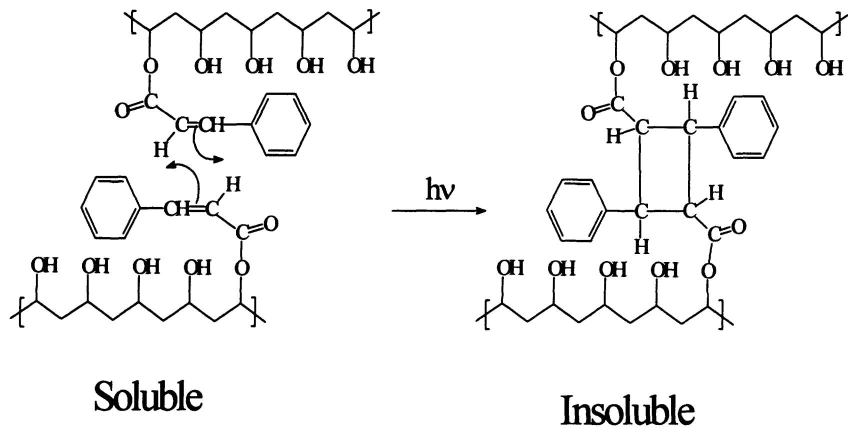
The exposure requirement for "dichromated gelatin" is orders of magnitude less than that required by the bitumen. There is some considerable "art" required to get high quality images with this resist material. Fox Talbot was one of the very best practitioners of this art and he was a processing expert by today's standards. He showed that high quality images could be generated in his resist material and transferred into the surface of stone. He recognized the importance of his discovery and was granted an early British patent (No. 565) in 1852. His work with dichromated gelatin spawned the photolithography industry. The printing of papers and art works proliferated during the 1900's and dichromated gelatin was the medium of choice for recording and transferring images into printing plates made of metal and stone for over 100 years.[4]

Although dichromated gelatin was a tremendously successful material, it had its shortcomings, the first of which was the "Dark Reaction". When the ammonium dichromate and gelatin are mixed, a slow crosslinking reaction begins even in the dark. The coatings are therefore only good for a few hours so the material could not be sold as precoated sheets. The second problem derives from the fact that gelatin is a protein, and as such, is not particularly useful as an etch barrier for strong acids or strong bases. It can be stabilized by "burning-in" the images after development. "Burning-in" involves heating the developed images to 300°F which causes them to char (cook). As you might imagine, the burning-in process does not improve image quality so it is not a wholly satisfactory solution to the etch stability problem.

When William Shockley and his co-workers at Bell Laboratories set out to make the first integrated circuits, it is not surprising that they turned to dichromated gelatin as the imaging material. Frankly, there was little else to choose from at the time. They discovered that their resist material had more than adequate resolution for the task but was not a very effective "resist". It did not serve well as a resist for hydrofluoric acid etching of silicon dioxide, a key step in their microfabrication process. So, the Bell labs team contacted Dr. Kenneth Mees, the Director of the Eastman Kodak Research Laboratory at Rochester, New York, seeking help. Dr. Mees turned to Louis Minsk for a response to this request. Minsk had been thinking for some time about a gelatin replacement with no dark reaction that would allow the sale of "presensitized" lithographic plates. He knew that gelatin was a polymeric material and he surmised that the hardening (tanning) of the dichromated gelatin was caused by light induced cross linking between adjacent chains of the protein. He combed the literature and found the only solid state photodimerization that was known at the time, the dimerization of cinnamic acid[5].

Louis Minsk conceived of a polymer that would, in one way or another, contain cinnamoyl groups hoping that on exposure to light, cinnamoyl groups attached to neighboring chains would dimerize and thereby crosslink the polymer matrix. When he turned these ideas into practice, the result was poly(vinylcinnamate) in which the cinnamoyl groups are attached to the vinyl backbone through ester linkages. Minsk was delighted to find that films of poly(vinylcinnamate) were insolubulized very efficiently upon exposure to the radiation from a mercury lamp. It should be noted that his system does not have a "dark reaction" and so can be stored indefinitely in the absence of light. Minsk had found a fine replacement for dichromated gelatin.

Louis Minsk



The photoreaction of poly(vinylcinnamate)

Poly(vinylcinnamate) was an immediate success. Sharp images with clean edges were easily generated and the images withstood exposure to strong enchants including hydrofluoric acid! Encouraged, Bell Labs started a small pilot production of semiconductor devices but the yield from the process was disappointing: the adhesion of poly(vinylcinnamate) to the glassy surface of the oxidized wafers was not adequate. Eastman Kodak had their first customer complaint.

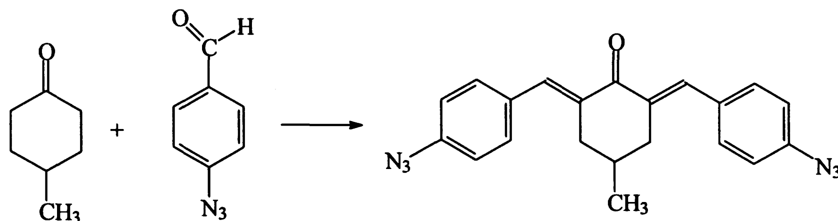
A variety of attempts were made to improve the adhesion of poly(vinylcinnamate) but it soon became clear that a new materials approach was needed. This time Dr. Mees sought the help of Martin Hepher, the Head of the Graphic Arts Department of Kodak Ltd. in Harrow, England. Martin was an experienced printing plate maker who immediately diagnosed the adhesion failure and suggested finding a way to make a light sensitive rubber adhesive. He discussed this problem with his lunch partner, Hans Wagner, an organic chemist. As it happened, a few weeks earlier Hans had read some papers by Professor Horner from Mainz University that described the photochemistry of azido-compounds. Horner had found that the azides undergo photolysis to generate very reactive intermediates that "graft on to almost any substrate." It was Hans' idea to synthesize a few bis-azides and mix them with a low molecular weight rubber of the sort used in the familiar rubber cements that are still sold today. He synthesized some of these materials, formulated them with rubber and

found that they produced excellent images that had perfect adhesion to glass and other surfaces including oxidized silicon wafers.

Martin Hepher, left and Hans Wagner, right. are credited with the invention of Kodak's KTFR resist .

The rubber in the formulation was ultimately replaced by a well defined and cyclized poly(cis-isoprene) of molecular weight of about 150,000. Cyclization is accomplished by treating the synthetic rubber with a Lewis acid. This process reduces the degree of unsaturation in the rubber and stabilizes it against oxygen mediated cross linking thereby improving the shelf life of the resist. The treatment also causes some chain scission, lowering the intrinsic viscosity of the material and allowing formulation of coatings with higher solid content. It also serves to raise the softening point of the polymer from about 30 degrees to nearly 60°C.

Of course, many bis-azides were auditioned for the application, but as is so often the case, the first bis-azide that Hans ever made, 2,6-bis(4-azidobenzal)-4-methylcyclohexanone (below) turned out to be the best! This formulation was sold by Kodak as "Kodak Thin Film Resist", KTFR[6] which was the work horse of the semiconductor industry from 1957 until about 1972 when the dimensions of the features in semiconductor devices reached about 2 micrometers, the limit of the resolution of KTFR.[7]

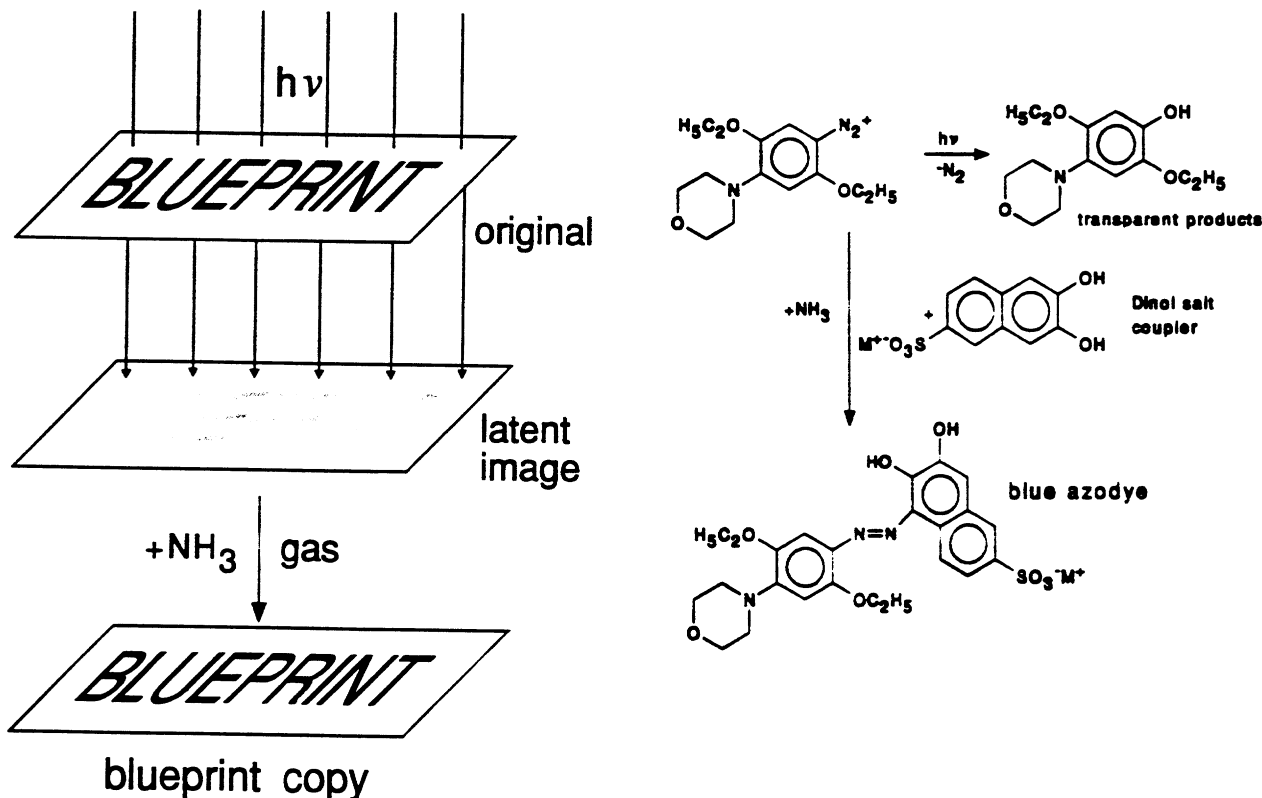


2,6-bis(4-azidobenzal)-4-methylcyclohexanone, Hans Wagner's bis-arylazide that was the basis of Kodak's KTFR resist.

In their quest for a higher resolution. KTFR replacement. lithographers tested many photosensitive coatings. one of which was a positive-tone material from the Kalle company in Wiesbaden. Germany which was used in positive printing plates. This material turned out to be the first diazonaphthoquinone/novolac resist for microlithography.

Kalle had been in the reprographics business for a long time. One of their main lines of business consisted of copying papers for engineering drawings. the original "blueprints". These materials were made up of a diazonium salt coated on paper together with an azocoupling agent. typically a naphthol. In the imaging process. the diazonium salt was imagewise destroyed by the irradiation. so that subsequent treatment of the paper with ammonia led to the formation of a blue azodye only in the unexposed parts. thus yielding a positive-tone image (below).

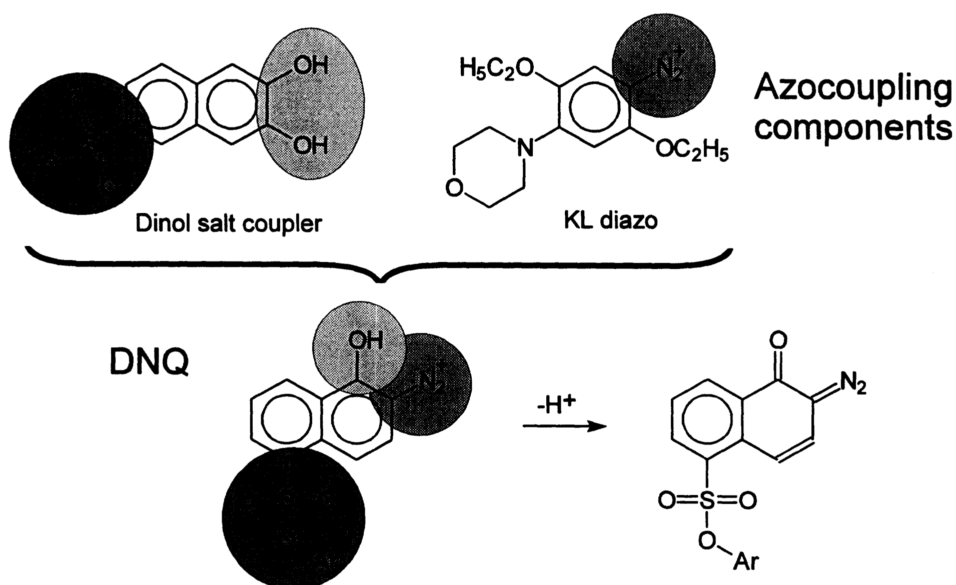
This principle was originally discovered in the beginning of this century by Gustav Kögel (1882-1945). a German monk who had been assigned the task of establishing whether several medieval vellum documents from the library of the monastery of Beuren had been erased and modified (forged)[8]. In his work. he often had to painstakingly copy medieval manuscripts letter-by-letter. a process that made him wish he could transcribe the original documents in some other way. After considerable experimentation. he found that using paper coated with certain diazonium salts, which were synthesized industrially at Kalle AG in Wiesbaden. he could copy the visible illustrations with sunlight. He worked with the Kalle chemists to use this chemistry to create a copying process which led to the diazo or blueprint papers. which were the first products based on light-sensitive organic compounds to be marketed. This basic process is still used today to duplicate engineering drawings as blue prints.



The chemistry of the process for making blueprint papers

The Kalle chemists synthesized a large number of diazonium salts in the following years. In the 1930s and 1940s. under the leadership of Oskar Süß, their work turned to the synthesis of diazonaphthoquinones. Many of the "diazos" made in that time may still be found today. in their original silver-blackened. rubber-stoppered and by now dust-covered flasks, in a dark and secluded cellar at Kalle. It is indicative of the storage stability of pure DNQs that some of them are still functional after all this time!

Oskar Süß, a leading chemist at Kalle (around 1940), and the inventor of DNQ/novolac technology. The name Süß means sweet in German and is often written as Süs or Suss because the English alphabet does not contain either the German umlat u (ü) or the special double s symbol ß.

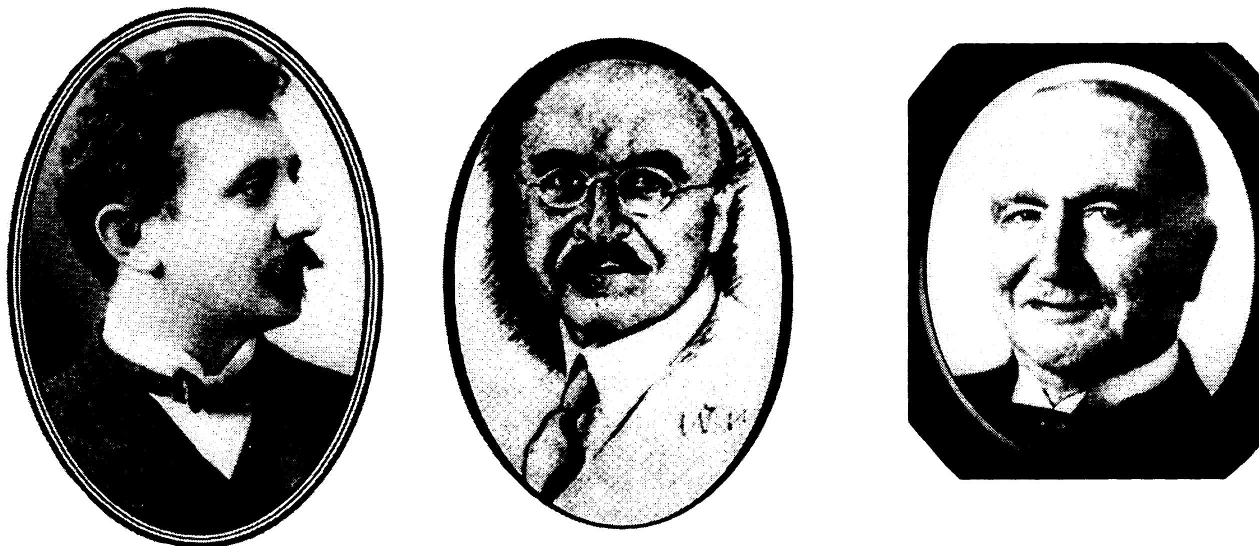


Putative genesis of diazonaphthoquinones from blueprint chemistry

In retrospect, one may conjecture that Süβ intended to combine the two functional groups involved in the azocoupling reaction into one molecule [9]. It is interesting to note that the sulfonic acid group, which later became important as a way of attaching the DNQ moiety to different ballasting groups, and which plays an important role in the dissolution inhibition phenomenon itself, was originally only present in order to enhance color brilliance via formation of the zinc chloride double salt.

The Kalle chemists also experimented with a large number of binders, among which the novolac resins manufactured by Albert Chemical Company, literally across the street from Kalle, were most important. Novolacs are condensates of phenol or cresols and formaldehyde. The term "novolac" is thought to originate from shellac, a natural

thermoplastic extracted from the sticky, resinous secretion of the tiny lac insect, *Laccifer lacca*. Lac or Lak also means lacquer or resin in a number of tongues, such as Dutch, German, or Swedish, prefixed by Latin or Italian novo, meaning new. These "new lacquers" had been discovered independently by Leo Baekeland, a Dutch chemist, and by C.H. Meyer, a private inventor in Aachen, Germany. Both inventions led to separate lines of products; Baekeland found that crosslinking the novolac with hardening agents yielded a thermoset plastic, which he called Bakelite. C.H. Meyer later went to work for Albert in Wiesbaden, Germany, where he found that the initial highly exothermic reaction of formaldehyde with phenol could be moderated by adding collophonium to the reagents. Moreover, the new resin could be mixed with linseed oil, which made it possible to use it as a base for lacquers and paints. This resin was commercialized under the name "Albertol" at about the same time the Bakelite Company in the U.S. and Bakelite GmbH in Germany started production (1910). Albertol was intended as a substitute for kopals, semi-fossil natural resins, which were secreted several thousand years ago by Caesalpinacea, a tree-like papilionaceous plant. The resin, found as lumps embedded in sandy soil, was collected manually in Zanzibar, the Congo or the Philippines, and found use in the manufacture of oil paints. As ersatz kopals, novolacs performed admirably in terms of film hardness and gloss, but since the novolac polycondensation has to be run at an excess of phenols in order to avoid gel formation, they had the unfortunate property of smelling rather strongly even after drying. Also, the color of the film was not stable, turning an initially clear coat through various yellow intermediate stages to a dark brown under the influence of light. The new resins were therefore not exactly a sparkling commercial success until World War I cut Germany off from its source of natural kopal resins. Under war conditions, production at Albert, the only factory in Germany that could provide raw materials needed by the paint industry, stepped up rapidly. The smell problem was finally solved by another Albert chemist, Ludwig Berend, who invented a non-smelling, solid phenol known today as Bisphenol A, and pioneered its use in specialized novolacs.

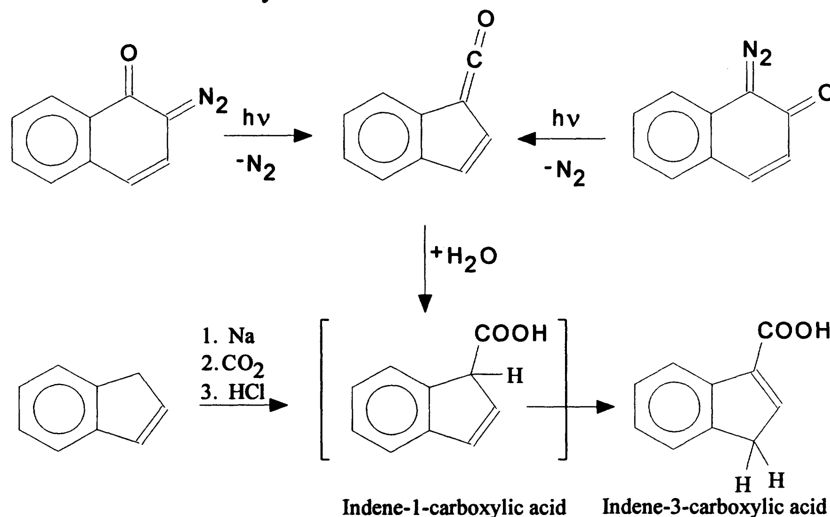


C.H. Meyer, (left) Leo Baekeland, (center) and Ludwig Berend, (right), pioneers in novolac synthesis.

Novolac manufacture then was a fairly crude affair by today's standards,. The reaction was carried out with excess phenol as a solvent, which was removed by heating the resin to over 200 °C. After cooling, the molten or semisolid resin was dropped (dumped) onto the factory floor, where workers broke it up by hand with pickaxes and sledgehammers. Lithographic resins were manufactured under essentially these same conditions at least until the late 1970's.

"...der Arbeiter zerkleinert das Harz von Hand..."; picture of workers breaking up chunks of Albertol novolac resin with pickaxes. From the Albert 125 Year Jubilee brochure

It was to the Albert novolac resins that the Kalle chemists turned in their search for a suitable resin to impart film forming properties and improved development properties to Süβ' lithographic material. However, the mixture of the novolacs with the new DNQ compounds gave only reddish-brown, dull tones in the azocoupling reaction, not the brilliant blue desired for blueprint papers. One day it was observed by chance (some say when cleaning glassware) that a mixture of diazonaphthoquinone-5-sulfonates with a novolac binder was much less soluble in aqueous bases when unexposed than in the exposed state. Oskar Süβ realized what was happening: the intact diazonaphthoquinone sulfonate inhibited the dissolution of the novolac binder, while its photoproducts increased the dissolution rate. Süβ knew that diazoketones undergo a chemical reaction known as the Wolff rearrangement[10], which yields a ketene intermediate, and he was able to substantiate the proposed mechanism by comparing the products formed from 1,2- and 2,1-diazonaphthoquinone sulfonates, which both should yield the same indene carboxylic acid[11].



Oskar Süβ' chemical proof of ketene intermediacy in DNQ photolysis. 2,1- and 1,2-isomers yield the same acid, which is only possible if both reactions proceed via a common intermediate. Süβ' structure assignment was not quite correct: Under the conditions used in microlithography, indene-1-carboxylic acid rearranges to the conjugation-stabilized 3-isomer. That Süβ did indeed have the 3-substituted isomer in hand is shown by the melting point reported in his original notebooks. However, it took over 30 years and the use of modern spectroscopic methods before this error was spotted.

There had been an interest in positive-tone printing plates since they made possible the immediate reproduction of an original without having to create an intermediate photographic negative. The new chemistry was applied to the problem. The first Kalle positive plate, consisting of a DNQ/novolac system on an anodized aluminum sheet, was introduced around 1950 under the Ozatec® tradename, and met with good market success. Its strong point was its high contrast and resolution, its drawback a certain fragility and initially a poorer resistance to wear, compared to the negative-tone systems,. In the USA, these printing plates were supplied by Azoplate, an affiliate of Hoechst AG (by then, Kalle had become a Hoechst AG subsidiary as well).

Lithographic lore has it that the diazonaphthoquinone/novolac resists made their way from the printing to the lithography industry through family ties. At that time, the offices of Azoplate, the American outlet for Kalle printing plates, were situated at Murray Hill, NJ, just across the street from Bell Labs. The father of a technician at Azoplate worked as a technician at Bell Labs. Apparently the father had complained one day about the poor resolution quality of the solvent developed KTFR resist systems then in use at Bell Labs, and the son had boasted of the properties of the Azoplate DNQ/novolac coating; anyway, one day the father took a bottle of the coating solution with him to Bell Labs, and the age of DNQ/novolac resists began [12].

The new materials were marketed by Azoplate under the tradename "AZ Photoresists[13]. The use of DNQ/novolac systems increased rapidly after the introduction of projection lithography. By 1972, the DNQ-based resists had completely supplanted the old workhorse of the semiconductor industry, the cyclized rubber/bisazide negative-tone resist, at least in the high-end applications. The changeover was quick and dramatic. Within one year, projection lithography with DNQ resists had conquered the market, causing turmoil at mask manufacturers and resist vendors alike. The main advantage the DNQ/novolac resists offered was higher resist contrast and absence of swelling during development. Characteristics which have contributed to the lasting success of DNQ/novolac systems are their high etch resistance and the environmentally favorable aqueous base developer. DNQ/novolac resists have been the resists of choice for the 16 KB to 16 MB device generations, making up over 90% of the photoresist world market for over a quarter century. The gradual performance improvements in this resist type, to the point where now a final resolution of a quarter micron can be demonstrated with conventional i-line illumination on high-NA steppers, have been instrumental in prolonging the life of near-UV lithography over a decade beyond what rash prognosticators had forecast for its demise.

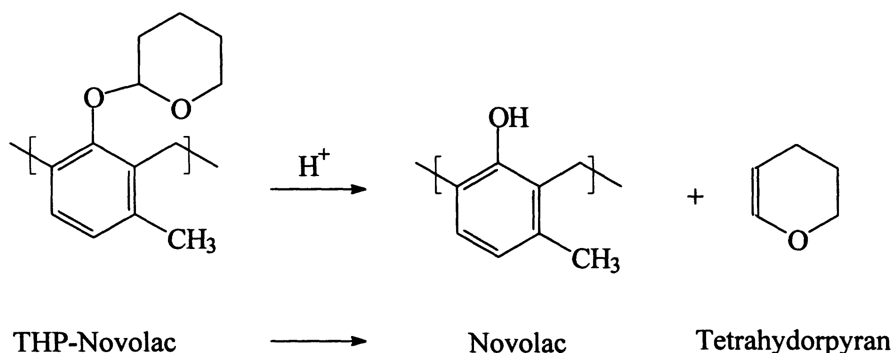
The history of deep UV resists has been well recorded in a number of excellent reviews[1h,14]. The work started with the report that it is possible to print images in Poly(methyl methacrylate) at 254nm[15]. This early report was followed by a number of attempts to develop materials based on acrylates and vinyl ketones. The first commercial deep UV resist, ODUR 10XX was sold by Tokyo Okah Kogyo and is based on poly(methylisopropenyl ketone). Other interesting approaches to the design of deep UV resists were based on 1,3-diacyl-2-diazocompounds[16] and ortho nitro benzylesters of carboxylic acids[17]

These systems were not really useful in conjunction with the Perkin Elmer 500 Micrascan® systems which were the first production worthy exposure tools capable of deep UV projection printing. The Perkin Elmer 500 tools use high pressure mercury lamps in the illuminators and such lamps generate less than 10% as much power in the deep UV (240-260nm or UV-2 mode) as they do in the near UV (350-450nm or UV-4 mode). Consequently, deep UV resists designed to support these tools must be an order of magnitude more radiation sensitive than the diazoquinone novolac resists if the productivity of the tool is to be sustained. Since the quantum efficiency for the conversion of the diazoquinone to acid is approximately 0.3, it is impossible to achieve more than about a threefold improvement in sensitivity based on a traditional resist design. This realization led to the design of "chemically amplified" resists[18,19].

In principle, systems with chemical amplification are those in which the initial radiochemical event produces a catalyst. This catalyst acts on the surrounding matrix to mediate a cascade of reactions or initiate a chain reaction that modifies the properties of the matrix in a way that can be exploited in relief image generation. In such systems, the quantum efficiency for the formation of the species responsible for the differential dissolution rate is the product of the quantum efficiency for the generation of the catalyst and the number of reactions that can be mediated by the catalyst before it is lost or inactivated.

Many imaging systems incorporate chemical amplification. Important examples include the Riston® resist systems used for circuit board manufacturing. These systems are based on free radical mediated crosslinking of acrylated polyols. A single photogenerated radical produces many cross links in these systems. In the early 1980's there were, however, very few

positive tone amplified systems. The person who first designed such a system was G. H. Smith of 3M Company. His early patent [20] describes the basis for acid catalyzed chemically amplified resists. The system he described involves the use of the tetrahydorpyranyl ether of novolac and an onium salt photoacid generator. Unfortunately, this work was never published and it was never exploited by 3M. The work was lost in the patent literature.

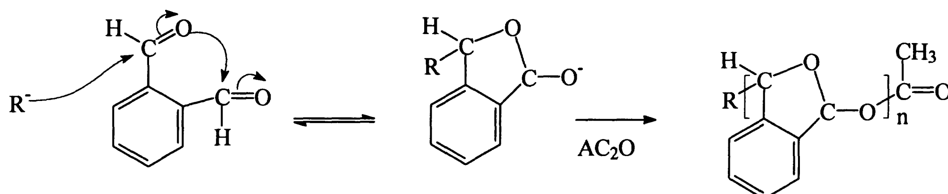


The chemically amplified resist system invented by G.H. Smith of 3M. Photogenerated acid cleaves the lipophylic tetrahydropyranyl ether to generate base soluble phenol.

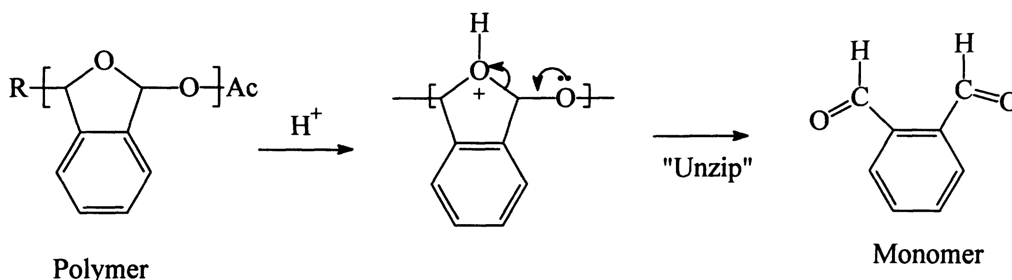
In 1978, Jean Fréchet, then a Professor at the University of Ottawa in Canada, came to spend a sabbatical year at the IBM San Jose Research Center (later the IBM Almaden Research Center) in San Jose, California. Fréchet and Grant Willson of IBM set out to design a chemically amplified deep UV resist. They were unaware of Smith's work and did not discover the Smith patent until filings were made on their work years later. The first approach that they took toward the design of the resist involved use of poly(phthalaldehyde) which undergoes an equilibrium cyclopolymerization and has a ceiling temperature of about -40°C. The idea was to prepare the polymer below its ceiling temperature, then cap it and isolate the intrinsically unstable product. In principle, any photochemical event that can regenerate the anionic chain end above the ceiling temperature should cause spontaneous depolymerization to monomer. They prepared the polymer by anionic polymerization and capped it with acylating agents. It was rendered photosensitive by incorporation of o-nitrobenzaldehyde as a co-monomer. Deep UV exposure of films of the capped copolymer resulted in spontaneous relief image formation, but the resulting images were not developed cleanly to the substrate. It was clear that the desired photochemistry had occurred. The chain had undergone scission and it had unzipped, but only in one direction! Unfortunately, the photochemistry generates an o-nitrosoester capping unit as one chain end. Hence, the unzipping occurs in only one direction.

Hiroshi Ito, who had extensive experience in anionic polymerization, came to the IBM Research Center as a post-doctoral fellow where he worked with Willson and Fréchet. It was Ito who suggested using an anionic mechanism to prepare the poly(phthalaldehyde) and a cationic mechanism to unzip it[18,19]. One needed only to find a neutral species which, upon exposure to deep UV radiation, generated an acid photo-product. The iodonium salts and sulfonium salts that were publicized in the work of James Crivello of General Electric[21] were attractive options in this regard. The very first formulation of poly(phthalaldehyde) with diphenyliodonium hexafluororarsenate provided a positive tone resist with unprecedented photosensitivity. Exposure of films of this formulation to deep UV radiation generated spontaneous relief image formation with doses as low as 2 mJ/cm^2. The depolymerization reaction is exothermic and sufficiently energetic to cause the phthalaldehyde monomer to vaporize. Self developed images were generated at doses two orders of magnitude lower than those required to image typical diazoquinone novolac resists.

These experiments produced an imaging system with very high photosensitivity. Unfortunately, it was not a resist system. The film remaining after exposure and spontaneous development does not resist much of anything. Attempts to examine the images under the scanning electron microsope only served to vaporize the material and contaminate the apertures of the microscope! However, the experiments did show that high sensitivity could be achieved without complete loss of resolution. In principle, a single molecule of acid catalyst could cause depolymerization of the entire coating, or at least one might expect to see a large bias in the imaging process. This was not observed. Sub-micron images were printed on the first attempts. Therefore, Willson, Fréchet and Ito were inspired to look for other systems in which this amplification phenomenon could be demonstrated--hopefully, systems that had greater engineering applicability.



Synthesis of polyphthalaldehyde by anionic initiation and endcapping.



Acid catalyzed scission and unzipping of poly(phthaldehyde)

The first practical system emerged quite quickly. It was based on poly(p-hydroxystyrene), a phenolic polymer that Willson and Fréchet were studying as a potential novolac replacement.[22] They had found that the t-butylcarbonate protected monomer was far more stable that the unprotected p-hydroxystyrene and could be purified and polymerized under controlled conditions. The resulting protected polymer was deprotected by treatment with acid, a process familiar to peptide chemists. Thus, the acid catalysis of the protecting groups was known. It did not require a huge leap to see that the acid catalysis used in the poly(phthalaldehyde) systems was directly applicable to poly(t-bocstyrene) PBOCST.

The PBOCST resist was an instant success. It could be imaged in either positive or negative tone by simply changing the developer, it had dry etch resistance, and it had very high photosensitivity. The first formulations of the material gave better negative tone images than they did positive. The positive tone images seemed to have T-shaped cross sections! Hence, the first commercial application of the resist was in negative tone. The monomer and polymer synthesis were scaled up by Eastman Kodak. Ultimately, many hundreds of pounds of the polymer were produced. It was formulated with triphenylsulfonium hexafluoroantimonate and used in negative tone to print the recessed oxide isolation level of IBM's 1 megabit DRAM.[23] This was the first full scale, commercial application of deep UV photolithography. The process provided a throughput of 100, 5 inch wafers per hour at a critical dimension of 0.9 microns and it produced millions of SIMMs.

Two orders of magnitude improvement in photosensitivity had been found. That allowed realization of the improved resolution that derived from operating at the shorter wavelength. It seemed unlikely even at that time that these improvements could be had "for nothing"! It was immediately assumed that the high sensitivity of these systems must be accompanied by a loss in resolution. Hence, a series of experiments were conducted to test the limits of the resolution in

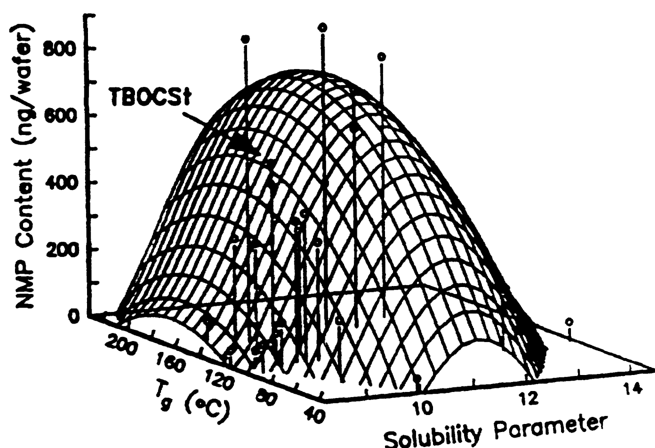
such systems[24]. The experiments involved electron beam exposure of the resist on very thin nitride membranes. It proved possible to print images in both positive and negative tone that were approximately 200 angstroms wide. The formulation had an intrinsic resolution limit that was about the same as PMMA. This was an unexpected result. The price that was paid for the increase in sensitivity seemed not to be in the currency of contrast.

The problem with this system did not really become apparent until it was in full scale manufacturing. The problem manifested itself in the form of fluctuating sensitivity. One minute the process seemed to be stable at 2 mJ/cm^2 and the next minute it required two or three times that dose to print to the mask dimension. Ultimately, the problem was called "aging" because it became clear that a delay between post apply bake and exposure resulted in a variation in sensitivity. It may seem obvious now that "it was something in the air" but at the time, it was certainly not obvious. Ultimately, as a result of very careful and controlled experiments by Scott MacDonald, Bill Hinsberg and Clint Snyder,[25] it was proven that the problem of varying sensitivity, the aging phenomenon, was the result of getting basic substances from the air.

This realization led to two activities that were carried on in parallel. First, carbon filtered enclosures were installed in the production line. Immediately after coating and baking, the wafers were transferred into these controlled environment storage spaces. Filtered air enclosures were also installed to protect the wafers in the input cassette on the exposure tool. Robotic transfer of the wafers from the output of the exposure tool to the post exposure bake plates had already been installed. This was the precursor of the cluster tool arrangements that are common in Deep UV exposure lines today. Once the filtered air system was installed, the process ran with high efficiency. The second activity that was triggered was a study designed to determine whether the process could be stabilized by changing the materials used in the resist formulation.

A system was assembled that allowed wafers to be exposed to a controlled amount of an impurity in air. The impurity studied in the most detail was N-methylpyrrolidone (NMP), since this substance was in highest concentration in the production facility. It should be noted here that highest concentration means only several parts per billion in this context, a level well below any health hazard threshold and near the detection limits. This experimental system was set up with radiolabeled NMP and many polymers were exposed to the contaminated air stream for like periods, then analyzed by scintillation counting to ascertain the extent to which they had absorbed NMP[25]. This set of experiments led to the hypothesis that the amount of absorbed solvent depends on the solubility parameter of the polymer and the contaminant and on the glass transition temperature, Tg, of the polymer[26].

It can be seen from the correlation that resulted that once again, the "best" system had been chosen in the first try. PBOCST is among the very fastest NMP getterers of all polymers tested. The implication is that if one were to change either the Tg or the solubility parameter of the polymer, a significant improvement in environmental sensitivity would be realized. Hiroshi Ito found an elegant way to test this hypothesis. He prepared the 3 and 5-BOCST isomers and compared the environmental stability of the corresponding polymers. The 3-isomer has a significantly lower Tg and is, as predicted, much less affected by exposure to low levels of NMP[27].



This figure shows the correlation between the amount of NMP taken up in a fixed time interval vs. the Tg and the solubility parameter for a set of polymers. Note that the PBOCST (TBOCST) resist material is among the most efficient gettering materials studied. A small change in either Tg or the solubility parameter causes a dramatic reduction in the propensity for the material to absorb NMP from the air. (from reference 26)

Ultimately there have emerged a variety of chemically amplified deep UV resists, all of which have greatly improved environmental stability and excellent

imaging performance. At this time. Deep UV lithography is growing at a pace limited by the availability of exposure tools. This technology has finally arrived.

One important piece of history that is being made now is in the area of 193nm resist materials. Neither the diazoquinone novolac systems nor the deep UV resists will function at this shorter wavelength. As before. the issue is one of optical transparency. Both systems are far too strongly absorbing at 193nm to be useful. Entirely new materials are being developed for this application. Interestingly, the first viable 193nm resist was originally designed for making printed circuit boards by visible laser exposure[28]. Bob Allen, Gregg Wallraff and their co-workers at IBM developed an acrylate analog of the PBOCST resist that was dye sensitized for exposure with visible light (514nm). When the dye was removed. the resist is quite transparent at 193nm and it produces excellent images at this exposure wavelength. The early development of 193 resists had recently been reviewed[29].

So, the history of photoresists materials continues to unfold at an ever increasing pace. Fresh. new inventions become parts of ancient history at a dizzying pace and new generations of scientists and engineers emerge to replace the dinosaurs. This is as it should be!

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