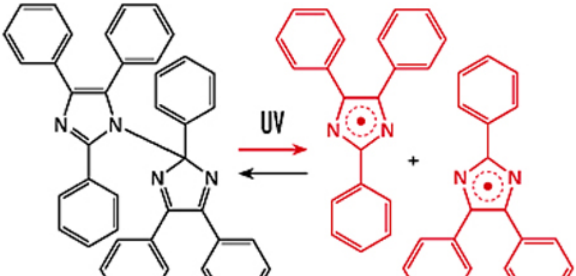
Rolf Dessauer

Photochemistry, History and Commercial Applications of Hexaarylbiimidazoles

All About HABIs



DIMER RADICALS

With Contributions from Bruce L. Booth, David F. Eaton, Thomas C. Felder, Bruce M. Monroe and Peter S. Strilko

A complete review of technology associated with hexaarylbiimidazoles
- includes CD with spreadsheets describing the patents and jouranl references
- includes DVD's containing interviews with inventors of the technology

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Greenville, Delaware, USA

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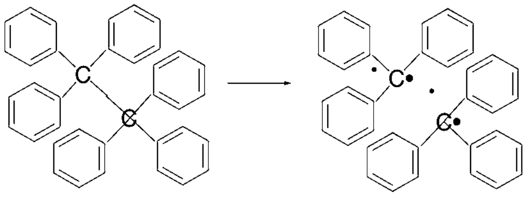
PREFACE

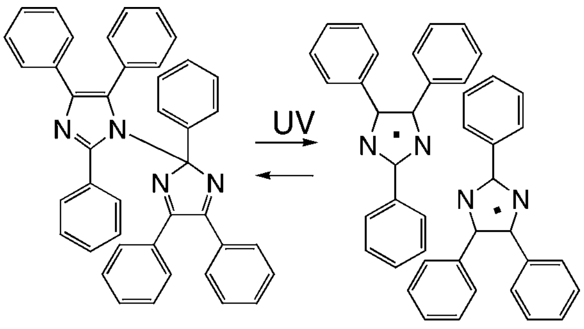
Free radicals are atomic or molecular species with unpaired electrons or an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions. Radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes.

Moses Gomberg, the father of free radical chemistry in 1900 identified the triphenylmethyl radical, the first organic free radical; it was found to be highly reactive with a very short half-life. Due to its reactivity toward oxygen, Gomberg could not isolate the triarylmethyl radical, but a yellow peroxide product. Despite this problem, Gomberg proposed the formation of the triarylmethyl radical, a trivalent carbon species.



Hexaphenylethane Triphenylmethyl radicals

Hexaarylbiimidazoles (HABIs) were discovered in the early 1960s and aroused worldwide interest because of their unusual physical properties: various stimuli such as heat, light and pressure converted these molecules to colored species, which were found to be relatively stable free radicals. Unlike Gomberg's triarylmethyl radicals, triarylimidazolyl radicals were oxygen insensitive. A research program directed at finding commercial applications for these materials at the DuPont Company resulted in the discovery that HABIs were useful as photo-oxidants and photopolymerization initiators. This in turn led to a number of very successful commercial products for the graphic arts, electronics, displays and communication industries.



HEXAARYLBIIMIDAZOLE MIDAZOLYL RADICAL

The development of these products resulted from an extensive study of HABIs as photooxidants in a proof paper product identified as DYLUX®. This was the first evidence that HABIs could be commercially produced to give very stable coated film and paper products. The availability of HABIs then encouraged investigators to apply HABIs as photoinitiators in products such as silver photographic films, holographic films, waveguides, displays, resists, etc.

I was fortunate in being to participate in this development from its inception. L.A. Cescon and I were credited with the invention of the photooxidation systems involving HABIs and leucodyes, and along with R.L. Cohen were able to show that these materials also acted as photopolymerization initiators. Cescon's basic studies with HABIs gave DuPont a uniquely powerful patent position, which precluded competitors from using these unique materials until the 1990s. Alexander Maclachlan and his colleagues in the DuPont Radiation Physics Laboratory undertook elegant mechanistic studies that gave us detailed insight into the reaction paths of HABIs and resulted in a unique imaging system that allowed formation of positive or negative mode images on the same material solely based on the sequence of irradiation with ultraviolet light (color-formation) and visible light (photodeactivation).

Rarely are industrial scientists able to stay with a significant technical development for over 40 years. I was able to do so and possess a unique insight into the historical development as well as the commercial expansion in this area.

It occurred to me that it would be of interest to the scientific community not only to record the development of this technology but also to add some human dimensions. I was able to maintain good records of the growth of this technology, and maintain friendship with many of my surviving collaborators. With modern videotaping technology it is easy to interview those who participated, and this collection contains such interviews which reveal the personal involvement of chemists, managers, engineers, physicists, electricians and even archivists, who have found one of the HABI products useful in recording watermarks of old paper documents.

While HABI chemistry is only a small portion of the field called photochemistry, it illustrates how product development proceeds form invention to production, to marketing and sales. It is also an illustration of how basic research done by scientists at the DuPont Company resulted in entirely new business opportunities.

Frequently, one or two contributors to technologies are rewarded, and the rest forgotten. I would like to acknowledge the excellent work done by so many of my collaborators, with especial gratitude to Drs. George Coraor (1960–1964), L.A. Cescon (1960–1965), R.L. Cohen (1963–1969), C.E. Looney (1961–1978 as consultant), A. Maclachlan (1961–1964), T.M. Sheets (1970–1986), P.S. Strilko (1963–1971), and later, J.V. Caspar (1992–2005), W.F. Mooney (1991–2005) and D.R. Logrando (1985–2004), B.L. Booth (1975–2005) and Dr. Thomas L. Felder (2001–2005), William S. Wartell (1969–1970). The dates inside the parenthesis indicate the period during which these people were involved.

I have included spreadsheets, which list all issued U.S. patents and patent applications up to December 31, 2005. These are organized to list titles, abstracts, first claims, inventors, assignees, U.S. and International Patent Classifications, and relevant dates. Also a spreadsheet lists all the abstracts reported in Chemical Abstracts with similar categories. I have also tried to list in a separate spreadsheet the Registry Numbers of some 200 differently identified materials.

As will be quite obvious to the reader, much of the literature of HABIs is reported in patents. DuPont's commercial success in this field rested initially on the Cescon patent, U.S. 3,784,557, which was significant in preventing competition to manufacture products that contained HABIs. Enclosed on the CD is a PowerPoint presentation of a lecture given at Columbia University and at the Interamerican Photochemical Society, highlighting the extraordinary huge database available in the U.S. Patent and Trademark Office. Finally, enclosed there also is a PowerPoint presentation of a lecture similar to the one I was asked to give when I received the Pedersen Award for my contributions to the development of HABI chemistry at DuPont.

Rolf Dessauer
Jan. 16, 2005

Shown is a sample of exposed DYLUX® 503 Proofpaper, folded to illustrate image formation by sequential exposure on both sides with ultraviolet light through a lithographic negative.

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INTRODUCTION

In thinking about the not-so-long ago past, it is remarkable how rapidly technology has changed since 1960, when hexaarylbiimidazoles were discovered. Consider how important the following have become in our lives: Personal Computers, Laser Printers, Color Television, CDs, Ink Jets, Xerox Copiers, Audio Cassettes, Lap Tops, Liquid Crystal Displays, Boeing 747s, Fax Systems Microprocessors Airbags, Global Position Systems, Video Cassette Recorders, Camcorders, Digital Cameras, DVDs and all the new information handling technologies including the Internet. Some of these products have already completed their life cycles.

Chemical research has changed, too. Forty years ago, chemists spent a great deal of time looking up past references relating to their work. Now, an enormous amount of information is available through computer terminals. Instrumentation has improved greatly. On the other hand, industrial chemists need to spend a lot more time in dealing with environmental issues. Certain solvents that were regularly used, e.g., benzene, have become pariahs.

In an ideal world, industrial scientists make inventions, the research management takes their results to the marketers, who identify applications, the sales forces are enthusiastic in their comments, and the manufacturing groups put their best people on the new programs to assure a good supply of high quality materials that could be sold to customers, who beat a path to the corporate doors.

The world, however, is not ideal. The DuPont Company, which supported an enormous amount of excellent research in this field during the 1960s and later, had many dedicated scientists, managers, marketers, sales people and manufacturing groups. Many times, the interactions between these groups were positive, but often they were not.

A personal opinion (RD): Most people have dedication and want to do good work, but the process of successful innovation requires more than that. In the author's opinion, it requires an enormous amount of personal involvement, time away from families, career risks, good timing, development of interpersonal relationships, and perhaps most importantly: Luck! Regrettably, Risk-Aversion wins out nearly every time. It is not the author's goal to deprecate other people's contribution, but rather a desire to present an honest assessment of the ups and downs of seeing an innovative program reach its ultimate success.

I was fortunate to be associated with a technology from its beginning on. Few industrial scientists have the opportunity to initiate programs, expand them, see them develop to useful products and live long enough to reflect on it all, and ultimately to be given credit for it all. I was also fortunate to be associated with a great many very talented people, without whom none of this would have happened.

Regrettably, most people do not have time to reflect on such developments long after they started, though there are exceptions. Dr. John H. Dessauer, who was director of research at

Haloid, later known as the Xerox Corporation wrote a witty book, *My Years with Xerox, the Billions Nobody Wanted* [1]. He was fortunate that not only was he given credit for much of what made Xerox an enormously successful corporation, but he was also rewarded famously, presumably because he was given stock in the fledgling corporation. He however also was the co-author of a scholarly book about electrophotography [2]. Long after he died I discovered that his family and mine were remotely related on my mother's side! I had always hoped to write a similarly successful book about the development of HABI (hexaarylbiimidazole) chemistry. I am delighted that Elsevier agreed to publish this book.

Some years ago, BASF Corporation ran TV commercials in which they pointed out that they are not known "*for the products that you buy, but rather, for how what they make the products you buy better*". HABI compounds fit into this category; they are not sold as products, but have played an important role in making certain products possible or better. For students of photochemistry, they might well serve as an outline of how two fields, printout images and photopolymerization were developed. Key to this is that HABI compounds possess a level of stability and versatility that has excited scientists for over 40 years.

An index of the importance of a chemical compound can be seen from how often it is cited in the literature, or more importantly, for industrial scientists, how often it is mentioned in patents. As can be seen in a later chapter, HABIs have seen a considerable growth in usage, with no sign of abatement, so many years after they were first described in the literature.

Why and how did this book come about? In 2001, I was awarded the DuPont's Pedersen Medal for my part in the development of this chemistry into successful commercial products. I was the 28th chemist in the history of the Company to be so honored. Later I also was the second recipient of the Plambeck Award, for contributions to photopolymer technology.

Prof. Douglas C. Neckers of Bowling Green State University (Ohio) subsequently invited me to give a lecture about this work, and remarked that he had not appreciated how much there was to this chemistry—DuPont scientists had published little in journals but there were hundreds of issued U.S. patents, which academic scientists have less concern with. After my presentation, Prof. Neckers suggested that I expand my experiences into a series of lectures, which I presented to his students in October 2003. He then remarked that it might be a good idea to consider writing a chapter for Advances in Chemistry, Vol. XXVIII [3], of which he was the editor. I agreed to write a chapter about DYLUX® Instant Access Imaging Materials, but was originally limited to 50 pages. Even though I grossly overran my allotted space, I concluded that it was not possible to condense some 1000 odd patents and a 1000 odd Chemical Abstracts references into so little space. To be honest, I had not even realized that there was so much literature out there.

As I was able in 2002 to look at patents electronically, it became immediately apparent that there was a huge amount of information, which regrettably no one had ever been assigned by DuPont to catalog. I had always maintained a file of Chemical Abstracts references, and dutifully entered these into loose-leaf books, and later, into computer spreadsheets. Until 2004 DuPont's Lavoisier Library had maintained a complete set of Chemical Abstracts, as well as an excellent collection of pertinent journals. Importantly, they had available the various indices, such as authors, formulas, chemical compounds, registry numbers, etc. While keeping up with everything was tedious work, it was still stimulating, perhaps especially because one could delight in seeing something keep growing over and over. Regrettably, a policy to save space resulted in the discarding of much of this, especially the Chemical Abstracts. The argument was presented that much of this information was available electronically, and would be easier to obtain via a computer terminal. This is indeed true, except that it is very difficult to find access to the necessary indices, and as some of my colleagues observed, the serendipitous joy of looking at what else is presented on the pages, above and below the reference of interest. Unfortunately, the disappearance of these references has made my task a lot more difficult, and hence this work cannot be as complete as might have been possible otherwise.

In the 1960s, the American comedian Bob Newhart became famous for a number of monologues in which he made fun of the difficulties of innovators in getting their inventions accepted. Thus, Abner Doubleday, the inventor of baseball was urged to find a game in which he would not need 18 men who would play at the same time, etc. I often thought that if Henry Ford had suggested that a major company would want to manufacture and sell automobiles containing an internal combustion engine, he would be advised that only fools would trust their lives to a device which would necessitate the passenger to sit on top of 20 gallons of a highly combustible fuel. And besides that, have someone build roads and highways before we go into mass production of automobiles! Thomas A. Edison would have been confronted with marketing types, who were worried about the possible lawsuits resulting when it turned out that artificial light would adversely affect people's eyesight, and besides that, all those wires that would be required to make incandescent light bulbs function, would constitute tripping hazards, and if they were concealed in the walls, they would certain be a fire hazard in case of short-circuits. Not to overlook the religious Right, who would have insisted that had the Lord wanted us to read at night, he would have turned the solar system around!

Well, we too experienced a certain amount of skepticism and opposition when we tried to find some uses for biimidazoles. Our thought, that we had invented a novel printout system was denigrated because the initial images were cyan, not black, and that the light fastness of the generated images was inadequate. Additionally, the photosensitivity was low compared to commercial imaging systems. It was difficult to persuade conservative managers that we should seek to combine the properties that we found attractive, and identify applications, where the instant access of the images, made without further processing, offered the potential customer advantages, and that there were applications where a cyan image was acceptable, and where contact exposures with a dedicated light source, would still offer the user something that he could not otherwise obtain.

It was thus a challenge to find applications for novel materials that had not been available to others. And if was necessary at an early stage, even in the golden 1960s, to propose applications that would be hugely successful, and justify the considerable expense in developing a novel technology. Fortunately, we were able to persist. There were some managers and visionaries who encouraged this development. And in time, the world found that our early work was significant.

A historical note! After World War II, DuPont was a leading manufacturer of dyes and pigments. Management was interested in identifying opportunities for the facilities used to manufacture these materials, frequently in batch processes, involving fairly complex chemistry. Where would be the future for colored materials in markets other than textiles or paper, which were then the principal applications for dyes and pigments?

During the 1960s, the world turned to plastics, which needed to be colored. Architectural structures were designed to be colored, and the coloration of anodized aluminum was considered an opportunity. As color-television became accepted, print media also turned color. This lead to new inks, printing products and methods of controlling the printing processes.

Automobiles were becoming more glass-enclosed, and the concept of making photochromic automotive windows that would darken in intense sunlight intrigued many. Buildings too had larger glass surfaces and modification of these was also considered. It was with these opportunities in mind, that a small effort toward the study of photochromic materials was undertaken in the Organic Chemicals Department of DuPont.

In the immediate post-war period, the U.S. Department of Defense was interested in photochromic materials for potential eye-protection in case of atomic or nuclear explosions. Considerably interest in this field was demonstrated at a government-sponsored symposium at Duke University in 1961. At that time, much research had been undertaken in a number of laboratories, Schoenberg in Egypt had developed novel spiropyrans. National Cash Register Company studied the use of these materials in data storage and data manipulation products.

Scouting at DuPont continued for a brief period, during which Dr. Lawrence A. Cescon saw a reference to Japanese work that described photochromic behavior of certain oxidation products of triarylimidazoles (lophines). Soon other laboratories in Japan, Germany, England and the United States embarked on studies of these materials.

In retrospect, it seems that most of the scientists who were active in this field were physical chemists or physicists. DuPont's Organic Chemicals Department had few physical chemists, but many synthetic chemists, and it was thus not long before several were turned loose to prepare many derivatives that would provide improved performance over those described by the Japanese workers. This was indeed fortunate, because the DuPont group made certain derivatives, containing 2-*o*-substitution in both imidazolyl rings. In time, these would become the HABIs of commercial utility.

It also became evident before long, that the application of HABIs in photochromic windows would be a daunting challenge. We noted that the radicals were excellent hydrogen abstractors, and we could not develop media that lacked abstractable hydrogen. Additionally, the color of the generated free radicals was weak, compared to "real" dyes, with extinction coefficients under 10,000, compared to dyes, such as Crystal Violet, with over 140,000.

Fortunately, the availability of a stable colorless (leucodye) derivative of a Crystal Violet like dye, allowed us to observe that we could generate intense color by combining the HABI with this. A photon would generate intense color. Over the next years, the DuPont group expanded on this finding, and developed a printout technology, which was on the edge of commercialization.

Even though there was an intense effort at DuPont's Photo Products Department to investigate the use of photopolymerization as a means of generating new products for the imaging industries, there seemed little interest there in critically evaluating the HABIs as initiators. We had submitted samples to our colleagues at the Parlin Photo Products Department, but their initial tests were unsuccessful, i.e., they could not effect polymerization of polyacrylates with HABIs.

In time, the group trying to develop novel printout systems was challenged to find materials with high photosensitivity, i.e., imaging speed, in order to broaden the application range. Even though no one really knew what new applications would be available for higher speed printout systems, we, like all scientists in this field suspected that higher speed would get into new areas of application. Could we ever attain the speed of silver photographic materials? Probably not. Still there were opportunities where a controlled exposure system employing printout that required no treatments subsequent to color formation. Cescon and Bob Cohen and the author one afternoon agreed that if we could increase the relatively slow deactivation speed of the system then under intense study, we might actually design a system in which much higher speed could be realized. This did indeed work, and in the end, we had found that under certain conditions, HABI acted as photopolymerization initiators.

In a parallel development, a group under Vaughn Chambers also observed that HABIs could indeed act as photopolymerization initiators.

The printout system that was developed at Orchem in time became a successful product as a monochrome proofing system. In 1971, many in the group, but not the author, were transferred to the Photo Products Department, but soon were given unrelated assignments. The Photo Products Department, however, enthusiastically employed HABIs in a wide range of photopolymerization applications, and developed a series of hugely successful products.

In 1974 the Cescon patent, which claimed a range of HABIS, including the important 2-*o*-phenyl substituted HABIs issued, and for nearly two decades, the DuPont Company had a virtual monopoly on this technology. Over 500 U.S. patents alone issued to DuPont! In 1975 the author found that certain HABIs, not covered by the Cescon patent offered some significant advantages, and this, as well as Sheets' derivative patent, issued in 1981 and 1986, respectively, extended the patent estate for DYLUX® proofing products.

In the early 1990s Fuji Photo Film Co., Ltd. combined microencapsulation technology, with some of the teachings of earlier DuPont patents, and developed a new proofing system. Eastman Kodak discovered that certain HABIs could be employed in silver photographic systems, where they helped in the bleachout of antihalation dyes.

In time, DuPont appeared to lose interest in photopolymerization technology, and from the 1990s onward, fewer and fewer DuPont patents were filed in this field. Since then, applications for HABI chemistry as shown in issued U.S. patents became an almost exclusive province for Asian companies, primarily Fuji Photo Film and Mitsubishi Chemical Co. The latter, under the leadership of T. Urano has published extensively in journals. The technology has returned to Asia, from whence it came!

Still, it seems worthwhile to make an effort to try to put all this together in a single publication, which traces both the historical, technical and commercial developments. It occurred to me that some of this could be presented as written documents, as PowerPoint presentations, electronic spreadsheets and video clips, in which some of the people involved could record their experiences. The Chemical Heritage Foundation of Philadelphia, PA, kindly supplied a small grant to further this latter activity and this is hereby acknowledged.

I have relied on some of my former associates and colleagues to help me with this, and their contributions are elsewhere recorded. I have frequently included pertinent patent references to illustrate the specific chemistry involved, and to allow the reader to follow up the details; this avoids any possible conflicts about disclosing proprietary information.

It is the overall goal of this book to show how technology can be advanced by dedication, imagination and perseverance. May others have the same opportunity and may the world progress as a result!

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[1] J.H. Dessauer, My Years with Xerox: The Billions Nobody Wanted. Mass Market Paperback, 1971.
[2] J.H. Dessauer and H.E. Clark, Xerography and Related Products. Focal Press, New York, London, 1965.
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2

INDUSTRIAL PHOTOCHEMISTRY FROM THE 1960s ONWARD

In 1960, when HABI research was initiated at the DuPont Company, a number of imaging technologies were investigated in laboratories all over the world. This included improvements in the maturing diazo chemistry, organic free radical chemistry, electrophotography, photochromism, dry silver technology, etc. The military and space programs in the United States supported some of these efforts, with the expectation that in time, dry processing systems would be developed.

D.F. Eaton, in a paper presented in 2005, concluded that "photopolymer science and technology are now over fifty years of age. In the time since the initial invention of photo-induced crosslinking and polymerization, major innovations have occurred in several industries as a direct result of the application of the new technology. In several cases, it can be unequivocally stated that the adoption of photopolymer technology in those industries has revolutionized the way the industry approaches manufacturing its products. In addition to lowering costs of manufacture and saving time and labor, the manufacturing processes in general have become safer for workers' health and more environmentally benign as a result of these changes."

In order to appreciate the importance of hexaarylbiimidazoles as components of imaging systems, it is desirable to review the state of the art at that time. In the end, the advantages of HABIs were that they provided chemists with a means of manufacturing very stable precoated films, obviating the need for wet coating of surfaces prior to exposure, that the chemistry permit sensitization, inhibition, stabilization, exposure systems that could give rise to positive or negative-working systems and the elimination of processing equipment in several applications, Now, some 45 years later, HABI chemistry is included in ever increasing numbers of issued patents, and with a constantly expanding body of knowledge in the non-patent literature.

2.1 WHAT WERE THE AIMS OF THESE NEW TECHNOLOGIES?

Silver-based imaging systems offer speed, reliability, enormous versatility, such as color, high resolution, image stability, under some circumstances, almost instant accessibility (Polaroid Systems), etc. However, they inevitably require processing, and though some systems have been invented that eliminate the need for wet processing, the combination of properties that the end product represents do not inevitably assure this technology to be universally accepted. Hence, an effort to look at alternate technologies.

During the early part of the 20th century, scientists began to develop optical systems that employed ultraviolet (UV) light of wavelengths between 200 and 400 nm; wavelengths sufficiently potent for rupture of chemical bonds.

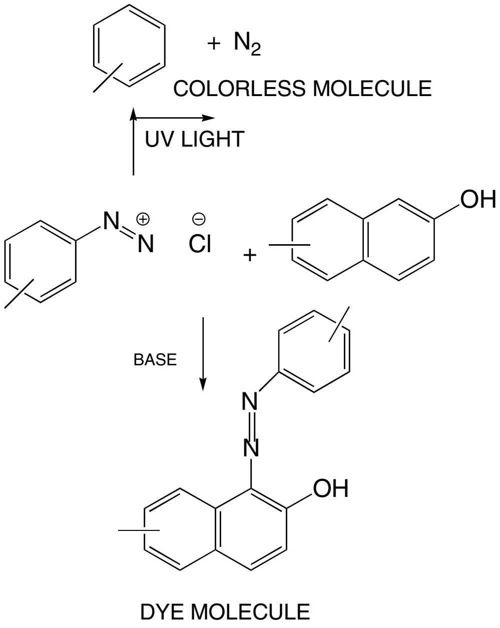
Before World War II, considerable effort was expended on the study and application of diazonium compounds, which were used in a variety of applications. In order to understand the state of the art, and what improvements came subsequently, it is worthwhile briefly to review what diazonium chemistry represented.

M.S. Dinaburg's extensive tome, *Photosensitive Compounds* (The Focal Press, London and New York) was originally published in Russia in 1964. It and Jaromir Kosar's *Light-Sensitive Systems* (John Wiley & Sons, New York) published in 1965 serve as excellent reviews of the status of industrial photochemistry up to that time.

The origins of diazo chemistry, as described by Kosar noted that azobenzene was discovered by Mitscherlich in 1834, and Griess in Germany began his research in this field in 1858 by synthesizing 4,6-dinitrobenzene-2,1-diazo oxide. Griess called this new class of compounds "diazo compounds".

Early diazo compounds were found to be very unstable, even to the point of explosive decomposition and, in the dry state had to be handled very carefully and only in small quantities. More stable diazo compounds are prepared from derivatives of *o*-aminophenols, *o*-aminonaphthols, etc. The tendency to decompose spontaneously depends on structural variations.

Comparatively stable diazo compounds were obtained by forming double salts with metal halides or nonmetallic fluorides. Zinc chloride, cadmium chloride, stannic chloride, or fluorboric acid were widely used. Fluorsulfonates and hydroborofluorides also have been suggested. The double salts are usually prepared by adding chlorides of heavy metals to the solution of diazo compound, and consist of a metal halo-anion complex and a diazonium cation with the general formula. The photochemistry of diazo materials is illustrated below. Note the process is positive working; the exposed areas do not form color (Scheme 2.1).



Scheme 2.1.

If the diazonium compound is struck by light, it will form a non-reactive product. If an unexposed aromatic diazonium compound reacts with a naphthol, under basic conditions to produce a dye molecule.

Inherently, the stability issues limited the applications for diazo chemistry and when better systems were developed, the diazo materials lost out. Still, they were relatively inexpensive, and saw enormous applicability up to the point where electrophotography offered a higher quality imaging system, which did not depend on a precoated paper and exposure to ammonia vapor.

One appealing aspect about diazochemistry was that the huge number of aromatic amines and phenolic compounds available to chemists allowed an almost unlimited possibility of creating novel compounds suited to specific needs.

The light to which the diazotype material is exposed must supply sufficient energy to destroy all the diazo in the non-image areas, and is thus completely responsible for the formation of the image. In silver halide layers, an average grain, consisting of roughly one and one half billion molecules, requires between one and two hundred quanta to become developable. Subsequent development reduces all the silver present in the grain and thus each absorbed quantum has affected millions of silver atoms. For this reason, in spite of the fact that the quantum efficiency in the diazotype process is of the same order as in silver halide photography, the energy required to form a “diazo image” is roughly a million times as great as that necessary to obtain an image in the silver halide process.

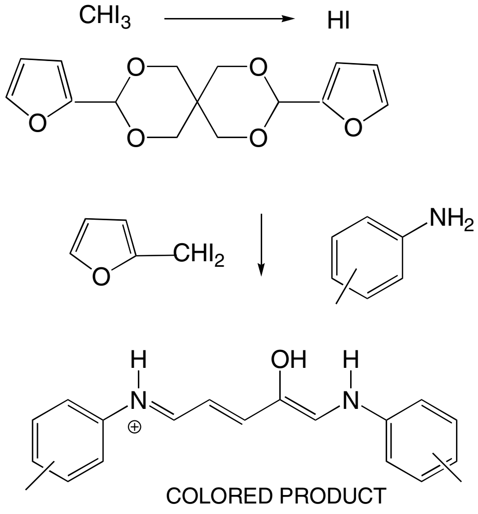
Because of these high-energy requirements, powerful light sources rich in ultraviolet rays must be used for exposing material sensitized with diazonium compounds. The most suitable and most generally used are high-pressure mercury-vapor lamps. The light output of these lamps is limited to very narrow bands—mercury lines having peaks at 3132, 3342, 3660, 4047, 4358, 5461, and 5770 Å. For standard diazotype papers, 3660 and 4047 Å are the most important, and have a destructive effect on the majority of benzene and naphthalene diazonium salts. Super-fast diazotype papers can be exposed with tungsten or fluorescent lamps, which emit a low percentage of ultraviolet light but more violet and blue.

Major technical achievements in imaging technology in the latter part of the 20th century were made by combining chemistry and engineering approaches.

2.2 VESICULAR FILM

A diazotype process, which does not depend on the formation of color, but rather on the liberation of nitrogen resulting from photolysis of diazonium compounds, is the vesicular process. Here, diazonium compounds are dispersed in a specific medium and on heating, under carefully controlled conditions, the nitrogen gas expands to form microscopic vesicles that as a result of a diffraction process scatter light. In a projection mode, good visual contrast is realized. Although prints on special papers could be prepared, this phase of the vesicular process did not gain wide acceptance. On the other hand, large quantities of such films, with the trade name KALVAR® were used as a medium for copying microfilm. The US Government used to keep all the records for the Social Security Administration until computer data storage became preferred. This technology has almost disappeared, although in the 1960s, it was very popular, and considerable research to improve it was then undertaken.

3M’s Thermofax technology, the first major copying development in post World War II United States preceded xerography, but was limited to reflex copying on a relatively flimsy



Scheme 2.2. S.D. Warren Fotoproof^{TM}.

paper base, and never achieved archival quality. It depended on the formation of an image pattern by locally causing a thermally initiated reaction to form a colored pattern. It was a step forward over the slow process of photocopying journals, namely photomicrographing documents, and then printing these out on silver based papers, requiring wet development. Here, a copier emitting infrared energy caused reflection of heat of the imaged areas, turning the paper dark. A severe limitation was that copying was essentially limited to black images as colored images did not absorb/reflect infrared energy/heat.

S.D. Warren's Fotoproof^{TM} (Scheme 2.2), which involved free radical chemistry, required a thermal after-treatment, which necessitated installation of venting equipment to remove toxic off-gases. Here photolysis of iodoform liberated an acid that reacted with furfurylidene derivatives to give an intermediate that reacted with an aromatic amines to give a highly conjugated colored product [J.A. Mattor et al., U.S. 3,413,121 (1968)]. At one time, this product, which gave excellent brown black images with high resolution was considered a serious competitor to DuPont's DYLUX® proof paper, but environmental considerations caused the product to be withdrawn.

In the realm of imaging technology, which relied primarily on novel photochemistry, a major effort was launched by Horizons Research Incorporated, a small research-oriented company in Cleveland, Ohio, who had received considerable help from the Department of Defense in their effort to develop photosensitive printout materials that could be used in reconnaissance photography; duplication of silver film, as well as direct capture.

This technology was described in many U.S. patents. Inherently, the concept was to employ halocarbons, e.g. bromoform, and aromatic amines and achieve complexes that could be thermally developed. The technology was designed to maximize the photosensitivity of the system, but inevitably had stability problems which limited its utility.

Their most recent patent issue dealing with printout images was

U.S. 4,187,105. Photosensitive Image Forming Composition Containing At Least One Substituted Bis-Diaryl Vinylidene Compound And/Or At Least One Substituted Bis-Diaryl Imine Compound. Wainer, Eugene and Lewis; James, M. February 5, 1980. A non-silver photosensitive image forming composition containing at least one substituted bis-diaryl vinylidene compound

> and/or at least one substituted bis-diaryl imine compound and tetraiodoethylene in a dried photosensitive layer thickness not exceeding 3 microns in layer thickness, the nature of the substitution being such that substantially any high extinction absorption peak or combination of high extinction absorption peaks is available from a family of compositions covering the range of 350 to 900 nm in wavelength, said composition being placed on a transparent or reflective substrate fitted with a compatible adhesive for the photosensitive layer not more than 0.5 micron in thickness and containing specialized stabilizers to permit precision information to be read out by a focused laser beam in either the transmissive or reflective mode, said precision information being placed on the film by exposure to precision light patterns followed by development and fixing with solvents and/or with heat not exceeding 115°C. Appl. May 23, 1978.

Electrophotography came into its own when the Haloid Corporation acquired technology that was being developed at the Battelle Institute, based on an invention by Chester Carlson. Initial interest was in using electrophotography in the manufacture of printing plates, but in time, the copying field was pursued—very successfully. Xerography made office copy and later home copy accessible, and also generated enormous business for suppliers of paper.

The development of the personal computer later created another huge market for imaging technology. Early printers involved dot-matrix printing technology. In the 1980s, laser printers began to appear on the market but were initially very expensive, but by 2005 had become quite inexpensive. The enormous success in the development of ink-jet technology made color printing in low volumes a considerable opportunity for the home-office environment. It would have been difficult to predict in the mid 1980s that most users would be able to print high quality colored documents for a reasonable prince—at home. The author attended a number of Diamond Conferences in the 1980s, which dealt with the generation of colored documents, and few of the attendees anticipated that the complex ink jet technology would become a household consumable! Again, the combination of chemistry and engineering made a difference.

Interest at that time was also devoted to photopolymerization, as a means to developing non-silver imaging systems. Here the driving force was application areas that were emerging, such as photoresists, color-proofing, lithographic plates, etc. Initially this involved dichromated colloids.

Published in 1989, Arnost Reiser's *Photoreactive Polymers: The Science and Technology of Resists* (John Wiley & Sons Inc.) gave a comprehensive introduction to the theory and applications of resists. It discussed applications of polymers in the imaging industry, especially printing, and the fabrication of solid-state electronic devices. Reiser listed the following photopolymerization initiators as of interest in the field at the time: anthraquinone, anthraquinone sulfate, benzophenone, benzoyl peroxide, 2-chlorothioxanthone, 2,2′-diethoacetophenone (DEAP), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2-ethylanthraquinone, 2-isopropylthioxanthenone, 2-*tert*-butylanthraquinone, acetophenones, alkyl ethers of benzoin, 2,2′-azobis(butyronitrile) (AIBN), azocompounds, benzylketals, benzoin derivatives, biimidazoles, derivatives of acetophenone, 3-ketocoumarins, ketoxime esters of benzoins, peroxides, 2-phenylacetophenone, thioxanthones, triazines. Since that time, progress has been made with cationic polymerization, which permits polymerization of different monomers in an oxygen environment.

The large number of classes of compounds that are listed by Reiser illustrates how much activity has been expended in this field. Many of these are no longer being employed. It is interesting that a large number of recently issued U.S. patents contain references to various HABI photoinitiators, as shown in Figure 2.1, because of the unique performance characteristics that are described throughout this book.

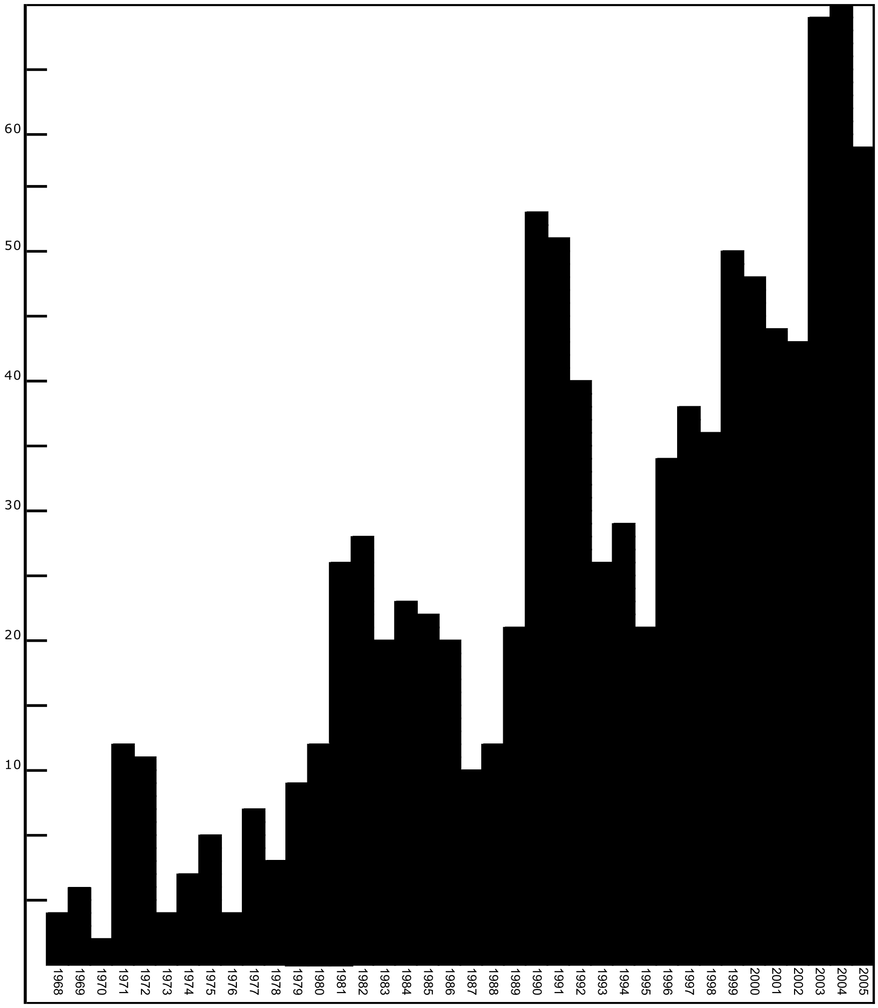


Figure 2.1. Growth of U.S. patents containing HABIs issued through 12/6/05.

The advances in photochemistry have also resulted in development of new business opportunities that could not have been considered before the development of modern photochemistry.

3

THE DUPONT COMPANY FROM 1960 TO 2000

The development and application of hexaarylbiimidazoles (HABIs) was the result of exploratory research at several DuPont Company laboratories starting in the 1960s. More than 200 scientists and engineers worked over a period of over 40 years to explore the chemistry, application and market development for HABI-based products.

Without the basic research on hexaarylbiimidazoles at DuPont, which established that these compounds could be valuable photooxidants, it is likely that they would have remained interesting laboratory curiosities, and probably be forgotten. Remarkably, with all the possible analogs or homologs of hexaarylbiimidazoles, no similarly effective materials were ever reported in the patent literature, in spite of probably intense efforts by other companies. DuPont's contribution to industrial photochemistry should therefore be acknowledged.

In the opinion of the author, the approach to industrial research exemplified in this field would not be possible in today's R&D climate. It is therefore appropriate to examine the conditions that made this work DuPont Company possible during this period.

Science and Corporate Strategy, DuPont R&D, 1902–1980, by Hounshell and Smith, 1988, Cambridge University Press (1989), examines the company's effort in the development of new products in considerable detail. Regrettably, in the photochemical field, the authors depended only on A.B. Cohen for insights into the product development, and not much on chemistry that made for novel commercially important products. Considering that HABI-based products were by 1988 covered by over 250 U.S. patents, with a sizable expense in filing and maintaining the patent estate, this is quite remarkable. Regrettably, the book did not go into the separate chemistries that would have given more insight into the contributions of Cohen's coworkers and their unique contribution that hexaarylbiimidazoles made in the success of photopolymer products, which were developed under A.B. Cohen's guidance! So, a new analysis might be worthwhile, if only to go into specifics!

The structure of the DuPont Company in the early 1960s played a unique role in the development of HABI technology. It was a far different organization then it became in later years. The DuPont of the 1960s willingly supported far-reaching research programs, with the expectation of some day reaping rewards. The 21st century companies speak endlessly of near term profitability, stockholder value and diversity—but not of long-range research of the kind that ultimately earns billions of dollars.

In the early 1960s, the DuPont Company was organized into a number of operating departments, which served different industries, and had manufacturing sites all over the United States. Sometimes, the products and markets of one department overlapped or conflicted with those of another. At the time, e.g., there were separate departments that manufactured and sold pigments; thus the Pigments Department served the plastics industry and the Organic Chemicals Department which manufactured dyes and some pigments, served the paper and textile industries. Both departments manufactured the pigment copper phthalocyanines, albeit, by different processes. Naturally there were some conflicts. However, researchers had relatively good access to the research of other departments.

There were several "non-operating" departments, such as the Central Research Department, the Engineering Department, the Development Department, etc., who were designed to offer special assistance to the "operating" departments, and in some cases, e.g., Central Research, received funding from the operating departments in order to carry out more esoteric research or to assist in supplying skilled specialists to assist in various developments.

Officially, there were line organizations, and in principle, the uppermost management communicated among the different departments and facilitated developments. More realistically, so many scientists in Wilmington had friends or acquaintance from college or graduate schools, social or religious associations, that inevitable one could learn a lot of what was going on by simply talking to one's friends. The HABI program too benefited from this type of interactions; Al Maclachlan, whose brilliant conception of the photofix concept for HABI/leucodye chemistry became acquainted with the author as a result of a cocktail party. Donald Johnson, who was a driving force for the company's 'aca'—automatic clinical analyzer heard about DYLUX® and arranged to have analysis results printed out on DYLUX® paper. Don was the author's neighbor at the time! A lesson to be learned: it is beneficial to be associated with people that have different backgrounds, but who can be helpful anyway.

The various operating departments differed in size, profitability and philosophy. The Organic Chemicals Department in the early 1960s was among the most profitable, manufacturing and selling tetraethyl lead and FREON® propellants. The dye business was not looked on as a business for the future, and therefore research in this area was primarily supported by the Textile Fibers Department, which required new dyes in order to color new fibers, such as DACRON®, ORLON®, LYCRA®, etc., as these were developed. In some cases, operating departments, which were developing new product lines, depended on other operating departments to manufacture intermediates, additives, etc., in order to avoid alerting the market of their new interests. In some areas, the operating departments worked as though they were separate companies.

At the end of World War II, the Allies thoroughly microfilmed all research and manufacturing reports of the then defunct I.G. Farben, the huge German chemical company. These were issued as BIOS and FIAT reports. The downside of this for some of the major chemical manufacturers was that anyone had access to excellent manufacturing processes without having to do the necessary research. As a result, the dye and pigment businesses for DuPont and similar companies became less profitable. Some efforts were made to scout for new application areas or new materials, and the proposed entry into the photochromic chemical opportunity was a result of that.

In addition to research laboratories at various plant sites, DuPont had a research center, the DuPont Experimental Station, at which by 1958 all departments had representation. Again, here was an effort made to have scientists more effectively communicate with each other and form associations that would facilitate their work. In the case of HABI research, this was a definite asset. An engineer, V.F. Hansen had prevailed upon the company's upper management to set up an institute for the study of radiation chemistry, called the Radiation Physics Laboratory (RPL) and was able to staff it with a number of outstanding scientists and engineers. RPL was equipped with expensive specialized equipment to assist in this field. As it turned out, the type of radiation studied there was of little commercial interest, but when RPL saw an opportunity to assist the company in investigating the effect of UV-radiation, their programs and reputations grew greatly. RPL lasted until around 1966, when it was absorbed into the Central Research Department and lost the autonomy that allowed scientists to do exploratory science. But by then, they had immeasurably contributed to the development and understanding of HABI chemistry.

In the mid-1960s the Company embarked on the venture concept, which is described elsewhere. It was not particularly effective.

The Organic Chemicals Department suffered of course when two of its principal products, tetraethyl lead and fluorocarbons were withdrawn from the market. In time, the Department was united with the Industrial Chemicals Department and Pigments Department, into the Chemicals, Dyes and Pigments Department. In time, different parts of the dyes business were sold to former competitors, and dye research ceased by 1980.

By then the production of DYLUX® had been assigned to the Photo Products Department, but the manufacture of leucodyes and photoinitiators and other critical ingredients remained there. This was still a lucrative business, but in time, Photo Products Department decided that the economics of DYLUX® and photopolymer products would be improved if vendors that had no similar large overhead, as did a DuPont operating department, supplied the ingredients. Of course, in the end that meant that there no longer were incentives for the Chemicals, Dyes and Pigments Department to undertake research in this area.

It is the author’s contention that improved new products result from the availability of custom-designed components, with adequate patent protection, rather than simple combinations of the least expensive ingredients. However, at a time of short-range objectives, this is a difficult viewpoint to defend.

The Photo Products Department was riding on the success of several of its HABI-based programs, and appeared to expand into new business areas. By 1978, the autocratic Dr. Robert Upson had retired as director of research, and his successor, Dr. C.F. Arrington left in 1983. Under new leadership, new areas of interest were pursued.

These included expansion into electronic materials, optical components, such as waveguides, holography, and a novel proofing approach, using xeroprinting.

New partnerships in various business areas were established, and a relationship with the Xerox Corporation was undertaken to pursue liquid toner chemistry for applications to the graphic arts and office supply markets. DX Imaging, a partnership between these companies was formed, and made good progress until financial difficulties; resulting from over-expansion forced its termination. In time, there was retrenchment in research and marketing. The former Photo Products Department became I-Technologies and in time was reorganized into specific business areas such as electronic products and printing & publishing. Except for a brief effort to develop a near-infrared version of DYLUX®, no significant further development of HABI chemistry was undertaken!

4

THE BEGINNINGS OF HABI CHEMISTRY AT DUPONT

The discovery of a photochromic oxidation product of triphenylimidazole by Hayashi and Maeda [1] stimulated wide interest in hexaarylbiimidazole dimers. At that time, an effort to develop photochromic windows and related products was underway at the DuPont Company under the direction of Dr. George R. Coraor, and Hayashi and Maeda's work was examined and duplicated. Fortunately, this interest attracted several synthetic chemists who were eager to develop related compounds with superior properties, what ever these might be. Obviously, for the proposed application, there was a need for a large number of reversals, different colors from the purple of the parent radical and different speeds of photolysis and recombination.

Cescon and Dessauer synthesized over 100 different biimidazoles, with the able assistance of Robert Jenkins and Edward Urban.

The photolysis of the various dimers was carried out in a wide range of different solvent and solid media, including the conventional solvents as well as binders such as polyvinyl butyral, cellulose acetate butyrates, etc. Inevitably the photochromic behavior was relatively brief due to the fatigue reaction, which we found to give rise to the parent triarylimidazoles.

Cescon proposed the synthesis of a photochromic polymer, based on the imidazole derived from terephthaldehyde. A bisimidazole was indeed synthesized, but on oxidation gave a deep blue color, which was identified as the monomeric oxidation product.

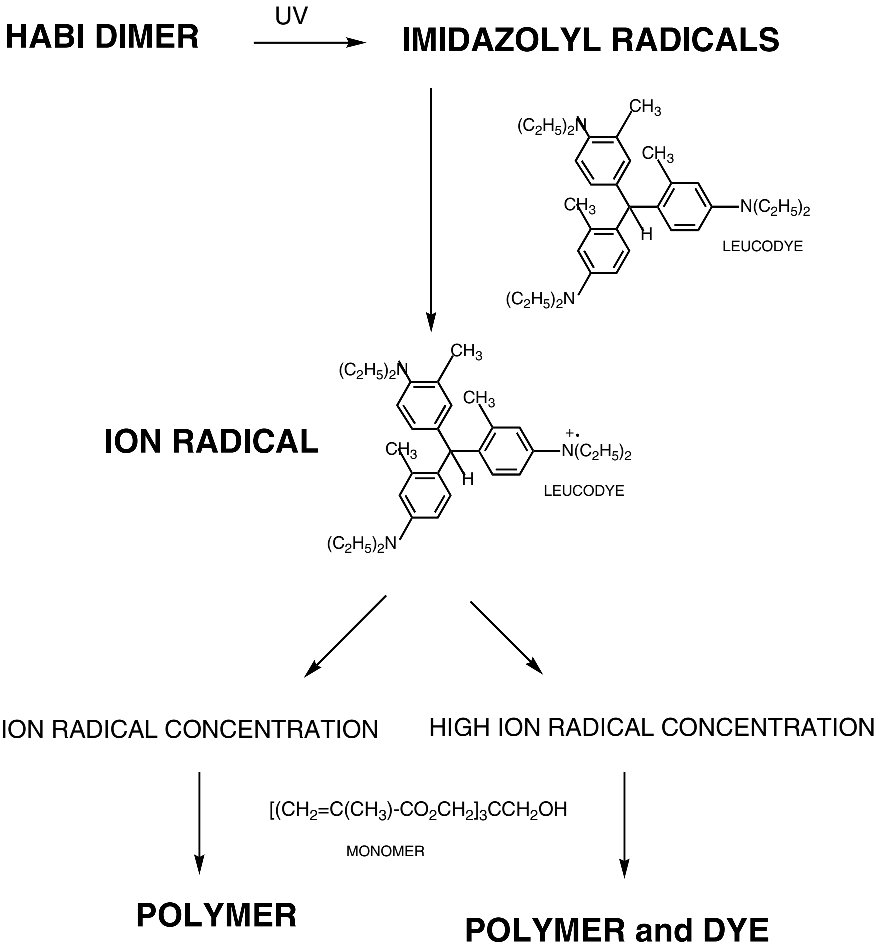
Dessauer was aware of a very stable triphenylmethane leucodye tris(*p*-*N*,*N*-diethylamino-*o*-tolyl)methane, which had been considered for a commercial product for the important spirit duplicating market. It was found by Cescon and Dessauer that the leucodye salt could be easily oxidized to give a deep blue color in solution, and a deep blue print when the exposure was carried out on filter paper that had been immersed in a solution of these components.

This then led to the investigation of the chemistry, rather than the physical properties of biimidazoles more broadly. Some of these studies were described in an article published in the Journal of Organic Chemistry in 1971 [2]. In time, interest in photochromism per se waned, and the reactions effected by efficient photooxidants became the primary objective of our research.

The expectation that HABIs could be used to initiate photo-polymerization was not realized for a long time. Photopolymerization was a field in which the DuPont Photo Products Department was active and we assumed that they would assist us in expanding the HABI chemistry in that area. Some cursory work—adding HABIs to vinyl acrylate monomers gave no evidence of photopolymerization.

Inevitably, increasing the sensitivity of color formation reaction became a goal of the program. Almost any application other than contact exposure was beyond the scope of this imaging technology. A research effort was made to develop a chain reaction during the color-forming step, but it was not successful. Another approach was needed.

As we began to formulate coatings with improved performance, we found that plasticizers played an important role in the effective color formation. Many different chemicals acted as plasticizers for the HABI/leucodye salt/cellulose acetate butyrate system; preferred were carbowaxes, phenolethers, sulfonamides, etc. The idea occurred to use a monomer as plasticizer, and to polymerize it in areas where color-formation was undesired. It was assumed that the polymerization was "fast", and that this approach might actually yield an increase in sensitivity, albeit in the "fixing" mode. We drew upon the work at Photo Products and selected then common photo-initiators, seeking such that would absorb in the visible wavelength range beyond the absorption of the HABIs. This work gave some indications of success. In order to assess the exact role of the visible sensitizer, an anthraquinone derivative, Cescon and Cohen omitted the latter and found that the polymerization still occurred [2]. In time they postulated that the earlier failure to effect polymerization when HABI was added to pure monomer came as a result of the omission of a co-initiator; in the HABI/leucodye salt/monomer system, the leucodye salt, an amine derivative, acted as coinitiator! Maclachlan postulated a mechanism for this as follows (Scheme 4.1).

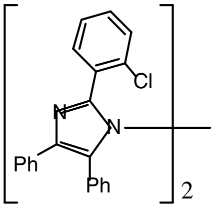


Scheme 4.1.

The ion radical formed by oxidation of the leucodye (by a triarylimidazolyl radical) can act as polymerization initiator (at low concentrations) or will disproportionate into dye and a colorless species and also act as polymerization initiator at high concentrations.

During the early 1960s, the Photo Products Department R&D division under Dr. V.C. Chambers, worked on a photopolymer based copying system, requested information about how black images could be made using the leuco-dye chemistry. This copy system was based on ingenious chemistry, in which a partially photopolymerized coating, containing a triphenylmethane dye, was thermally transferred onto a piece of plain paper. Chambers employed neutral shade forming leucodyes and HABIs, and his technician observed that the polymerization reaction, which was an imagewise reflex exposure, had higher speed as a result of the presence of the HABIs and leucodyes.

> **68:17429y. Photopolymerizable compositions and elements.** E. I. DuPont de Nemours & Co. (by Glen A. Thommes, Peter Walker, and Vaughan C. Chambers, Jr.). **Fr. 1,481,819** (Cl. C08f, G 03c), May 19, 1967; U.S. Appl. June 3, 1965, and March 4, 1966; 14 pp. Photopolymerizable compns. for use in the production of color images contain $\geqslant 1$ nongaseous ethylenically unsatd. monomer capable of undergoing free-radical addn. polymn. with chain propagation; $\geqslant 1$ free radical-producing electron donor, e.g. a leuco dye, a tertiary amine a mixt. of a leuco dye and a photoreducible substance, or a mixt. of a leuco dye and triethanolamine; a 2,4,5-triphenylimidazole dimer; and optionally an energy-transfer substance to improve the sensitivity and (or) an additive to eliminate or reduce the induction period. The compn. is dispersed in a thermoplastic binder and contains various dyes, pigments, thermographic compns., and chromogens, and is coated on any appropriate support. Thus, a standard soln. was prepd. from a 10% cellulose acetate butyrate (20.5% Ac, 26% butyryl, 2.5% OH, and viscosity 9.0–13.5 poises) soln. in Me_2CO 110.0, a 10% cellulose acetate (39.4% Ac 55% HOAc, viscosity 130–82 poises) soln. in Me_2CO 32,5, pentaerythritol triacrylate 30.0, poly(ethylene oxide) (mol. wt. 400) (in 14 ml. MeOH) 2.0 g., and Me_2CO to make 200.0 g. The standard soln. 5.0, the **I** dimer 2-(o-chlorophenyl)-4,5-diphenyl-imidazole 80,



I

> and CBr_4, 100−mg. were mixed, coated as a 0.15-mm. layer on a 0.03-mm. poly(ethylene terephthalate) support precoated with a layer of vinylidene chloride–Me acrylate–itaconic acid terpolymer, and dried for 30 min. at ambient temp. to give a 0.03-mm. film. The laminated product was contacted with an original, exposed to a photoflood lamp at a distance of 40.6 cm. for 30 sec., delaminated, developed, and passed with a receptor paper through 2 rollers heated at 125° to transfer the under exposed zones from the photopolymer layer to the receptor sheet thereby forming a well-contrasted and defined image on the paper.

The reason Chambers and Cescon et al. had success and Dr. M. Burg in earlier work did not was that our system included a tertiary amine, which acted as co-initiator. HABIs themselves indeed do not initiate polymerization, but do so most effectively, when paired with a co-initiator.

Even though the project was terminated because office copy arena became exclusively an opportunity for electrophotography, DuPont applied for a patent, which was the first of many that identified HABIs as photopolymerization initiators. Other aspects of HABI chemistry were investigated at DuPont's Central Research Department by Nacci and Pazos.

Abele and Grossa et al. in DuPont's Neu Isenburg laboratory investigated a phototackification system in which exposed areas of coatings became sticky relative to the unexposed areas. A possible rationalization was that one component of the system, a dihydropyridine derivative became an oil as a result of oxidation, and that this oil promoted adhesion. However, this can be called to question, because we also found that if the ratio of HABI to DHP was significantly altered, the opposite behavior resulted, i.e., the exposed areas became non-tacky relative to the exposed areas. While considerable effort was expended in developing this chemistry, no mechanistic studies were ever reported.

REFERENCES

[1] T. Hayashi and K. Maeda, J. Chem. Phys. 32, 1568 (1960); Bull. Chem. Soc. Japan 33, 566 (1960).

[2] L.A. Cescon, G.R. Coraor, R. Dessauer, E.F. Silversmith, A.S. Deutsch, H.L. Jackson, A. Maclachlan, K. Marcali, E.M. Potrafke, R.E. Read and E.J. Urban, Journal of Organic Chemistry 36 (16), 2262, 2267 (1971) (received February 12, 1970) and subsequent publications.

5

THE HABI LITERATURE

There is a considerable amount of literature dealing with hexaarylbiimidazoles (HABIs). References to these compounds were found in over 130 journal articles as shown in Chemical Abstracts (CA); there were about 1050 patents abstracted in Chemical Abstracts. Most significantly, a very large database exists in the issued (over 1200) and applied patents (over 500) that can be examined on the U.S. Patent and Trade Mark Office website. Several chapters in survey books describe various aspects of HABI Chemistry.

R. Dessauer wrote a chapter "The Invention of DYLUX® Instant Access Imaging Materials and the Development of HABI Chemistry—A Personal History" in *Advances in Photochemistry*, Vol. 28, editors D.C. Neckers, T. Wolff and W.J. Jenks, Wiley-Interscience (2005).

R. Dessauer and C.E. Looney described some aspects of HABI chemistry in a chapter "Low Amplification Imaging Systems" in *Imaging Processes and Materials Neblette's Eighth Edition*, Van Nostrand-Reinhard (1989).

Koko Maeda, contributed a chapter "Hexaarylbiimidazolyl: The Choice Initiator for Photopolymers, History of Synthesis and Investigations of Photochemical Properties", and Yi Lin, Andong Liu, Alexander D. Trifunac and Vadim Krongauz'c chapter "Investigation of Electron Transfer Between Hexaarylbiimidazoles and a Visible Sensitizer" in Krongauz and Trifunac's *Processes in Photo-Reactive Polymers*, Chapman Hall (1995).

None of these treat the impact that HABI chemistry had on industrial photochemistry, nor do they go into much detail into the patent aspects of HABI based photooxidation, photopolymerization, phototackification and other reactions. Also of necessity, they do not go into much detail about the different compositions that are involved in making this chemistry happen.

This author has had a considerable interest in the importance of patents in industrial chemistry. Why this is so is perhaps well illustrated in a later chapter.

During the 1960s, when this research started, examination of issued patents was a tedious process. The search rooms of the U.S. Patent and Trademark Office (USPTO), first in the Commerce Department Building in Washington, DC, and later, in the more modern facilities in Crystal City, VA, contained thousands of pigeon-holed shelves, in which copies of the various issued patents were stacked by U.S. patent classification numbers. A patent would appear in each assortment in which its classification number was found. One could then purchase a copy and study it at one's leisure, although there usually was a delay in obtaining copies, as the high speed electrostatic copiers were only gradually introduced. Still, our group was able to build up a small library of patents dealing with the pertinent areas: photochromism and leucodyes. It was not much later, that patents could be scanned electronically, making the

Table 5.1. HABI compounds listed by USPTO as of 7/20/06

Search term	Hits
Arylimidazole	133
Biimidazole	432
Bisimidazole	186
DYLUX	26
HABI	186
Hexaarylbiimidazole	243
Hexaarylbisimidazole	64
Imidazole dimer	215
Imidazolyl dimer	114
Lophine dimer	68
Tetraphenyl biimidazole	50
Tetraphenylbiimidazole	129
Tetraphenyl bisimidazole	9
Triarylimidazolyl	183
Triarylimidazole	331

whole search process incredibly easier. Still, only patents dating from 1976 onward could be so studied.

The author had collected the patent literature diligently, and developed a spreadsheet.[1] Regrettably, long chemical names are generally not searchable in the USPTO database. As a matter of fact, it is amazing how many synonyms for HABIs must be searched, I have identified the terms that were searched, and the number of hits (Table 5.1).

It is color coded by company. The various columns identify patent number, international classification, assignee, inventors, issue date, filing date, U.S. classification number, abstract and 1st claim. While this is undoubtedly only a partial picture of the scope of the technology, it does summarize over 10,000 pages of examined technology. There is a wealth of information here that can be easily searched and one can distinguish between the different important applications of HABI chemistry:

- Leucodye oxidation—printout systems
- Phototackification—add-on toning
- Photobleaching in silver systems
- Photopolymerization.

One can easily delineate patents dealing with different application areas, e.g. photoresists, printing plates, proofing systems, etc.

A similar spreadsheet was developed for filed and issued U.S. patent applications, going back to January 1, 2004. Some of these applications have by now been issued as issued patents.

An effort to design a similar spreadsheet to cover the Chemical Abstracts literature has also been made.

It is the author's experience that many chemists are not too familiar with the ease which such information can be gathered. Here is a simple primer.

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[1] The spreadsheet containing all the different patents is attached on a CD.

The U.S. Patent and Trademark Office is located in Crystal City, VA, and more importantly on the Internet as USPTO.com. It offers an extensive database, which can be accessed easily. One can search by inventors, assignees, titles, keywords, patent classes, etc. It is updated every Tuesday.

Unfortunately, only patents issued after 1975 can be searched electronically and searching for chemical structures is complicated by the fact that trivial names abound. In compiling a database for HABIs, I found different patents which identified lophine dimers, imidazole dimers, imidazolyl dimers, DYLUX®, bisimidazoles, biimidazoles, etc.

When one goes to USPTO.com, one finds (Fig. 5.1).

One click later (Fig. 5.2).

One needs to fill in **Fields** from the following list:

All fields
Abstract
Patent Number
Application Serial Number
Assignee Name
Assignee State
International Classification
Primary Examiner
Inventor Name
Inventor State
Government Interest
PCT Information
Reissue Data
Referenced By
Other References
Description/Specification

Title
Issue Date
Application Date
Application Type
Assignee City
Assignee Country
Current US Classification
Assistant Examiner
Inventor City
Inventor Country
Attorney or Agent
Foreign Priority
Related US App. Data
Foreign References
Claim(s)

Thus, one click later (Figs. 5.3, 5.4).

One can click for all patents, but only those issued after 1976 can be searched electronically. Earlier patents exist as PDF documents.

Some patents use trivial names to identify critical components.

It is also useful to consider using the Current U.S. Classification system to search for related materials. These numbers are somewhat arbitrary, but can be better understood by searching the USPTO web site. For example, all photochemical patents dealing with microencapsulation are in class 430/138; those involving infrared exposure are 430/944, and those using laser beams 430/945. Class 281.1 contains radiation sensitive composition comprising ethylenically unsaturated compounds.

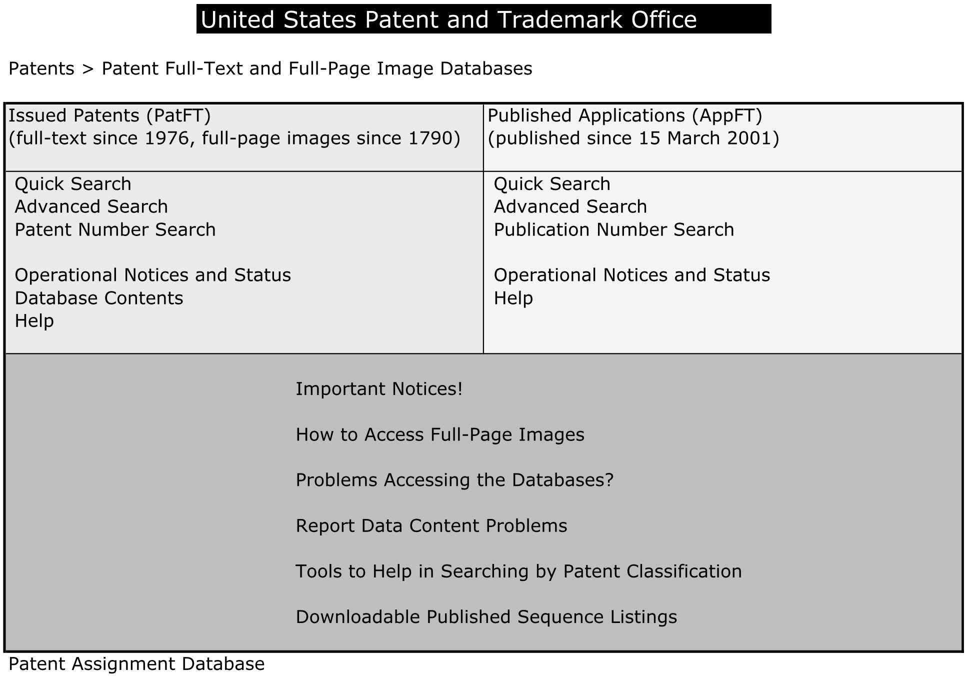

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Figure 5.1.

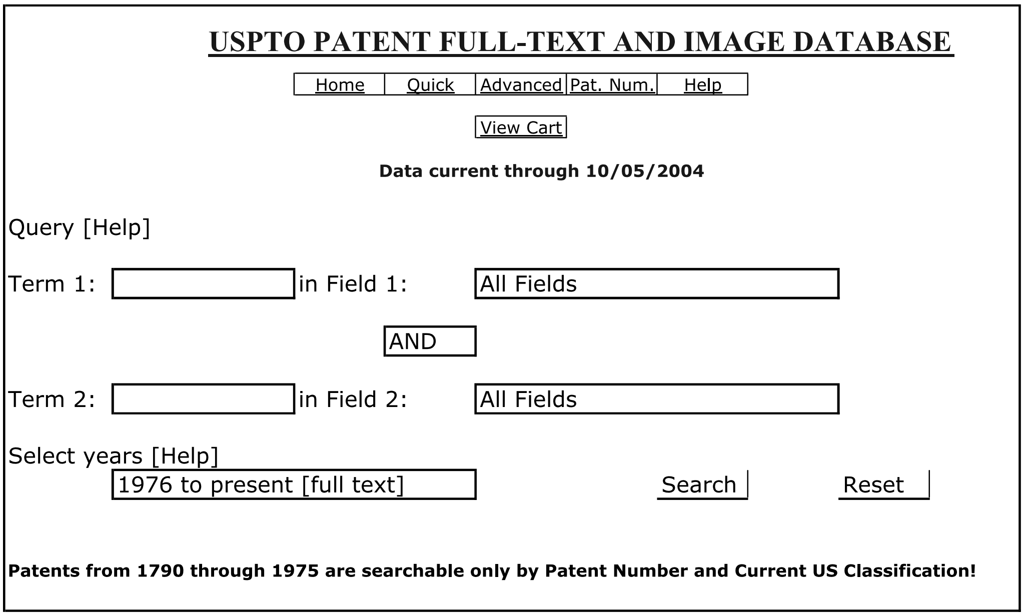

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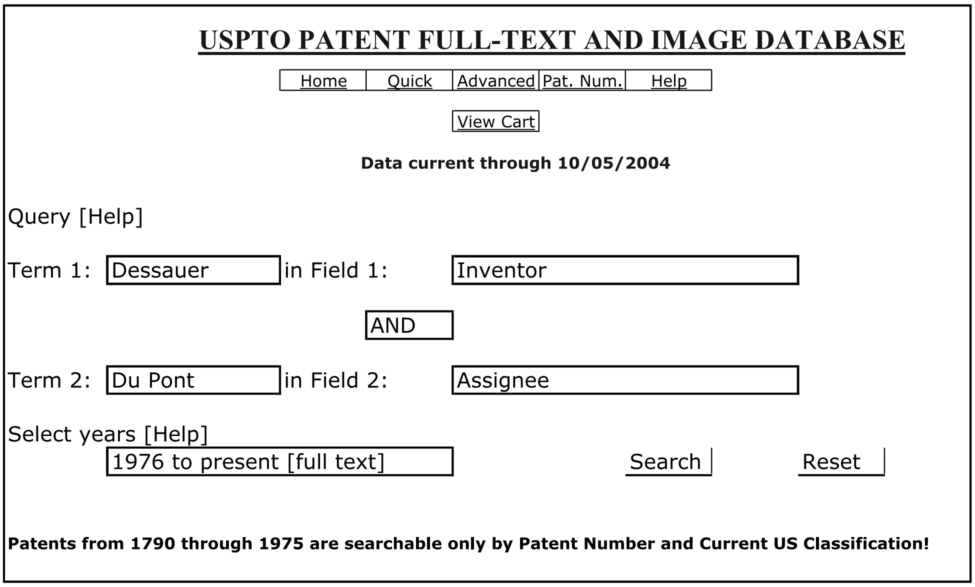
Figure 5.2.



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Term 1: Dessauer in Field 1: Inventor

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Term 2: Du Pont in Field 2: Assignee

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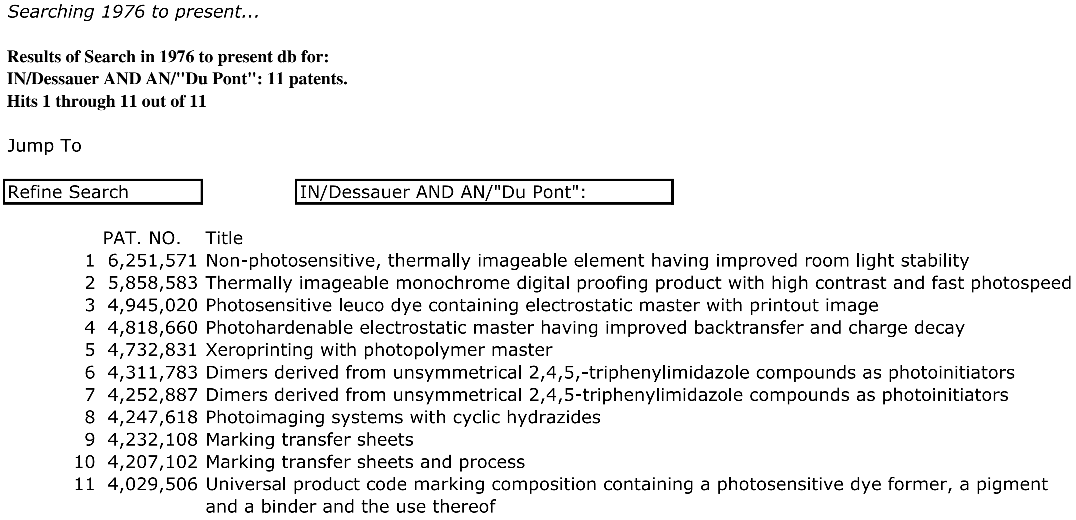
Figure 5.3.



Searching 1976 to present...

Results of Search in 1976 to present db for:
IN/Dessauer AND AN/"Du Pont": 11 patents.
Hits 1 through 11 out of 11

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IN/Dessauer AND AN/"Du Pont":

	PAT. NO.	Title
1	6,251,571	Non-photosensitive, thermally imageable element having improved room light stability
2	5,858,583	Thermally imageable monochrome digital proofing product with high contrast and fast photospeed
3	4,945,020	Photosensitive leuco dye containing electrostatic master with printout image
4	4,818,660	Photohardenable electrostatic master having improved backtransfer and charge decay
5	4,732,831	Xeroprinting with photopolymer master
6	4,311,783	Dimers derived from unsymmetrical 2,4,5,-triphenylimidazole compounds as photoinitiators
7	4,252,887	Dimers derived from unsymmetrical 2,4,5-triphenylimidazole compounds as photoinitiators
8	4,247,618	Photoimaging systems with cyclic hydrazides
9	4,232,108	Marking transfer sheets
10	4,207,102	Marking transfer sheets and process
11	4,029,506	Universal product code marking composition containing a photosensitive dye former, a pigment and a binder and the use thereof

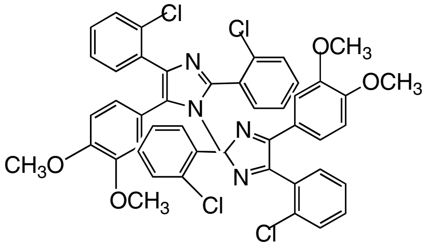
Figure 5.4.

5.1 NOMENCLATURE

Chemical Abstracts lists HABIs primarily as either derivatives of

(a) 1,1′-biimidazole,
(b) 2,2′-biimidazole,
(c) dimers of imidazoles, and most correctly,
(d) as the 1*H*-imidazole derivative, which is likely the correct structure for most of these dimers, where the bonding between rings is presumed to be 1,2′, the correct name of the dimer is 1*H*-imidazole-2,4-(2-chlorophenyl)-1-[bis(2,4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2*H*-imidazol-2-yl)]-5-(3,4-dimethoxyphenyl) for the compound of structure, given in Scheme 5.1.

When looking in the Chemical Abstracts indices, the more readily understandable biimidazole or bisimidazole structure is easily discernible, while searching for the more difficultly, but correctly named 1,2′ isomer is quite complex. It is thus not surprising that a lot of the earlier and even more recently identified HABIs are probably incorrectly named as 1,1′-derivatives.



Scheme 5.1.

6

A SURVEY OF HABI PUBLICATIONS

There has been continued interest in the chemistry of hexaarylbiimidazoles as can be seen from the plot of journal references found in Chemical Abstracts from 1960 to 2003 (Fig. 6.1).

6.1 1960

A New Phototropic Substance and its ESR. Taro Hayashi, Kodo Maeda, Shoji Shida and Kazuo Nakada. J. Chem. Phys. 32, 1568 (1960). Oxidn. of 1 g. lophine (2,4,5-triphenylimidazole) by 12 g. KOH in 100 cc, EtOH or by Br in EtOH gave a phototropic substance (I) considered to be an imidazole derivative. When 450 vcc. 1% $K_3Fe(CN)_6$ aq. soln. was added during 1 hr. with stirring by an O stream to the above KOH mixt. of I, the initial violet color disappeared. Working up gave yellow prisms, m. 199–201°, mol. wt. 200, λ 267 mm in EtOH. The red violet color was presumably due to the free radical, $C_{21}H_{15}N_2$, and the yellow form may have been a labile mesoionic form of lophine.

Preparation of a New Phototropic Substance. Taro Hayashi and Kodo Maeda, Univ. Ochanomizu, Tokyo, Bull. Chem. Soc. Japan 33, 565–6 (1960). Oxidn. of 1 g. lophine (2,4,5-triphenylimidazole) by 12 g. KOH in 100 cc, EtOH or by Br in EtOH gave a phototropic substance (I) considered to be an imidazole derivative. When 450 vcc. 1% $K_2Fe(CN)_6$ aq. soln. was added during 1 hr. with stirring by an O stream to the above KOH mixt. of I, the initial violet color disappeared. Working up gave yellow prisms, m. 199–201°, mol. wt. 200, λ 267 nm in EtOH. The red violet color was presumably due to the free radical, $C_{21}H_{15}N_2$, and the yellow form may have been a labile mesoionic form of lophine.

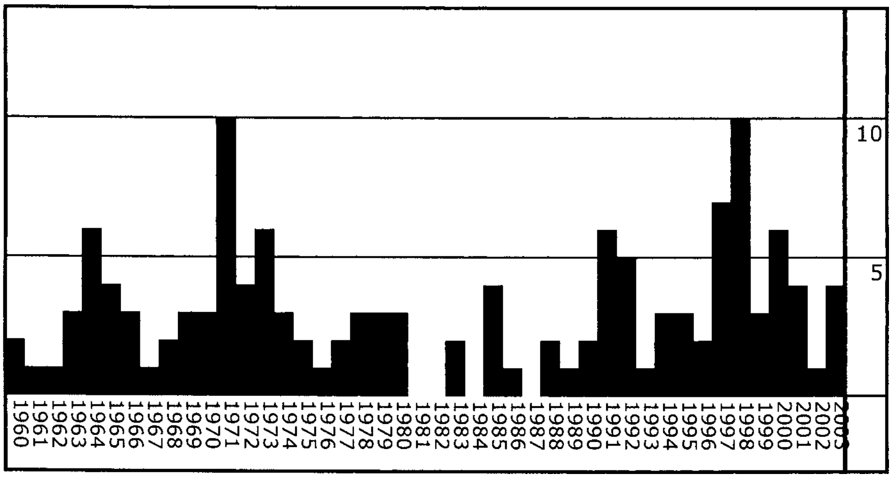
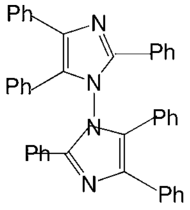


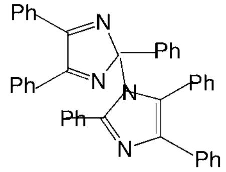
Figure 6.1. HABI references listed in chemical abstracts by year.

Soon after Hayashi and Maeda's original paper appeared, scientists became interested in the unusual properties of the oxidation product of triphenyl imidazole and related compounds. What was especially of interest was to make structural assignments based on spectroscopic and other data.

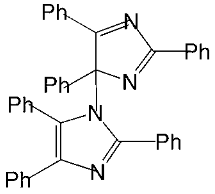
Below are depicted the 6 possible combinations based on bonding of the two imidazole rings.



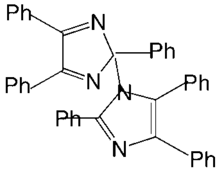
1,1'



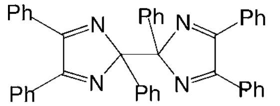
1,2' piezochromic and photochromic



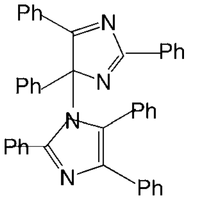
1,4' photochomic



1,2' piezochromic and photochromic



2,2' nonphotochromic



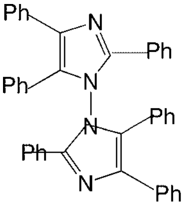
2,4'

6.2 1961

1,1′-Bipyrrole, 1,1′-Biimidazole and their Dissociation into Radicals. Herbert Zimmermann, H. Baumgärtel, and F. Bakke. Tech. Hochschule, Munich, Ger., Angew. Chem. 73, 808 (1961). Reaction of the K-salt of 2,3,4,5-tetraphenyl pyrrole in ether under N and Cl gives 60–80%, 1′-biphenylpyrrole (I). I in soln. is in equil. with the tetraphenylpyrryl radical as shown by its abs. spectrum. In toluene at 20° the equil. const. Is 3.8 x 10^{-4} mole/l., and DH is +14 kcl./mole. Similarly obtained with iodine in place of Cl, was 1,1′-bi(2,4,5-triphenyl-imidazole) (II), m. 193°, contg. no active H, also in equil. with its radical. Also prepd. were 1,1′-bis(2-p-tolyl-4,5-biphenylimidazole) (III), m. 190° and 1,1′-bis(2-p-methoxy-4,5-biphenylimidazole) (IV), m. 146°, both of which in soln. show equil. with their radicals which are blue to violet in color. The equil. const. k and dissocn. enthalpy DH of the imidazoles in toluene are (compd., k, DH): II, 0.95 x 10^{-4} mole/l. at 90°, +19 kcal./mole; III, 1.75 x 10^{-4} mole/l. at 90°, +15 kcal./mole; IV, 4.6 x 10^{-4} mole/l. at 60°, +14 kcal./mole.

6.3 1962

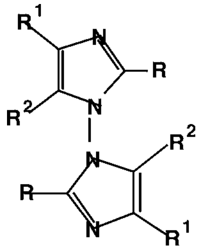
Mechanism of Chemiluminescence of 2,4,5-Triphenylimidazole. Taro Hayashi and Kodo Maeda (Ochanomizu Univ., Tokyo). Bull. Chem. Soc. Japan 35, 2057–8 (1962). The anion of 2,4,5-triphenylimidazole, formed in alc. KOH soln., yielded the free radical 2,4,5-triphenylimidazyl (I) by air oxidn. I was produced by dissociation of the N–N bond in dimeric Ia. I reacted with mol. O to yield a peroxide (II). II decompd. to benzoic acid and NH_3 with the emission of light. I is the essential intermediate in the process of chemiluminescence.



1,1' Ia

6.4 1963

Synthesis of 1,1′-Biimidazoles and Dissociation into Radicals. Helmut Baumgärtel and Herbert Zimmermann (Tech. Hochschule, Munich, Ger.). Z. Naturforsch. 18b (5), 406–12 (1963). 2,4,5-Trisubstituted-1,1′-biimidazoles (I)



I

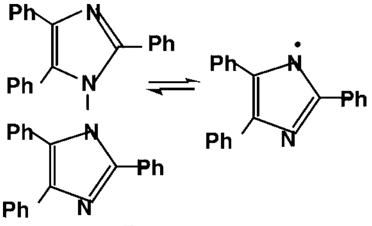
are prepd. by treating an N-haloimidazole with the Na salt of the corresponding imidazole in Et_2O. Unsubstituted imidazole does not react in this way. The Na salt is prepd. by the addn. of the calcd. amt. of Na to the imidazole deriv. dissolved in liquid NH_3 or dioxane. Addn. of Br to the Na salt dispersed in anhyd. Et_2O yields I, which dissociates into 2 imidazolyl radicals (II). Diln., temp., and light favor the formation of II. Thermodynamic data of the dissocn. have been studied; DS ranges in general between 25 and 30 cal./°mole. The following I were prepd. in about 50% yield (R, R^1, R^2, and m.p. given): Ph, Ph, Ph, 195°; p-tolyl, Ph, Ph, 190°; p-$MeOC_6H_4$, Ph, Ph, 146°; Ph, p-$MeOC_6H_4$, p-$MeOC_6H_4$, 175°; p-$MeOC_6H_4$, p-$MeOC_6H_4$, p-$MeOC_6H_4$, 120°; p-tolyl, p-tolyl, p-tolyl, $\sim$ 180° (obtained only in 95% purity); p-$Me_2NC_6H_4$, Ph, Ph, 103° (very unstable, excluded from thermodynamic studies). 1,1′-Bi(2-phenyl-4,5,9′,10′-phenanthrimidazole), m. 170°, was also prepd.

Chemical Luminescence. Taro Hayashi (Ochanomizu Univ. Tokyo). Kagaku (Tokyo) 33 (3), 114–19 (1963). A review with more than 17 references.

Storage of Light Energy by a Solution of Photochromatic-1,1′-biorg-(2,4,5-Triphenylimidazyl) at Low Temperatures. Taro Hayashi and Koko Maeda (Univ. Ochanomizu, Tokyo). B. Chem. Soc. Japan 36 (8), 1052–3 (1963). The storage of light at low temps. was observed in 10^{-2} or 10^{-4} M solns. of 1,1′-biorg-(2,4,5-triphenyl-imidazyl)triphenyl-imidazyl) (I) in benzene, cyclohexane, toluene, n-heptane, and CCl_4. Solns. were prepd. in the dark, degassed, cooled to -20 to $-195°$, and irradiated with sunlight for several min. After warming to 0–15°, solns. became reddish purple, and gave strong electron spin resonance signals, attributed to the radical 2,4,5-triphenylimidazyl. The duration of energy storage by frozen solns. of I was 6 hrs. at 0° and approx. 100 hrs. at −70°. Similar observations were made for solns. of 2-(p-methylphenyl), 2-(p-methoxyphenyl), 2-(p-chlorophenyl), 2,4,5-trisorg(p-methyl phenyl), and 2,4,5-trisorg(p-chlorophenyl) analogs of I. The mechanism of light energy storage involved stored energy insufficient to split the N–N bond at low temps. becoming adequate after thermal energy at elevated temps. was provided.

6.5 1964

Mechanism of the Photochromism and Thermochromism of 2,2′,4,4′,5,5′-Hexaphenyl-1,1′-Biimidazole. Taro Hayashi, Kodo Maeda, and Midori Morinaga (Ochanomizu Univ., Tokyo). Bull. Chem. Soc. Japan 37 (10), 1563–4 (1964) (Eng.), cf. CA 54, 24674c, 23747d. The rate of decrease in absorbance at 347 nm which is produced by sunlight irradiation of C_6H_6 solns. of the title compd. (I) was measured at 19.0–50.5°.

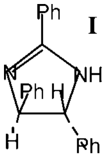


I

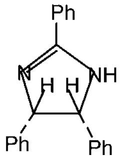
The decay of absorbance followed 2nd-order kinetics and was attributed to the recombination of 2,4,5-triphenylimidazolyl radicals. The activation energy of the recombination reaction was 7.3 kcal./mole. Equil. consts. for the thermal dissocn. reaction were estd. from absorbance at 554 nm due to thermochromism, to be 0.31 × 10^{-4} (49.0°), 4.7 × 10^{-4} (53.8°), and 1.1 × 10^{-3} (60.4°). DH for the reaction was estd. to be 23 kcal./mole.

Kinetic Study of the Photochromism of 2,2′,4,4′,5,5′-Hexaphenyl-1,1′-Biimidazolyl with Electron Spin Resonance. Taro Hayashi, Koko Maeda, and Makoto Takeuchi (Univ. Ochanomizu, Tokyo). Bull. Chem. Soc. Japan 37 (11), 1717–18 (1964) (Eng.). The title reaction, followed by the E.S.R. spectrum, involves a second-order recombination of triphenylimidazolyl radicals.

The Mechanism of Dehydrogenation of 2,4,5-Triphenyl-4,5-Dihydroimidazole Over Solid Catalysts. Taro Hayashi, Mineko Kuyama, Emiko Takizawa, and Masako Hata (Univ. Ochanomizu, Tokyo). Bull. Chem. Soc. Japan 37 (11), 1702–4 (1964) (Eng.). Amarine (I) has been completely dehydrogenated, in the absence of O, by refluxing xylene, toluene, C_6H_6, or Me_2CO solns. with Raney Ni whereas no dehydrogenation of *dl-iso*-amarine (II)



I



II

occurred under the same conditions. I was also dehydrogenated in the absence of O by refluxing solns. with Pt black, Pd black, or active C. The dehydrogenation of I, carried out by refluxing a soln. in C_6H_6 with S powder, was accompanied by the evolution of H_2S. I was adsorbed with active C from a soln. in C_6H_6 at room temp., whereas hardly any II was adsorbed under the same conditions. The mechanism of dehydrogenation of I, (cis isomer), and the failure of the trans isomer to dehydrogenate are discussed in terms of adsorption in the catalyst surface.

Chemiluminescence. Taro Hayashi (Ochanomizu Univ., Tokyo). Kagaku (Kyoto) 19, 32–7 (1964) (Japan.), cf. CA 61 12807f. A review with 14 references.

Chemiluminescent and Thermochemiluminescent Lophine Hydro-Peroxide. Joseph Sonnenberg and Dwain M. White (Gen. Elec. Res. Labs., Schenectady, N.Y.). J. Am. Chem. Soc. 86 (24), 568–6 (1964) (Eng.); cf. White and Harding, following abstr. The lophyl radical (I) (2,4,5-triphenylimidazoyl radical) and 3% H_2O_2 gives 59% lophyl hydroperoxide (II). Irradiation of a $CHCl_3$ soln. of lophine at 18° in the presence of methylene blue and O also yields II. II is a hydroperoxide rather than an endoperoxide as suggested by Dufraisse (D, et al., CA 51, 9333a). Substitution of cumyl or tert-Bu hydroperoxide for H_2O_2 yields analogs of II. II is thermochemiluminescent above 110° and chemi-luminescent on treatment with d base. For II, chemiluminescent reaction and thermal degradation yields N,N′-dibenzoylbenzamidine. II action spectra from thermochemiluminescence and chemiluminescence are essentially identical with chemi-luminescence of lophine.

The Chemiluminescence of Lophine and its Derivatives. Emil H. White and Maurice J.C. Harding (Johns Hopkins Univ., Baltimore, Md.). J. Am. Chem. Soc. 86 (24), 5686–7 (1964) (Eng.); cf. Sonnenberg and White, preceding abstr. Substituted lophine hydroperoxides were synthesized from substituted imidazoles, which (as well as the corresponding hydroperoxides) yield light on the same wavelength on reaction with base and or base alone. lophine anions are probably the common intermediates in both reactions. Salts of diaroylarylamidines are products of both reactions, which suggests that they are the light emitters in the chemiluminescence.

6.6 1965

Mechanism of Photochromism. Taro Hayashi (Ochanomizu Univ., Tokyo). Yakugaku Zasshi 85 (1), 1–7 (1965) (Japan.). A review with 27 references.

Mechanism of the Piezochromism of Hexaphenylbiimidazole. Toro Hayashi and Koko Maeda (Ochanomizu Univ., Tokyo). Bull Chem. Soc. Japan 38 (4), 685–6 (1965) (Eng.). Hexaphenylbiimidazole exhibits photochromism, thermo-chromism, and piezochromism. The color change is effected by grinding or by pressure (10–50 kg./cm.^{2}). In each instance, the color is due to the triphenylimidazolyl radical.

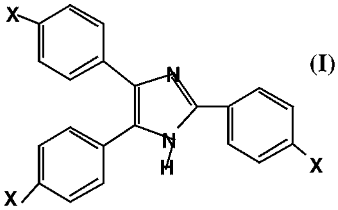
The Mechanism of the Photochromism and Thermochromism of 2,2′,4,4′,5,5′-Hexa-Phenyl-1,1′-Biimidazolyl in a Solid State. Taro Hayashi Koko Maeda, and Takako Kanaji (Ochanomizu Univ., Tokyo). Bull. Chem. Soc. Japan 38 (5), 857 (1965) (Eng.). Pale yellow 2,2′,4,4′,5,5′-hexaphenyl-1,1′-biimidazolyl (I) becomes reddish purple upon irradiation or when heated in the solid state. On the basis of the E.S.R. and absorption spectrum measurements of a sample irradiated at 15°, the mechanism of photochromism of I, in the solid state, was concluded to be the radical dissociation of its N–N bond to triphenylimidazolyl radicals (II). The same mechanism can be applied to the thermochromism in the solid state. The photochromic color gradually reverted to its original pale yellow color at about 40°. The rate of recombination of II in the dark at 46 and 62.5° did not obey the rate expression of the 2nd-order reaction.

Infrared Absorption Spectra of Photochromic and Piezochromic Systems of the Dimers of Triarylimidazolyls. Taro Hayashi and Koko Maeda (Ochanomizu Univ., Tokyo). Bull. Chem. Soc. Japan 38 (12), 2202–3 (1965) (Eng.). The compds., such as $C_{42}H_{30}N_4$, m. 199–200°, $C_{48}H_{42}N_4$, m. 194–5, $C_{42}H_{24}N_4Cl_2$, m. 213–14°, and $C_{42}H_{28}N_4Cl_2$, m. 219–20° produced by the oxidation of 2,4,5-triphenyl-, 2,5,5-tri-p-tolyl-, 2,4,5-bis(p-chlorophenyl)- and 2-(p-chlorophenyl-4,5-diphenyl)-imidazole, resp., exhibit photochromism, thermochromism, and piezochromism (CA, 54, 23, 747d). These compds. are dimers of triarylimidazo radicals, and the colors exhibited are due to the radicals formed by photo, thermal, or mechanical dissocn. One or more absorption bands were observed in the spectra of the photo- or piezochromically colored systems that were not found in I dimers. The ir spectra of the dimers indicate that they; not the hexaaryl-N,N′-biimidazolyls previously reported, I rather hexaaryl-2,2′-bi-2*H*-imidazolyls.

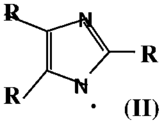
6.7 1966

Oxidation of Triarylimidazoles. Structures of the Photochromic and Piezo-Chromic Dimers of Triarylimidazyl Radicals. D.M. White and J. Sonnenberg (Gen. Elec. Res. & Develop. Center Schenectady, N.Y.). J. Am. Chem. Soc. 88 (16), 3825–9 (1966) (Eng.). Two dimers of the 2,4,5-triphenylimidazyl radical have been prepd. and characterized. One compd., an isoimidazyliso imidazole (I), is photochromic and thermochromic. The isomeric compd., a bis(isoimidazole) (II), is a piezochromic solid which rapidly dissociates to triphenylimidazyl radicals in soln. Interconversions of I and II have been carried out and indicate that I is more stable than II both in soln. and in the solid state. Various substituted triarylimidazoles have been converted to dimers with analogous photo- and piezochromic properties. 15 references.

Triarylimidazolyls and Triarylimidazole Dyes. Helmut Baumgärtel and Herbert Zimmermann (Univ. Munich, Ger.). Chem. Ber. 99 (3), 843–9 (1966). The dehydrogenation of the aryl substituted imidazoles (I) with PbO_2 in nonpolar solvents, or, better, the reaction of the Na salts of I with Br, yielded deeply colored free radicals of the type II which are in soln. in equil. with their dimers (III). The equilibria were measured spectrophotometrically. Oxidn. of I (X = MEt_2N) (IV)



(I)



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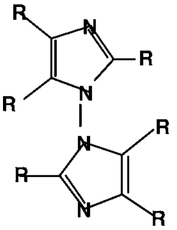

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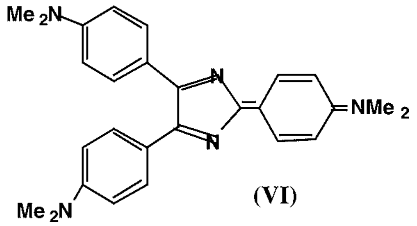


(VI)

gave a deep red dye cation whose chem. properties resemble those of Crystal Violet. I (X = O_2N) (V) has acidic properties and formed with bases or with alkali metal deep red dye anions. (p-$Me_2NC_3H_4CO)_2$ (20 g.), 10 g. p-$MeNC_6H_4CHO$, and 50 g. NH_4OAc in 250 cc. HOAc refluxed 4 hrs., cooled, and added dropwise to 800 cc. concd. NH_3 yielded 22 g. yellow IV, m. 245° (dioxane). Na salt (0.55 g.) of I (X = Ph) in 40 cc. dry Et_2O treated with 24 mg. dry Br in a stream of N and filtered, and the deep green free radical soln. concd. gave 0.12 g. yellow-green III (R = p-PhC_6H_4), m. 184° (decompn.). I (X = Cl) (0.84 g.) in 30 cc. 1:1 tetrahydro furan–Et_2O gave similarly, with 0.15 g. Br, a deep blue free radical soln. which, when concd., yielded 0.20 g. yellow III, (R = p-ClC_6H_4), m. 201° (decompn.). IV (0.212 g.) in 50 cc. dry Et_2O shaken 0.5 hr. with 0.12 g. PbO_2, filtered, and evapd. at room temp., yielded 0.17 g. olive-green III (R = p-$Me_2NC_6H_4$), m. 160° (decompn.). IV (0.425 g.) in 100 cc. 70% EtOH treated with 2 g. PbO_2, and the resulting green radical soln. treated with stirring with 0.126 g. iodine in 40 cc. EtOH, stirred 20 min., filtered and evapd., and the residue chromatographed on silica gel yielded 0.37 g. red, cryst. VI, m. 170° (decompn.). VI (2.95 g.) in 150 cc. HOAc treated with stirring with 20 g. Zn dust, stirred 0.5 hr. filtered, and added dropwise to 500 cc. concd. NH_4OH gave 1.9 g. IV. V (1.0 g.) with 0.46 g. Na in 40 cc. dry dioxane refluxed 0.5 hr. under N gave 0.91 g. black, cryst. Na deriv.

Kinetics of the Photochromic Decay Reaction of Solutions of 2,2′,4,4′,5,5′-Hexaphenyl-Biimidazolyl. M.A.J. Wilks and M.R. Willis (Univ. Nottingham, Engl.). Nature 212 (5061) 500–2 (1966) (Eng.). The kinetics of the photochromic decay of solns. of the title compd. is shown to be

3/2 order, falling to first order. The following kinetic scheme is suggested to explain the

$$\mathrm{L.X} \xrightarrow{k_1} \mathrm{L.} + \mathrm{X};$$

$$\mathrm{L.} + \mathrm{L.X} \xrightarrow{k_2} \mathrm{L}^+ + \mathrm{L.X}^-$$

$$\mathrm{L.X}^- \xrightarrow{k_3} \mathrm{L.} + \mathrm{X}^-$$

$$2\mathrm{L.} \xrightarrow{k_4} \mathrm{L}_2$$

results, where L. signifies 2,4,5-triphenyl imidazolyl, L_2 the photochromic dimer, and X, some other species in soln., probably the radical–dimer complex, $L.L_2$. The following, kinetic data were obtained using this mechanism: 1.5 order rate const. (C_6H_6, 31.7°) 3.3×10^{-1} mole^{-5} sec.$^{-1}$, (CH_2Cl_2, 27°) 3.9×10^{-1} mole^{-2} sec. ^{1}; 1st order rate const. (C_6H_6, 31.7°) 3.2×10^{-1} sec.$^{-1}$, (CH_2Cl_2, 27°) 2.5×10^{-1} sec.$^{-1}$; activation energy (1.5 order) 14 ± 2 kcal./mole (C_6H_6), 11 ± 2 kcal./mole (CH_2Cl_2).

6.8 1967

Mechanism of Reversible Photochemical Color Change of Bis(Triphenyl-Imidazolyl) at Low Temperature. Taro Hayashi and Koko Maeda (Ochanomizu Univ., Tokyo). Bull. Chem. Soc. Jap. 40 (12), 2990 (1967) (Eng.). E.S.R. and phosphorescence data on the reversible color change of bis-(triphenylimidazolyl) (I) solns. on irradn. in the rigid state at or near −196° is due to formation of a cation radical produced by photolytic loss of an electron from the N atom of I. The electron is trapped in the rigid solvent and the weak after-glow and bleaching of the bluish-purple color observed on increasing the temp. from −196° are attributed to recombination of the trapped electron with the cation radical to I through a triplet state.

6.9 1968

Kinetics of the Photochromic Decay Reaction of 2,2′,4,4′,5,5′-Hexa-Phenylbiimidazolyl. Wilks, M.A.J; Willis, Martin R. (Univ. Nottingham, Nottingham, Engl.). J. Chem. Soc. B 1968, (12), 1526–9 (Eng.). Kinetic studies on the title reaction show that the reaction is 3/2 order in radical concn. falling to 1st order. A chain mechanism involving both ions and radicals is suggested. Studies on the 3/2 order rate const. and equil. const. in mixed solvents of varying dielec. const. indicate that polar intermediates are involved. The 3/2 rate const. is also weakly dependent on the concn. of photochromic dimer.

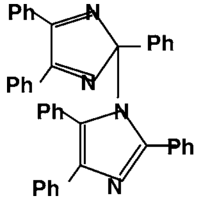
Interpretation of the High-Resolution Electron Spin Resonance Spectrum of the 2,4,5-Triphenylimidazolyl Radical. Wilks, M.A.J.; Willis, Martin R. (Univ. Nottingham, Nottingham, Engl.). J. Phys. Chem. 1968, 72 (13), 4717–18 (Eng.). The computer simulated spectrum produced on the basis of the H. Ueda (1964) interpretation of the E.S.R. spectrum of the 2,4,5-triphenylimidazolyl radical indicates that the Ueda interpretation is incorrect. E.S.R. spectra of several deuterated compds. based on the 2,4,5-triphenylimidazolyl radical were recorded. The spectrum of 2,4,5-trideuteriophenylimidazolyl contained 5 partially resolved lines with a splitting of about 1.63 gauss. Spin ds. were calcd. by a McLachlan calcn. Best fit with no., intensity, and sepn. of lines was obtained by using a slightly higher proportion of the spin d. on the para proton. A 100% Gaussian line-shape and 0.15 Gauss line-width at half-power for any line were used.

6.10 1969

Radical Mechanism of the Photochromism of Bis(2,4,5-Triphenyl-Imidazolyl). Hayashi, Taro; Maeda, Koko (Ochanomizu Univ., Tokyo, Japan). Nippon Kagaku Zasshi 1969, 90 (4), 325–43

(Japan.). A review of the authors' work on the photochromism of the newly synthesized compd. bis(2,4,5-triphenylimidazolyl). 13 references.

Photochromism of Organic Compounds. I. Kinetics and mechanism of photochromic reactions of 2,2′,4,4′,5,5′-hexaphenyl-1,2′-biimidazole. Prokhoda, A.L.; Krongauz, V.A. (Fiz.-Khim. Inst. im. Karpova, Moscow, USSR). Khim. Vys. Energ. 1969, 3 (6), 495–501 (Russ.). The title compds. (I) in EtOH, C_6H_6, C_6H_{12} with or without O irradiated (10^{-4} to 10^{-5} einsteins 1.$^{-1}$ min^{-1}) at room temp., liq. N temp., and optical d. (D) at 347 nm for 2,4,5-triphenylimidazolyl (II)



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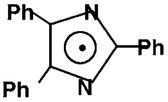


II

followed a linear relation kinetically (a plot of $\log \mathrm{t}_{1/2}$ vs. $\log l/D$ was linear); the $\mathrm{t}_{1/2}$ (half life of II) and quantum yields to give II was calcd. For combination of II to I, ESR spectra and UV spectra gave $1/D - 1/D_0 = (\mathrm{k}/\mathrm{eR}^1)^{\mathrm{t}}$, where $D \to D_0$ as $\mathrm{t} \to 0$, k is the radical (II) recombination rate const. eR extinction coeff. for II at 347 nm, and 1 thickness of the absorbing layer. Formation of 2,4,5-triphenylimidazole from II by abstracting H from the solvent mol. was confirmed.

Nitrogen-Containing Heterocyclic Free Radicals. VII. Use of Diphenyl-Picrylhydrazine for Studying the Dissociation Rate of Dimers of Triphenylimidazolyl Radicals. Tanaseichuk, B.S.; Stanovkina, K.V.; Sunin, A.N.; Rezenova, L.G. (Mord. Gos. Univ., Saransk, USSR). Zh. Org. Khim. 1969, 5 (11), 2054–5 (Russ.). The ability of diphenyl-picrylhydrazine (I) to form free radicals was used in the study of 5-(2,3,5-triphenyl-imidazol-l-yl)-2,3,5-triphenylimidazole (II) dissocn. The rate of the optical d. change at 530 nm of I–II mixts. gave the dissocn. rates at 65, 74.5, or 85°. The dissocn. activation energy was 23 kcal/mole. The process consists of a slow dissocn. of II to 2,3,5-triphenylimidazole free radicals (III) and the rapid formation of I free radicals and 2,3,5-triphenylimidazole.

6.11 1970

DuPont Dylux® Photosensitive Products. Dessauer, R., Image Technol. 1970, 12 (2), 27–31 (Eng.). The photosensitive coatings contain a mixt. of org. compds. Colored images are obtained by exposure to UV radiation without chem. processing, and light is used to stabilize the nonimaged areas. By control of the sequence of exposures, either pos. or neg. images can be obtained.

Photochromism of Organic Compounds. IV. Behavior of a 2,2′,4,4′,5,5′-Hexaphenyl-1,2′-Biimidazolyl-Triphenyl Imidazyl Radical System in Solutions. Prokhoda, A.L.; Krongauz, V.A. (Fiz.-Khim. Inst. im. Karpova, Moscow, USSR). Khim. Vys. Energ. 1970, 4 (2), 176 (Russ.). Spectrophotometric and EPR methods showed that recombination in the dark of the free triphenylimidazyl radicals (I) in benzene in the presence of the title biimidazolyl deriv. (II) is a 2nd order reaction at the II concn. of $\sim 10^{-5}$ M and a 1.5th order reaction at the II concn. $\sim 10^{-4}$ M. This is explained by an intermediate complex formation between I and II; the complex reacts with I in forming 2 mols. of II and its concn. (as detd. by the II concn.) affects the reaction order. The splitting of H from the EtOH mol. by I has the rate const. of $\sim 1.6 \times 10^{-4}$ in the dark at 23° and $\geqslant 3.5 \times 10^3$ L/mole-sec in irradiating the system (2 M EtOH in benzene contg. I and II) by the light with λ 546 nm. Excited I are assumed to participate in the H splitting, the quantum yield being ~ 0.007 mole/Einstein. The formation of triphenylimidazole was studied in dependence on the time of the irradn. with UV radiation of solns. of II. Both excited and ground state mols. of II take part in the reaction, the quantum yields of which are 0.2–0.3 and 0.3–0.4 mole/Einstein at $\sim$ 303–313 and 365 nm, resp. The photodecompn. of II to radicals by $\sim$ 253.7 and 365 nm radiation was studied with benzene and benzophenone as the sensitizers, resp. The quantum yields depend on the starting II concn. and reach the satd. values of ~l and ~ 0.01 mole/Einstein at the II concns. of $\sim 10^{-2}$ and $\sim 10^{-4}$ N in the 1st and 2nd cases, resp.

Nitrogen-Containing Heterocyclic Free Radicals. VIII. Rate of Dissociation of Dimers of Triarylimidazolyl Radicals. Tanaseicliuk, B.S.; Rezepova, L.G. (Mord. Gos. Univ., Saransk, USSR). Zh. Org. Khim. 1970, 6 (5), 1065–8 (Russ.). The oxidn. of 2-(RC_6H_4-substituted)-4,5-diphenylimidazole I) (R is H, p-Me, m-Me, p-Br, m-Br) with $K_3Fe(CN)_6$ in alc. KOH gives I free radicals, which dimerize. The equil. free radicals dimers depends on R. Linear equations were obtained relating Hammett σ consts. with the dimer dissocn. rate consts.

6.12 1971

Photochromism of Organic Substances. V. Kinetics of the Photodissociation of Bis(Triphenylimidazolyls) in Benzene Solutions. Prokhoda, A.L.; Krongauz, V.A. (Fiz.-Khim. Inst. im. Karpova, Moscow, USSR). Khim. Vys. Energ. 1971, 5 (3), 262–3 (Russ.). The kinetics of photodissocn. (A = 303–313 nm) of bis(tri-phenylimidazolyl) and its 5 derivs. in C_6H_6 soln. in non-steady state conditions was studied. The mechanism involving the formation of isomeric forms of imidazols was proved exptl.

Flash Photolysis of a Substituted Hexaarylbiimidazole and Reactions of the Imidazolyl Radical. Coraor, G.R.; Riem, R.H.; MacLachlan, A.; Urban, E.J. (E. I. du Pont de Nemours & Co.). J. Org. Chem. 1971, 36 (16), 2272–5. The rate of reaction of 2-(o-chlorophenyl)-4,5-diphenylimidazolyl radicals (L•) with additives was studied in various solvents. Evidence based on measured rate consts., including kinetic D isotope effects, prove that the rate detg. step in the reaction L• + aromatic amine is an electron change reaction at the amino N, while in the reaction L• + hydroquinone the rate-detg. step is H abstraction.

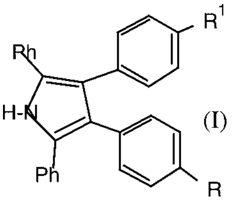
Reactions of Triarylimidazolyl Free Radicals. Coraor, G.R.; Cescon, L.A.; Dessauer, R.; Deutsch, A.S.; Jackson, Harold Leonard; MacLachlan, A.; Marcali, K.; Potrafke, E.M.; Read, R.E.; et al. (Exp. Stn., E. I. du Pont de Nemours and Co., Wilmington, Del.). J. Org. Chem. 1971, 36 (16), 2267–72 (Eng.). Triaryl-imidazolyl free radicals oxidize electron-rich substances by rapid electron abstraction from tertiary amines, iodide ion, and metal ions and H atom abstraction from phenols, mercaptans, primary and secondary amines, and activated C–H compds. The rate consts. for electron abstraction from tertiary amines were related to σ^+ values via oxidn. potentials which were detd. by cyclic voltammetry.

Properties of Triarylimidazolyl Radicals and their Dimers. Coraor, G.R.; Cescon, L.A.; Dessauer, R.; Silversmith, E.F.; Urban, E.J. (Exp. Stn., E. I. du Pont de Nemours and Co., Wilmington, Del.). J. Org. Chem. 1971, 36 (18), 2262–7 (Eng.). The electronic spectra of 2,4,5-triarylimidazolyl radicals (I) are strongly influenced by substitution on Ph rings. The rates of disappearance of I in benzene at 27° vary over 100 fold with substitution of Ph rings. Any ortho substituent in the aryl group increases the rate const. relative to position isomers, a fact consistent with radical destabilization by ortho substituents through steric disruption of ring coplanarity.

Substituent Effects on the Reactivity of Triarylimidazolyl Free Radicals Toward Tris(2-Methyl-4-Diethylamino-Phenyl)Methane. Cohen, Robert L. (Exp. Stn., E. I. du Pont de Nemours and Co., Wilmington, Del.). J. Org. Chem. 1971, 36 (16), 2280–4 (Eng.). The effect of aryl substituents on the reactivity of substituted triarylimidazolyl free radicals, photolytically generated from their corresponding dimers, in an electron exchange reaction with an aminotriphenylmethane substrate was studied by flash photolysis, The reaction rate was retarded by electron-donating substituents and enhanced by electron-withdrawing groups on the imidazolyl radical. Bulky substituents ortho to the imidazole ring, also increased the reactivity.

Nitrogen-Containing Heterocyclic Free Radicals. X. Synthesis of 2,5-Diaryl-3,4-Diphenylpyrroles and Study of Free Radicals Based on them. Tanaseichuk, B.S.; Vlasova, S.L.; Morozov, E.N. (Mord. Gos. Univ. im. Ogareva, Saransk, USSR). Zh. Org. Khim. 1971, 7 (6), 1264–7

(Russ.). p-$RC_6H_4COCH(OH)Ph$ (R = MeO, EtO, Me, Et, Cl) condensed with p-$R^1C_6H_4COCH_2Ph$ (R^1 = MeO, EtO, Me, Br) in AcOH containing NH_4OAc, giving the corresponding 3,4-diphenyl-2,5-diarylpyrroles (I)

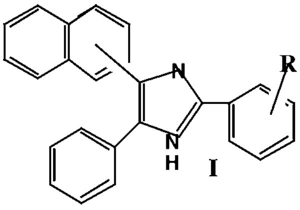


(I)

in 30–60% yield. PbO_2 oxidn. of I afforded the corresponding free radicals, which has absorption max. at 560–630 nm. Decolorization of these radicals in air was 2nd order in radical; the logarithm of the rate const. correlated with the sum of the Hammett σ consts. of R and R^1.

Biimidazole-Sensitized Photooxidation of Leuco Triphenylmethane Dyes. Maclachlan, Alexander; Riem, R.H. (Exp. Stn, E. I. du Pont de Nemours and Co., Wilmington, Del.). J. Org. Chem. 1971, 36 (1G), 2275–80 (Eng.). Oxidn. of tris(2-methyl-4-diethylamino-phenyl)-methane by photogenerated 2-(o-chloro-phenyl)-4,5-diphenylimidazolyl radical ($L\cdot$) was studied by flash photolysis. An electron-exchange reaction involving $L\cdot$ occurs at an unprotonated amino N of the leuco dye and is responsible for the first oxidn. step. Subsequent reactions do not involve the $L\cdot$ radical and depend only on the structure of the leuco dye and environmental effects. The influence of pH on both the course and rate of the dye-forming reaction is discussed.

Nitrogen-Containing Heterocyclic Free Radicals. XI. Synthesis of Diaryl Naphthyl Imidazoles. Bardina, A.A.; Tanaseichuk, B.S.; Khomenko, A.A. (Mord. Gos. Univ., Saransk, USSR). Zh. Org. Khim. 1971, 7 (6), 1267–71 (Russ.). $PhCH_2COC_{10}H_{7\text{-}a}$ and -b were oxidized to the diketone (I)



I

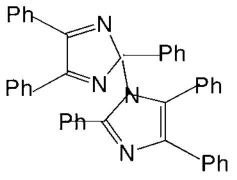
by SeO_2, I condensed with 10 RC_6H_4CHO to form the corresponding 4(5)-phenyl-5(4)-naphthyl-2-arylimidazole (II) in 55–81% yield. PbO_2 oxidn. of II in benzene yielded the corresponding free radicals, which had absorption max. at 610–45 nm; the EPR spectra were independent of R•.

Nitrogen-Containing Heterocyclic Free Radicals. XIII. Bis[4(5)-Biphenylyl-5(4)-Phenyl-2-Arylimidazolyl] Compounds. Tanaseichuk, B.S.; Bardina, A.A.; Maksakov, V.A. (Mord. Gos. Univ. im. Ogareva, Saransk, USSR). Zh. Org. Khim. 1971, 7 (7), 1508–11 (Russ.). p-PhC_6H_4COBz condensed with RC_6H_4CHO (R = H, p-Me, m-Me, p-Br, m-Cl, p-MeO, p-NO_2, m-NO_2) in HOAc contg. NH_4OAc to give 2-RC_6H_4, 4-Ph, 5 p-XC_6H_4-trisubstituted imidazoles (I) in 73–85%, yield. Oxidn. of I by alk. aq. alc. $K_3Fe(CN)_6$ yielded the corresponding bis(triarylimidazol-1-yls). The dissocn. rates of the latter into free radicals correlated with the Hammett σ consts. of R; the activation energy of dissocn. was 20.3–2.0 kcal/mole.

Nitrogen-Containing Heterocyclic Free Radicals. XIV. Dissociation Rate of Diaryl-Bi-Naphthylimidazolyl Radicals. Tarnseichuk, B.S.; Bardina, A.A.; Khonienko, A.A. (Mord. Gos. Univ. im. Ogareva, Saransk, USSR). Khim. Geterotsikl. Soedin. 1971, 79, 1255–7 (Russ.). I (R = H, p-Me, m-Me, p-Br, m-Cl) were synthesized by oxidn. of the corresponding beta-naphthyldiarylimidazoles with $K_3Fe(CN)_6$ in alc.–H_2O soln. of KOH. The effect of R on the values of dissocn. rate consts., k, and activation energy. E, was detd. in toluene at 70, 70, 75, and 80°, equation was found, whereas E for all compds. was 17–19 kgs/mole.

6.13 1972

Chemiluminescence of Organic Compounds. I. Structures of Three Isomeric Dimers of 2,4,5-Triphenylimidazolyl. Tanino, Hideo; Kondo, Tadao; Okada, Kunisuke; Goto, Toshio (Dep. Agric. Chem., Nagoya Univ., Nagoya, Japan). Bull. Chem. Soc. Jap. 1972, 45 (5), 1474-80 (Eng.). In addn. to the piezo-chromic and the photochromic dimers (I) of 2,4,5-triphenyl imidazolyl, II (photochromic) and III



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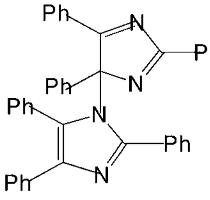
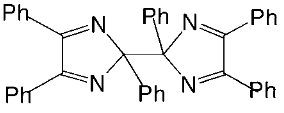


1,4' photochomic

II



2,2' nonphotochomic

III

non-photochromic were prepd. Several para-substituted derivs. of the dimers were also prepd. On treatment with HCl–EtOH, I underwent heterolytic cleavage and gave a mixt. of 2-ethoxy-2H- and 4-ethoxy-4H-2,4,5-triphenylisoimidazole, and 2,4,5-triphenylimidazole.

Long Exposure Density Reversal in a Dye-Forming Imaging System in Viscous Media. Gordon, Michael D.; Looney, Catharine E. (E. I. du Pont de Nemours & Co.). Photographic Science and Eng. 1972, 16 (2), 151–6. Sensitometric curves of imaging systems based on formation of org. dyes in viscous media show long exposure "d. reversal." In such cases the concn. of the product dye increases monotonically, reaches a max., and then decreases with continuing exposure and finally stabilizes. The conditions are: (1) a high rate of absorption of photons; (2) a large excess of photoinitiator; and (3) a highly viscous medium. The obsd. "d. reversa1" does not arise from dye instability but is a natural consequence of reaction kinetics in the viscous system.

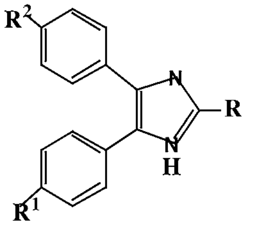
Heterylimidazoles. I. Synthesis of 2-Heteryl-4,5-Diarylimidazoles. Rozin, Yu.A.; Blokhin, V.E.; Pushdareva, Z.V.; Sukhova, M.E. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1972, (5), 681–2 (Russ.). Reaction of benzyl (I) with $AcONH_4$ and isomeric quinoline-carboxaldehydes in AcOH yielded 2-(α-quinolyl)-4,5-diphenylimidazoles. Analogous reactions with p-tolyl gave 2-(α-quinolyl)-4,5-di-p-tolylimidazoles. Reaction of I with AcONH and acridine-9-carboxaldehyde in AcOH gave 2-(9-acridinyl)-4,5-diphenylimidazole.

Computer Simulation of the Chemical Dynamics in a Complex Imaging System. Looney, Catharine E.; Gordon, Michael D.; Laird, J.P.; James, E.W. (Org. Chem. Dep., E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.). Photogr. Sci. Eng. 1972, 16 (6), 433–42 (Eng.). A computer simulation has been successfully applied to Dylux films and papers under a wide variety of imaging conditions and formulation variables. The math. models of both UV-activated color formation and visible light deactivation involve multistep reaction sequences. Fine adjustment of the estd. rate consts. is accomplished by optimizing the fit between computer and actual exptl. results. Once so established, the model permits computer generation of practical sensitometric curves as functions of intensity, wavelength (mono- and polychromatic) for various sample thicknesses and concns. of actives. The program includes light absorption characteristics of any transient inter mediates as well as those of sensitizers, actinic species, screeners, and products. Specific examples of the effects of the independent variables on the sensitometric properties of Dylux are discussed.

6.14 1973

Heterylimidazoles. II. Synthesis of 4,5-Diarylimidazoles and Hetero Analogs of Hexa-Arylbiimidazoles. Rozin, Yu.A.; Blokhina, V.E., Pushkareva, Z.V.; Elin, V.I.; Sukhova, M.E. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1973, (8), 1105–8 (Russ.).

Heterocycle-contg. imidazoles (I; R = 3-, 4-, 6-, 7-, 8-quinolyl, 9-acridinyl, R^1 = MeO, Br, H, R^2 = MeO, Br, NO_2) were prepd. in 10–82% yields by condensation of the appropriate heterocyclic aldehyde with p-$R^1C_6H_4COCOC_6H_4R^2$-p in AcOH contg. NH_4OAc. Biimidazoles (II; R = H, Me, MeO, R^1 = 3-, 4-, 5-, 6-, 7-quinolyl, 9-acridinyl)



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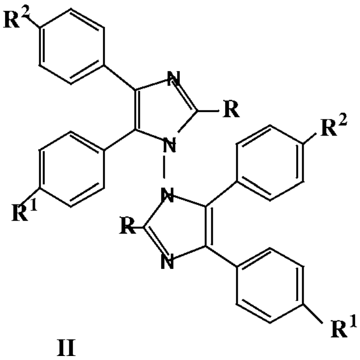
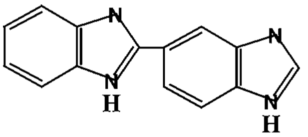


II

were obtained in 20–36% yields by base catalyzed oxidn. of the appropriate I with $K_3Fe(CN)_6$.

Photochemistry of Heterocyclic Compounds. I. Photodehydro-Dimerization of Benzimidazole. Cole, E.R.; Crank, G.; Sheikh, A-Salam (Dep. Appl. Org. Chem., Univ. N. S. W., Kensington, Aust.). Tetrahedron Lett. 1973, (28), 2659–60 (Eng.). Irradn. of 1% benzimidazole in EtOH gave 16% 2,4′-bisbenzimidazole (I) and 25% 2,5-bisbenzimidazole (II).



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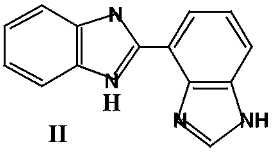


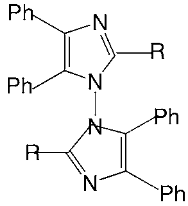
II

Structures were confirmed by NMR, UV, and IR spectra.

Synthesis and Study of 4(5)-Phenyl-2-α-Naphthyl-5-(4)-R-Phenyl-Imidazyl Radicals. Bardina, A.A.; Tranaseichuk, B.S., Sb. Nauch. Tr., Ivanov. Energ. Inst. 1972, No. 14, 111–16, Ref. Zh. Khim. 1973, Abstr. No. 16B941. Synthesis of 4(5)phenyl-2-α-naphthyl-5(4)-R-phenyl imidazoles (R = H, p-Me, p-OMe p-OEt, p-Br, p-Cl) is described. Oxidn. of the obtained imidazoles with K ferricyanide in H_2O–alc. soln. of alkali gave the dimers which were dissocd. in PhMe to the corresponding radicals. The reaction rates of dissocn. of the dimers were detd. Spectrometrically at 70, 75 and 90° and the Arrhenius activation parameters A and Ea calcd A (min^{-1}) and Ea (kcal./ mole) changed from 2.4×10^7 and 13.9 for bis[4(5)-phenyl-2-α-naphthyl-5(4)-methoxy-phenylimidazolyl] to $\leqslant 2.7 \times 10^6$ and 15.8 for bis(4,5-diphenyl-2-α-naphthylimidazolyl).

Biphenylyls and α-Naphthyldiarylimidazolyl Radicals as Stabilizers of Oxidative Thermal Degradation of Polymers Synthesized from Cellulose Ethers. Bardina, A.A.; Tanaseichuk, B.S.; Vinogradov, S.V.; Belyakov, V.K., Sb. Nauch. Tr., Ivanov Energ. Inst., Ref. Zh. Khim. 1973, Abstr. No. 14S462. 2-Naphthyl and 2-biphenylyl 4(5)-phenyl-5(4)-R-phenylimidazolyl dimers (R = 4-OMe, 4-OEt, 4-Me, H, 4-Br, 4-Cl), showed higher stabilizing properties for cellulose ethers than 2,6-di(α-methylbenzyl)-4-methylphenol. The best from these stabilizers was bis[2-biphenylyl-4(5)-phenyl-5(4),4-tolylimidazolyl] [51542-00-8]. The substituents in the phenolic ring in the position 4(5) of the imidazole cycle slightly affected the stabilizing capability of the dimers. The monomers of the above compds. showed a low stabilizing capability.

Synthesis and Properties of Hetero Analogs of 2,2,4,4′,5,5′-Hexaaryl-Biimidazolyls. Rozin, Yu.A.; Blokhin, V.E.; Pushkareva, Z.V. (USSR). Khim. Khim. Tekhnol., Obl. Nauchno-Tekh. Konf., [Mater], 4th 197:3 (Pub. 1973), 2.45–6 (Russ.). Edited by Kudryashov, S.F., Permsk. Politekh. Inst., Perm, USSR. Dissocn. kinetics of I (R = Ph, 1-$C_{10}H_7$, 2-$C_{10}H_7$, 3-, 4-, 5-, 6-, and 7-quinolyl, 9-acridinyl)



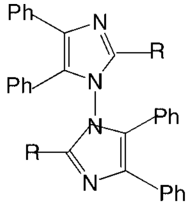
I

were detd. in PhMe at 70 and 80°.

Hetero Analogs of Triarylimidazoles and Hexaarylbiimidazolyls as Inhibitors of Radical Polymerization. Surovtsev, L.G.; Blokhin, V.E.; Rozin, Yu.A.; Lukina, G.A.; Bulatov, M.A. Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR. Khim. Tekhnol. Geterotsikl. Soedin Goryuch. Iskop., 2nd 1973, 203–4 (Russ.). The title compds. I and II (R^1 = H, Br, Me, OMe; R^2 = quinolinyl, 9-acridinyl) exhibited an inhibiting influence on the radical polymn. (60°) of styrene [100-42-5] and benzyl methacrylate [2495-37-6], with the strength of inhibition depending on the monomer nature and the substituents in I and II. Electron acceptor substituents led to decreased inhibiting action by I and II. The biimidazoles were generally stronger inhibitors than the I imidazoles.

6.15 1974

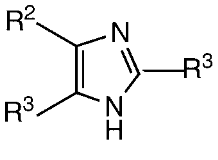
Heterylimidazoles. IV. Homolytic Dissociation of Hexaaryl-Biimidazolyls and their Heteroanalogs. Rozin, Yu.A.; Gryazev, V.F.; Blokhin, V.E.; Pushkareva, Z.V.; Martina, G.E. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1974, (11), 1536–9 (Russ.). The logarithms of the 1st order homolytic dissociation rate consts. of I (R = Ph; 1- and 2-naphthyl; 3-, 4-, 5-, 6- and 7-quinolinyl)



I

exhibited a linear correlation with the polarog. oxidn. half-wave potentials of the corresponding imidazole anions. I (R = 9-acridinyl) deviated from this correlation. The results were discussed in terms of the relative stabilities of dimers and radicals.

Heterylimidazoles. III. Polarographic Oxidation of 2-Heteryl-4,5-Diarylimidazoles Anions. Rozin, Yu.A.; Blokhina, V.E.; Pushkareva, Z.V.; Elin, V.I.; Sukhova, M.E. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1974, (7), 990–2 (Russ.). A linear dependence between the half-wave potentials and s consts. of the substituents R^1, R^2 and R^3 was found for compds. of general formula I,



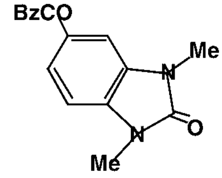
I

where R^1 and R^2 are MeO, Me, H, Br, and NO_2 and R^3 is quinolyl bonded in all its possible positions and 9-acrydinyl.

Heterylimidazoles. IV. Homolytic Dissociation of Hexaarylbiimidazolyls and Their Hetero Analogs. Rozin, Yu.A.; Gryazev, V.F.; Blokhin, V.E.; Pushkareva, Z.V.; Martina, G.E. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1974, (11), 15369. The logarithms of the 1st order homolytic dissocn. rate consts. of I (R = Ph, 1- and 2-naphthyl, 3-, 4-, 5-, 6-, and 7-quinolinyl) exhibited a linear correlation with the polarog. oxidn. half-wave potentials of the corresponding imidazole anions. I (R = 9-acridinyl) deviated from this correlation. The results were discussed in terms of the relative stabilities of dimers and radicals.

6.16 1975

Heterylimidazoles. V. Synthesis and Properties of Hetero-Analogs of Triaryl-Imidazoles. Rozin, Yu.A.; Blokhin, V.E.; Sokolova, N.M.; Pushkareva, Z.V.; Surovtsev, L.G. (Ural. Politekh. Inst. im. Kirova, Sverdlovsk, USSR). Khim. Geterotsikl. Soedin. 1975, (1), 86–9 (Russ.). The condensation of glyoxal I with RCHO and NH_4OAc gave imidazoles II



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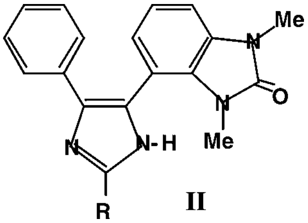
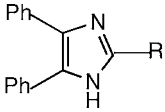


II

(R = Ph, p-anisyl, p-$Me_2NC_6H_4$, p-$Et_2NC_6H_4$, 3,4-$(MeO)_2C_6H_3$, p-ClC_6H_4, p-BrC_6H_4, m-, p-$O_2NC_6H_4$, α-naphthyl, β-hydroxy-α-naphthyl, N,N′-dimethylbenzimidazol-5-yl).

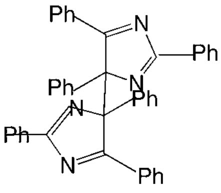
Syntheses of Imidazoles with Liquid Ammonia. 6. N-Substituted Imidazoles. Stoeck,V.; Schunack, W. (Fach-bereich Pharm., Univ. Mainz, Mainz, Ger.). Arch. Pharm. (Weinheim, Ger.) 1975, 308 (1), 72–4 (Ger.). N-Substituted imidazoles cannot be prepd. by reaction of imino esters and α-substituted carbonyl compds. in liq. NH_3 as shown by reaction of benzoin with $PhCH_2NH_2$ in the presence or absence of PhC(OEt):NH · HCl to give $\leqslant$ 25% lophine (I).

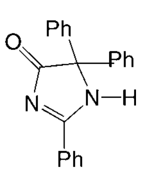


I

6.17 1976

Electrochemical Oxidation of 2,4,5-Triphenylimidazole in Organic Media. Libert, Michel; Caullet, Claude (Inst. Sci. Haute-Normandie, Mont-St.-Aignan, Fr.). Bull. Soc. Chem. Fr. 1976, (3–4, Pt. 1), 345–8 (Fr.). Electrochem. oxidn. of 2,4,5-triphenylimidazole in $MeNO_2$ or MeCN gives, in the 1st step, a radical cation which eventually leads to the dimer I. I can undergo further electrochem. oxidn. In the presence of H_2O or at higher temps. (87–88°) ketone II is also formed.





I II

6.18 1977

Electrochemical Formation and Cleavage of Bisimidazolyls. Lang, Ulrike, Baumgärtel, Helmut (Inst. Phys. Chem., Univ. Freiburg, Freiburg/Br., Ger.). J. Electroanal. Chem. Interfacial Electrochem. 1977, 78 (1), 133–43 (Eng.). Bis(2,4,5-triphenylimidazolyls) result from the dimerization of 2,4,5-triphenylimidazolyls and from the nucleophilic attack of 2,4,5-triphenylimidazole anions upon 2,4,5-triphenylimidazolylium cations. The isomeric bis(imidazolyls) consist of imidazole and iso-imidazole systems. Imidazoles undergo only anodic oxidn., isoimidazoles only cathodic redn. Therefore the bis(imidazolyls) may be analyzed from their electrochem. behavior. 2,2′,4,4′,5,5′-Hexaphenyl-1,2′-diimidazole [7189-41-5] and 2,2′,4,4′,5,5′-hexaphenyl-1,4-diimidazole [63245-02-3] undergo reductive bond cleavage in an *ece* (chem. reaction between 2 charge transfer reactions) mechanism from which 2,4,5-triphenylimidazole anions result. The electrochem. properties of one of the bis(imidazolyls) agree with that of 1,4,5-triphenyl-2-(2,4,5-triphenylisoimidazol-4-yl)imidazole [63245-03-4] and not with that of bis(2,4,5-triphenylimidazolyl)-2,4′ as reported in literature.

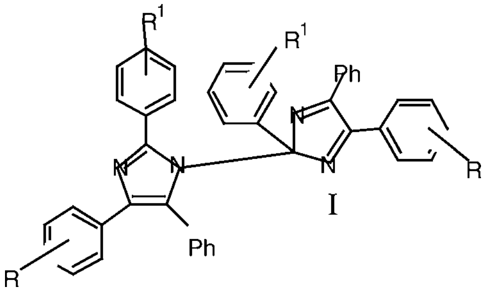
Study of 2-Heteryl-4,5-Diarylimidazoles as Inhibitors of the Radical Polymerization of Styrene. Surovtsev, L.G.; Blokhin, V.E.; Rozin, Yu.A.; Lukina, G.N.; Bulatov, M.A. Ural. Politekh. Inst., Sverdlovsk, USSR. Izv. Vyssh. Uchebn. Zaved., Khim. Tekhnol. 1977, 20 (11), 1676–9 (Russ.). The rate of radical polymn. of styrene [100-42-5] was retarded in the presence of the title imidazoles I (R^1 = H, Me OMe, Br; R^2 = H, Me, OMe, Br, NO_2; R^3 = acridinyl, quinolinyl, Ph). The logarithms of the inhibition consts. of I were in a linear relation with the a consts. of the substituents in the 4- and 5-positions of I and the oxidative potentials of I anions.

6.19 1978

Thermally Induced Reactions of Imidazole Derivatives VII. Thermal Rearrangements of 4,4-Triaryl-5-Methylthio-4H-Imidazoles in the Absence of Hydrogen Sources. A novel type of hexaarylbiimidazolyl. Domany, Gyorgy; Nyitrai, Jozsef; Lempert, Karoly; Voelter, Wolfgang; Horn, Hans. Inst. Org. Chem., Tech. Univ. Budapest, Budapest, Hungary. Chem. Ber. 1978, 111 (4). Thermolysis of either I or II (R = 4-ClC_6H_4 throughout) gave III via a free radical mechanism.

Absorption Spectrum of 2-[p-(4,5-Diphenyl-2-Imidazolyl)Phenyl]-4-Ethoxy-4,5-Diphenyl-4H-Imidazole. Sakaino, Yoshiko; Kakisawa, Hiroshi, Fac. Educ., Gunma Univ., Maebashi, Japan. Nippon Kagaku Kaishi 1978, (10), 1449–51 (Japan.). The longest wavelength electronic absorption bands of 2-aryl-4,5-diphenylimidazoles (e.g. I through IV) show bathochromic shifts when more electron-attractive substituents are introduced in the 2-Ph group. The substituent effect is related to that in the intramol. charge-transfer bands of 1-(p-substituted phenyl)pyrroles. The longest wavelength absorption band of the title compd. (I) is an intramol charge-transfer band. The solvent and temp. effects are consistent with this interpretation.

Studies on Nitrogen-Containing Heterocyclic Free Radicals. XXI. Dissociation Constants of Dimers of Triarylimidazolyls. Tanaseichuk, B.S.; Belozerov, A.I.; Tikhonova, L.G.; Shishkin, V.N.; Bardina, A.A.; Butin, K.P. (Mord. Gos. Univ., Saransk, USSR). Zh. Org. Khim. 1978, 14 (10), 2029–35 (Russ.). Dissocn. of I

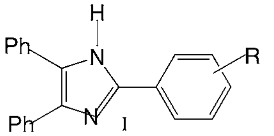


I

(R = H, R^1 = H, 3-Br, 4-Br, 3-Cl, 3-Me, 4-Me, 4-MeO; R^1 = 4-Ph, R = H, 4-Br, 4-Cl, 4-MeO, 4-Me, R = 4-Ph, R^1 = H, 3-Br, 4-Br, 3-Cl, 3-Me, 4-Me) was studied spectrophotometrically in one or more of C_6H_6, PhOMe, $PhNO_2$, and PhMe; thermodn. parameters were detd. In all cases DH° and DS° increased in the solvent order $PhNO_2 < C_6H_6 <$ PhOMe. The effect of aryl substituents agreed well with the Hammett equation (σ^+ const.). There was a linear relationship between the equil. const. and the rate of dissocn.

6.20 1979

Study of Intra- and Intermolecular Interactions of 2,4,5-Arylimidazole Derivatives by Electron and IR Spectroscopic Methods. Kirlicheva, V.G.; Egorochkin, A.N.; Tanaseichuk, S.B.; Belozerov, A.I. (Inst. Khim., Gorkij, USSR). Zh. Obshch. Khim. 1979, 49 (8), 1802–7 (Russ.). The electronic spectral peaks of 4 series of compds., I–IV (R = 4-MeO, 4-Me, 4-Br, 3-Br, $4\text{-}NO_2$, $3\text{-}NO_2$, etc.),



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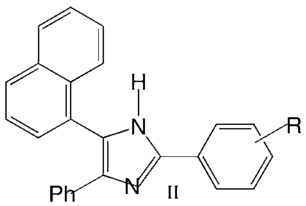

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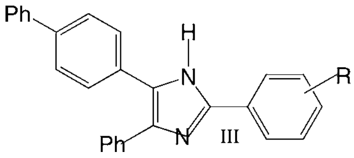
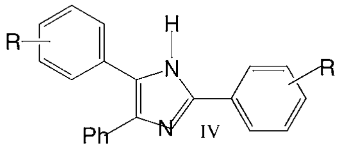


III



IV

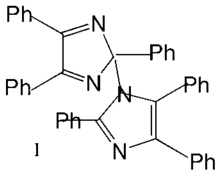
were obtained in different solvents at 77 and 293 K. Frequency shifts ($\Delta\nu$) of the NH group IR band on complexation with THF were also obtained, and 4 linear correlations of $\Delta\nu$ with σ consts. were described. Direct polar conjugation between the substituents in positions 2 and 4 was indicated.

Modulation of Biimidazole-Leucodye Photochemical Reaction by Photo-polymerization. Dessauer, Rolf; Looney, Catharine (Chem., Dyes Pigm. Dep., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898, USA). Photogr. Sci. Eng. 1979, 23 (5), 287–9 (Eng.). A photoimaging system is reported in which the diffusion controlled color-formation reaction is modulated by the polymn. of the essential plasticizer. Polymn. of the plasticizer by light-induced reactions allows pos. or neg. image formation depending on the sequence of exposures; an intense exposure leads to simultaneous color-formation and deplasticization, while low-intensity exposure results only in polymn. without color formation.

Crystalline Matrix Photoimaging. Hertler, W.R.; McCartin, P.J.; Merrill, J.R.; Nacci, G.R.; Nebe, W.J., du Pont de Nemours, E. I., and Co. Photogr. Sci. Eng. 1979, 23 (5), 297–301. A new class of photoimaging systems based on photopolymn. in predominantly cryst. coatings is described. The coatings can be made by spreading a melted monomer-initiator mixt. on a substrate, cooling, and crystg. After light exposure, the unchanged monomer is washed away with a solvent leaving a photopolymer image. Light sensitivity is ~ 20 J/cm^2, making these systems potentially useful in lithog., resist, and other applications. Mechanism studies show that photopolymn. does not take place in the crystal lattice but in liq. or liq.-like inclusions in a cryst. matrix. The size and compn. of the liq. inclusions are normally detd. by the phase relationships of the monomer and initiator. However, both can be varied over a wide range by properly selecting the monomer and initiator m.ps. and by incorporating small amts. of addnl. materials. Since only the inclusions need to be polymerizable, the matrix need not be a monomer and use of a wide variety of cryst. materials is demonstrated with considerable improvement in performance.

6.21 1980

Photochemical and Thermal Interconversions of Three Dimers of 2,4,5-Triphenylimidazolyl (Lophyl). Goto, Toshio; Tanino, Hideo; Kondo, Tadao (Dep. Agric. Chem., Nagoya Univ., Nagoya, Japan). Chem. Lett. 1980, (4), 431–4 (Eng.). Two photochromic R^1 lophyl dimers, I and II, are interconverted by UV irradn., while these two dimers and thermochromic dimer III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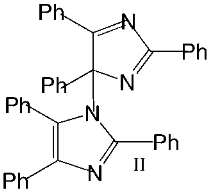
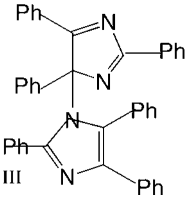

II


III

can be equilibrated in C_6H_6 at 100°. Compns. at equil. using the corresponding 3 dimers of 2-(p-tolyl)-4,5-diphenylimidazolyl are I:II = 96:4 and I:II:III = 14:18:68.

Radical Recombination Kinetics: An Experiment in Physical Organic Chemistry. Pickering, Miles (Princeton Univ., Princeton, NJ 08544, USA). J. Chem. Educ. 1980, 57 (11), 833–4 (Eng.). A lab. expt. is given on the recombination kinetics of the triphenylimidazyl radical. Photochromism is displayed in the expt.

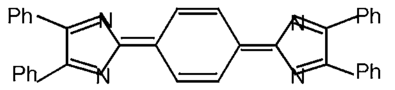
Electrogenerated Chemiluminescence in Mechanistic Investigations of Electroorganic Reactions. Pragst, Fritz; Kaltoffe, Brigitte. Sekt. Chem. Humboldt-Univ. DDR-104 Berlin, Ger. Dem. Repub., J. Electroanal. Chem. Interfacial Electrochem. 1980, 112 (2), 339–45 (Eng.). In the simultaneous cathodic redn. of bis(2,4,5-triphenylimidazolyl-1,2′) (L_2) and some arom. hydrocarbons A in DMF, the emission of A is obsd. This electrogenerated chemiluminescence (ECL) originates from electron transfer between A^- and imidazolyl radicals L•, which are formed via cleavage of L_2^- into L• and L^-.

6.22 1983

New Photochemical Reactions Leading to Spatial Dissipative Structures. Gimenez, M.; Micheau, J.C. (Lab Chim.-Phys. II, Univ. Libre Bruxelles, B-1050 Brussels, Belg.). Naturwissenschaften 1983, 70 (2), 90–2 (Eng.). Spatial dissipative structures were formed during visible or UV light irradn. of shallow layer solns. of photochromic (reversible) or chromogenic (irreversible) compds. The origin of the structures was independent of the mechanisms involved in the chem. reaction.

Structures and Chromotropic Properties of Imidazole Derivatives Produced from 3,6-Bis(4,5-Diphenyl-2H-Imidazol-2-Ylidene)Cyclohexa-1,4-Diene. Sakaino, Yoshiko (Dep. Chem., Gunma Univ., Maebashi, Japan). J. Chem. Soc., Perkin Trans. 1, 1983, (5), 1063–6 (Eng.). Addn. reaction of bis(imidazolylidene)cyclohexadiene I with AcOH in C_6H_6 for 15 min. gave acetoximidazole II (RR^1 = R^4R^5 = bond, R^2 = OAc, R^3 = Ph) (III). Reaction of III with KOH in EtOH–CH_2Cl_2 overnight gave 60% II (RR^5 = bond, R^1 = H, R^2R^3 = O, R^4 = Ph), which on oxidn. with PbO_2 or hexacyanoferrate (III) gave dimer IV. Oxidn. of I with PbO_2 in AcOH C_6H_6 contg. Na_2SO_4

over-night gave bis(imidazolyl)benzene V.



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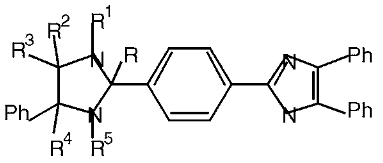
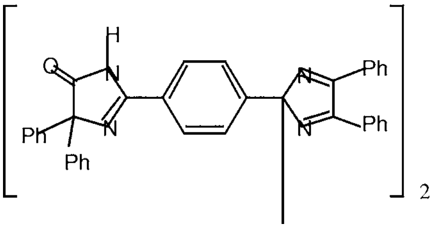
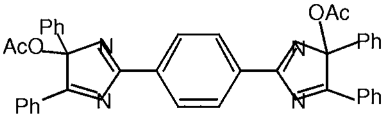


II



IV



V

UV irradn. of III and V gave I. IV showed chromotropism due to radical dissocn. of the dimer during irradn., heating, or grinding. Particularly rapid reversible photochromic behavior was obsd. for IV.

6.23 1985

A Photoacoustic Study of Photochromic Reactions in the Crystalline and Adsorbed States. Guesten, H.; Heinrich, G.; Ache, H.J. (Inst. Radiochem., Kernforschungszent. Karlsruhe, 7500 Karlsruhe, Fed. Rep. Ger.). J. Photochem. 1985, 28 (3), 309–14 (Eng.). The use of photoacoustic spectroscopy in the study of the absorption spectra and thermal kinetics of photochromic reactions in the cryst. and adsorbed states was demonstrated in the following photochem. reactions E-α-(2,5-dimethyl-3-furylethylidene) (isopropylidene) succinic anhydride into 7,7′-dihydro-2,4,7,7′-pentamethylbenzo[b]furan-5,6-dicarboxylic anhydride, 2-(2′-dinitrobenzyl)pyridine into its blue tautomeric form, bis-(2-o-chlorophenyl-4,5-p-methoxyphenyl)diimidazolyl-1,1 into its stable free imidazolyl radical and *trans*-1,2-bis[quinolinyl-(2)]ethylidene dioxalate into its violene radical cation. By using the dual illumination technique the absorption spectra and thermal lifetimes of short-lived photochromic species can be recorded by means of photoacoustic spectroscopy.

Kinetics in a Continuously Stirred Photochemical Tank Reactor. Gregoire, F.; Lavabre, D.; Micheau, J. C.; Gimenez, M.; Laplante, J.P. (Lab. Interact. Mol. React. Chim. Photochim., Univ. Paul Sabatier, F-31062 Toulouse, Fr.). J. Photochem. 1985, 28 (2), 261–71 (Eng.). The continuously stirred photochem. tank reactor (REPAC) is a new semiautomatic app. for photochem. measurements. From the kinetic anal. of steady-state regimes, this open system allows detn. of the quantum yields, the thermal-return rate consts. and the spectra of photoproducts. Moreover, the kinetic anal. of transient regimes affords further information on the mechanism of the photochem. process. The possibilities of the REPAC are shown using various photochromic compds. Theor. anal. of the kinetic rate equations in the REPAC shows that quite unusual behavior, such as unstable steady states or photochem. oscillations, can be exhibited. Nonlinear photochem. reaction schemes are likely to show such behavior.

Free Radicals. XXIII. Reaction of Triphenylimidazoyl with CH-Acids. Tanaseichuk, B.S.; Belozerov, A.I.; Sanaeva, E.P.; Butin, K.P. (Mord. Gos. Univ., Saransk, USSR). Zh. Org. Khim. 1985, 21 (8), 1616–21 (Russ.). The title radical can abstr. H from β-dicarbonyl compds. having a high enol content. The rate of abstraction increases with pK of the enol. Radical formation was confirmed by spin trapping with 2,4,6-$Br_3C_6H_2NO$.

6.24 1986

A New High-Speed Photopolymerization System. Mitchell, R. David; Nebe, William J.; Hardam, William M. (Photosyst. Electron. Prod. Dep., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898, USA). J. Imaging Sci. 1986, 30 (5), 15–17 (Eng.). In a novel high-speed photopolymer imaging system an imagewise exposure to long wavelength radiation forms a photopolymn. sensitizer. A second overall exposure to shorter wavelength, which is not absorbed by the sensitizer precursor polymerizes the image areas where sensitizer was formed. This system has high speed not only because the high intensity overall exposure generates the image polymer, but also because the sensitizer promotes formation of addnl. photopolymn. sensitizer. This allows an imaging step in which only a very low radiation dose is required to generate enough sensitizer for the second overall exposure. Imaging energies as low as 0.1 mJ/cm^2 were achieved; the mechanism an system requirements are discussed.

6.25 1988

Photocyclization of Triphenylimidazole in a Polymer Film. Testa, A.C. (Dep. Chem., St. John's Univ., Jamaica, NY 11439, USA). J. Photochem. Photobiol. A 1988, 43 (1), 105–108 (Eng.). The photocyclization of triphenylimidazole in a poly(vinylbutyral) film was obsd. during absorption and fluorescence studies. The quantum yield was about 35 times less than that in soln.

Multicolor Imaging Process and Materials For. Anon. (USA). Res. Discl. 1988, 293, 695–8 (Eng.). A multicolor imaging process is based on a material producing color images upon exposure to > 2 different kinds of imaging energy (electro-magnetic from IR to X-ray, thermal, mech., or elec.). Thus, a poly(ethylene terephthalate) was coated with a layer contg. p-dimethylaminophenyl-1,3-dioxo-2-indanylmalodinitrile, azo dye thermochromic compd. and pressure-sensitive capsules contg. a leuco dye, and overcoated with a photosensitive layer contg. pyrenequinone mixt., bis(chlorophenyl)tetraphenylbiimidazole, tris(diethylaminotolyl)methane, toluenesulfonic acid, and tri-methylnitrilo-propionate to provide scratch-resistant photo-, thermo-, and pressure-sensitive multi-color recording material. The material was imagewise exposed with UV to provide cyan image, flash exposed with Xe lamp, contacted imagewise with a thermal print head to produce yellow image, and with a printing head contg. a row of electromagnetically driven styli to provide magenta dye sepn. image.

6.26 1989

Dimerizations of p-Rich N-Heteroaromatic Compounds and Xanthine Derivatives. Sekine, Toshikazu; Higuchi, Yoshihiro; Yamada, Tomoko; Murakoshi, Isamu (Fac. Pharm. Sci., Chiba Univ., Chiba, Japan 260). Chem. Pharm. Bull. 1989, 37 (8) 1987–9 (Eng.). N-Methylimidazole, benzimidazole, and N-methylbenzimidazole condensed dehydrogenatively to afford the corresponding sym. dimers when heated in the presence of Pd-Pt/C catalyst and pyridine N-oxide. Imidazole, pyrazole, and N-methylpyrazole did not dimerize under the same conditions. The same reactions using caffeine and 1,7-dimethylhypoxanthine gave the corresponding dimers.

6.27 1990

Photopolymers for Holography. Smothers, William K.; Monroe, Bruce M.; Weber, Andrew M.; Keys, Dalen E. (Exp. Stn. Lab., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19880-0352, USA). Proc. SPlE—Int. Soc. Opt. Eng. 1990, 1212 (Pract. Hologr. 4), 20–9 (Eng.). Photo-sensitive films composed of dye, initiator, acrylic monomers, and polymeric film-forming binder, and their use in recording vol. phase transmission and reflection holograms are described. Systematic variation of monomer–binder combinations reveals that the max. attainable index modulation (hologram efficiency) increases with increasing difference between the refractive indexes of monomer and binder. Addn. of plasticizer is also useful for increasing index modulation. Thermal and wet chem. processing methods for altering hologram properties are described.

Optical-Recording Materials Having New Functions. Sato, Hiroyasu (Fac. Eng., Mie Univ., Tsu, Japan 514). Kokagaku 1990, 14, 8–19 (Japan.). A review with 2 refs. on topics related to optical information recording. These included; light and magnetic field control of a dispersion of photochromic hexaphenylbiimidazolyl in PMMA, and fluorescence of polydiacetylene Langmuir–Blodgett films with adsorbed cyanine dyes which can shift the fluorescence wavelength. The guidelines of developing new functional materials are discussed.

6.28 1991

Improved Photopolymers for Holographic Recording. I. Imaging Properties. Monroe, Bruce M.; Smothers, William K.; Keys, Dalen E.; Krebs, Robert R.; Mickish, Daniel J.; Harrington, Albert F.; Schicker, Scott R.; Armstrong, Mark K.; Chan, Dominic M.T.; Weathers, Carolyn I. (Imaging Syst. Dep., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19880 0352, USA). J. Imaging Sci. 1991, 35 (1), 19–25 (Eng.). Improved photopolymers for holog. recording are described along with a brief review of the basic technol. Holog. diffraction gratings with high refractive index modulation are prepd. from photopolymers contg. a liq. arom. monomer, such as 2-phenoxyethyl acrylate, and an aliph. binder such as cellulose acetate butyrate. Higher refractive index modulation are attained when a second, solid, arom. monomer that contains heavy atoms or polycyclic arom. group is used in combination with the liq. arom. monomer. Holog. mirrors with high refractive index modulations are produced from materials that contain poly(vinyl acetate) or poly(vinyl butyral) binder. The refractive index modulations of mirrors formed in the poly(vinyl acetate)- and poly(vinyl butyral)-contg. materials can be enhanced by treatment with an org. solvent or by thermal treatment.

Improved Photopolymers for Holographic Recording. Mechanism of Hologram Formation. Monroe, Bruce M. Imaging Syst. Dep., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19880 0352, USA). J. Imaging Sci. 1991, 35 (1), 25–29 (Eng.). Holog. photopolymer recording materials that contain liq. monomer, a binder, and a photoinitiator system were investigated. The largest refractive index modulations are obsd. for compns. in which there is a large difference in refractive index between the monomer and the binder. Addn. of a solid monomer to the liq. monomer increases the obsd. refractive index modulation if the added monomer increases the difference in refractive index between the monomer mixt. and the binder. Ways for altering the refractive index within a sample are discussed with ref. to these materials.

Kinetics of Anisotropic Photopolymerization in Polymer Matrix. Krongauz, Vadim V.; Schmelzer, E. Richard; Yohannan, Robert M. (Exp. Stn. Lab., E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19880 0352, USA). Polymer 1991, 32 (9), 1654–62 (Eng.). The photopolymn. of N-vinylcarbazole initiated with o-chlorohexaphenyldiimidiazole in a plasticized polymeric matrix is examd. The photopolymn. rate and yield vary greatly with the distance from the film surface because of the high optical d. of the film and the presence of O. Monomer and O migrate toward the illuminated surface of the film where most of the excitation and reagent consumption takes place. The unidirectional illumination creates a spatially anisotropic distribution of reactants and products. A semiempirical computer model of the spatial dependence of photopolymn. kinetics is presented. Photopolymn. kinetics are studied as a function of film thickness, light intensity and rate of monomer diffusion. Calcns. explain the exptl. obsd. kinetics and predict the time-dependence of the polymer distribution in the film.

Photodissociation of Hexaarylbiimidazole. 1. Triplet-State Formation. Qin, X.Z.; Liu, A.; Trifunac, A.D.; Krongauz, V.V. (Chem. Div., Argonne Natl. Lab., Argonne, FL 60439, USA). J. Phys. Chem. 1991, 95 (15), 5822 (Eng.). The mechanism of photodissocn. of 2-chlorohexaaryl-biimidazole was studied by laser flash photolysis in org. liqs. and by EPR methods in polymer and low-mol.-wt.

org. matrixes. At low temps. (~ 10°K) the UV irradn. produced triplet hexaarylbiimidazole rather than the radicals. No triplet-state decompn. into radicals was obsd. supporting the result of indirect measurement reported by other researchers. At higher temps., the radicals formed from the dissocn. of the singlet state dominate. This is the first direct observation of the hexaarylbiimidazole triplet reported to date. The results are explained by considering the mol. structure and hexaarylbiimidazole mobility.

EUROSPRINT Proofing System. Froehlich, Helmut H. (Du Pont de Nemours G.m.b.H., 6078 Neu Isenburg, Fed. Rep. Ger.). Proc. SPIE—Int. Soc. Opt. Eng. 1991, 1458 (Print. Technol. Images, Gray Scale, Color), 51–60 (Eng.). EUROSPRINT laminated toning film, which is used in proofing to tone CHROMALIN (TM) photopolymer film is described. Development of this dry peel-apart system and its performance are described.

Peculiarities of Anisotropic Photopolymerization in Films. Krongauz, Vadim V.; Schmelzer, E. Richard (Exp. Stn Lab., E. I. du Pont de Nemours and Co., Wilmington, DE 19880-0352, USA). Proc. SPlE—Int. Soc. Opt. Eng. 1991, 1559 (Photopolym. Device, Chem., Appl. 2), 354–76 (Eng.). A detailed numeric anal. is presented of the mechanism of anisotropic photopolymn. in films. A substantial deviation is obsd. from uniformity in distribution of forming polymer. The microscopic observation of the imaged photopolymer reveals formation of the ridge at the boundary of the illuminated region. These peculiarities of the anisotropic photopolymn in polymer matrix can lead to undesirable problems with resoln. in the imaging and electronic systems based on polymer films. The diffusion from the dark regions to the illuminated ones makes the boundaries of the polymd. region more defined. The migration of monomer leads to image contrast enhancement since the yield of polymer is higher than that which could be obtained in the absence of monomer diffusion.

6.29 1992

Photodissociation of Hexaarylbiimidazole. 2. Direct and Sensitized Dissociation. Liu, An Dong; Trifunac, Alexander D.; Krongauz, Vadim V. (Chem. Div. Argonne Natl Lab., Argonne, IL 60439, USA). J. Phys. Chem. 1992, 96 (1), 207–11 (Eng.). Photodissocn. of a widely used photopolymn. initiator, 2-chlorohexaarylbiimidazole (I), is studied in CH_2Cl_2 soln. in the absence and presence of the visible light photosensitizing dye, 2,5-bis(2,3,6,7-tetrahydro-1H, 5H-benzo[*ij*]quinolizin-l-yl)methylenecyclopentanone (II). Laser flash photolysis at 480 nm is employed. In the absence of II triarylimidazolyl radicals (L•) are produced. In the presence of II, an increase in L• formation is obsd. This increase occurs by the dissocn. of the I radical anion formed by electron transfer from the excited singlet state of II to I. The obsd. formation of L• radicals exhibits a linear dependence on I concn. The rate const. of electron transfer obtained from this dependence is equal to $(2.2 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$. No reaction between the excited triplet state of II and I is found.

Photoinduced Electrification at the Contact Interface Between Photosensitive Layer and Insulator Films. Shirai, Yasuo; Suzuki, Miho; Matsuo, Shigeharu; Miyagawa, Toshio (Fac. Eng. Tokyo Inst. Polytech., Atsugi, Japan 243-02). Nippon Kagaki Kaishi 1992, (2), 215–20 (Japan.). The behavior of electrification induced by photopolymn. at the contact interface between a photosensitive layer and an insulator film was studied with the aim of developing a new recording material and a method for prepg plastic electrets. The photosensitive system to induce electrification was made of a photosensitive layer, comprising a polymer as a binder, an initiator for photopolymn. (HABI), a chain-transfer agent, and acrylic monomer, which was coated on an Al plate, and a polymeric insulator film as a contact material was then laminated on the photosensitive layer. A neg. or pos. charge was induced on the polymd. layer surface by peeling off the cover film after imagewise exposure according to the triboelec. series of the contact films. A neg. charge was obtained with nylon 66 and poly(vinyl alc.), which tended to be pos. in the triboelec. series. In contrast, a pos. charge was obtained with cellulose triacetate or polyethylene film that tended to be neg. The quantity of the charge induced on the layer also depended on the triboelec. series of the films, and on the thickness and the compn. of the photosensitive layer. The above and other exptl. results suggested that the photoinduced electrification was attributed to the contact tribocharging involving the contraction of the photosensitive layer.

Investigation of Electron Transfer Between Hexaarylbiimidazole and Visible Sensitizer. Lin, Yi; Liu, Andong; Trifunac, Alexander D.; Krongauz, Vadim V. (Chem. Div. Argonne Natl. Lab., Argonne, IL 60439, USA). Chem. Phys. Lett. 1992, 198 (1–2), 200–6 (Eng.). Photoinduced electron transfer between the hexaarylbiimidazole (HABI) and visible sensitizer 2,5-bis[(2,3,6,7-tetrahydro-lH,5H-benzo[ij]quinolizin-1-yl)methylene]cyclopentanone, in liq. soln. was studied esptl. The relative fluorescence quantum yield of the sensitizer mol. was measured as a function of HABI concn. An exponential dependence on HABI concn. was obsd. for the sensitizer fluorescence yield, from which the crit. distance for the electron transfer interaction was detd. to be 12 Å. The time-dependent fluorescence quenching was studied with the time correlated single-photon counting technique. The dynamics of the electron transfer process was detd. by comparing the exptl. data to existing models of electron transfer in liqs. The inclusion of the relative diffusion between the electron donor and acceptor mols. is necessary to fit all the observations and to obtain accurate transfer parameters.

Photoinduced Electrification at the Contact Interface Between Photo-Polymerizable Layer and Metal Films. Shirai, Yasuo; Suzuki, Miho (Fac. Eng., Tokyo Inst. Polytech., Abugi, Japan 234–02). Nippon Kagaku Kaishi 1992, (10), 1186–8 (Japan.). The behavior of electrification induced by light at the contact interface between a photopolymerizable layer and metal films was studied with the aim of developing a novel photofunctional material. Surface potentials from −10 V to −500 V were induced on the photopolymd. layer by peeling off the contact metal film after imagewise exposure, depending on the work function (3.63–5.1 eV) of the metals. The behavior of this photoinduced electrification however, can not be accounted for by the contact charging model unlike the case that insulator films are used as contact materials. Some exptl. results suggest that this photoinduced electrification is attributed to the charge transfer involving the reaction of a metal and the radicals produced photochem. in the photosensitive layer.

Photochemical Behavior of Hexaarylbiimidazole in Solid Polymer Matrixes. Morita, Hiroshi; Minagawa, Shigenori (Fac. Eng., Chiba Univ., Chiba, Japan 260). J. Photopolym. Sci. Technol. 1992, 5 (3), 551–6 (Eng.). Bis(2-o-chlorophenyl)-4,5-diphenylimidazole] (I) in poly(Me methacrylate) PMMA matrix by UV irradn. produced 2-(o-chlorophenyl)-4,5-diphenyl) imidazolyl radical having UV absorption at 348 nm, which changed into 2-(o-chlorophenyl)-4,5-diphenylimidazole (II) showing UV absorption at 300 nm and emission band at 438 nm. Furthermore, the prolonged irradiation of II produced 2-o-chlorophenyl-9,10-phenathroimidazole having emission band at 440 nm. Meanwhile, irradn. of I in the bromo- and chloromethylated polystyrene matrix gave an absorption spectrum around 260 nm by crosslinking reaction of the polymer induced by I in addn., to absorption and emission spectra described above.

6.30 1993

Photopolymers in Electrostatic Imaging Applications. Blanchet, Graciela B.; Dessauer, R. (E. I. du Pont de Nemours, Cent. Res. Dep., Wilmington, DE 19898, USA). J. Imaging Sci. Technol. 1993, 37 (3), 238–45 (Eng.). In this work the authors discuss the feasibility of using photopolymers as electrostatic masters in electrophotog. because they provide the advantage of permanent image formation necessary for multiple copy applications. For the compns. described here, multiple copies can be achieved without any measurable degrdn. in image quality or image resoln. In addn., the latent image of photopolymer masters can be precisely tailored by independently adjusting the elec. properties of the exposed and exposed regions, which, in turn, control the dot gain and dot range of the image on paper. A detailed description of the chem. and phys. characteristics of photopolymer electrostatic masters is presented here. The effects of temp. and humidity on the elec. properties and, consequently, on image quality are also described.

6.31 1994

Visible Light Photopolymerization Initiated by Hexaarylbiimidazole (HABIs). Yang, Weidong; Yang, Yongyuan; Wang, Junshen; Zhang, Cunlin; Yu, Meiwen. Institute of Photographic

Chemistry, Academia Sinica, Beijing, Peop. Rep. China. J. Photopolym. Sci. Technol. (1994), 7 (1), 187–92. Kinetics of Me methacrylate (MMA) photopolymn. was studied using 2,5-bis(4′-diethylaminobenzylidene)cyclopentanone (DEAP) and 2,5-bis(4′-dimethylaminobenzylidene)cyclopentenone (DMAP) as visible light sensitizers and 2-chlorohexaarylbiimidazole (o-Cl-HABI) as polymn. initiator. The photopolymn. study were carried out in toluene soln. at 30°C. The polymn. rate was proportional to the concn. with exponent of 0.85, −0.28, 0.30, 1.0 for DEAP, o-Cl-HABI, 3-mercapto-4-methyl-4H-1,2,4-triazole additive, MMA, resp. The photopolymer materials can record stable hologram with sensitivity of 30–300 mJ/cm^2 and resoln. of 4000 1/mm.

Characterization of the DuPont Photopolymer for Three-Dimensional Holographic Storage. Curtis, Kevin; Psaltis, Demetri (Department of Electrical Engineering, California Institute of Technology, Pasadena, CA 91125, USA). Appl. Opt. 1994, 33 (23), 5396–9 (Eng.). DuPont's HRF-150 photopolymer film is investigated for use in three-dimensional holog. memories. Measurements of sensitivity, hologram persistence, the lateral spread of the photoinitiated reaction, and the variation of diffraction efficiency with modulation depth, spatial frequency and tilt angle, and intensity are reported. We obsd. that the diffraction efficiency of the HRF-150 photopolymer for a given exposure decreases with increases in intensity and grating tilt angle. The holograms were nondestructively reconstructed for long periods of time at room temp. The photoinitiated reaction spread less than 100 μmeters over a period of 16 h.

ESR Study of Lophyl Radicals in Dry Films. Khudyakov, Igor V.; Turro, Nicholas J.; Weed, Gregory C.; Caspar, Jonathan V. (Department of Chemistry, Columbia University, New York, NY, USA). ICPS 94 Phys. Chem. Imaging Syst., IS&T's 7th Annu. Conf. 1994, 2, 682–6 (Eng.). IS&T—The Society for Imaging Science and Technology: Springfield, VA. 2-(2′-Chlorophenyl-2′-(2′-chlorophenyl)-4,4′,5,5′-tetraphenylbisimidazoles (o-Cl-HABI and other hexaarylbisimidazoles are commonly termed HABIs) have been used as free radical initiators in photopolymer imaging for more than 2 decades. In the present work we investigated the photochem. of a representative HABI, o-Cl-HABI. HABI undergo thermolysis, direct and sensitized photolysis in both the liq. and the solid phase with the formation of corresponding lophyl radicals. ESR was used to study formation and decay kinetics of these radicals in photoexposed E'MMA films contg. triacetin, TMPTA, N-phenylglycine, 2-mercaptobenzoxazole, leuco Crystal Violet and o-Cl-HABI.

6.32 1995

ESR Study of Lophyl Free Radicals in Dry Films. Caspar, Jonathan V.; Khudyakov, Igor V.; Turro, Nicholas J.; Weed, Gregory C. (Central Research and Development Department, E. I. du Pont de Nemours and Company). Macromolecules (1995), 28 (2), 636–41. Photolysis of 2-(2′-chlorophenyl)-2′-(2′-chlorophenyl)-4,4′,5,5′-tetraphenylbisimidazole (D) into corresponding lophyl free radicals (R•) was studied by steady-state and time-resolved (TR) CW ESR in dry films of PMMA at 6–400 K and in a frozen liq. soln. at 77 K. Steady-state ESR expts. demonstrate the formation of spatially proximate electronically interacting radical pairs (RPs) R•. . .R• as well as the formation of spatially isolated free radicals R•. The ratio of amts. of photogenerated R• to R•. . .R• depends upon the temp. and the properties of the film. This ratio increases with increasing temp., and at the same temp. the ratio is larger in films contg. a plasticizer (triacetin). At low temps. (6–200 K) RPs are obsd. and are characterized by zero-field splitting (ZFS) values of $2D \approx 250$ G (corresponding to intraradical distance of $r \sim 6$ Å) and $E \leqslant 10$ G. Films which do not contain a plasticizer demonstrate ESR spectra of RPs with $2D \sim 100$ G ($r \sim 8$ Å) at room, and even at elevated, temps. (up to 400 K) as well as ESR spectra of RPs of two types ($r \sim 6$ and 8 Å) at reduced temps. Thus, the measurement of ZFS parameters of RPs produced by the photolysis of D in films can be used to characterize photopolymer film. TR ESR spectra of the triplet state of D were obsd. in films at 53 K. Simulation of the spectra leads to ests. of $2D \sim 2200$ G and $E \sim 165$ G. Decay kinetics of the lophyl radicals in films was satisfactorily described by polychromatic second-order kinetics with a rectangular distribution of reactivity. The estd. max. difference in activation energies for a film without a plasticizer is ca. 4 kcal/mol, suggesting a range of recombination rate consts. of ca. 10^3.

Some Aspects of the Role of Amines in the Photoinitiated Polymerization of Acrylates in the Presence and Absence of Oxygen. Bradley, Grant; Davidson, R. Stephen (The Chemical Laboratory, The University of Kent, Canterbury, UK CT2 7NH). Recl. Trav. Chim. Pays-Bas 1995, 114 (11/12), 628–33 (Eng.). Triethanolamine (1), methyldiethanolamine (2) and dimethylethanolamine (3) are used in conjunction with the 2-(2-chlorophenyl)-4,5-diphenylimidazolyl radical and triplet benzophenone to initiate the polymn. of lauryl acrylate. The radical abstrs. a hydrogen atom from the amine to generate an α-aminoalkyl radical. Hydrogen-atom abstraction occurs rather than electron followed by proton transfer, which is confirmed from the order of reactivity of the amines towards the lophyl (triarylimidazoyl) radical i.e. $2 \gg 1 > 3$. The imidazolyl radicals abstr. hydrogen from thiols in a similar fashion more effectively to give thiyl radicals which initiate polymn. of the acrylate. The effectiveness of the amines to reduce oxygen inhibition is $1 < 3 < 2$. The ability of the amines to act as synergists in the polymn. of thin films of lauryl acrylate initiated by lophyl radical and triplet benzophenone is assessed. The efficiency of the amines is $2 > 1 > 3$ for reaction with lophyl radicals whereas with triplet benzophenone the three amines gave similar amts. of polymer. For amines 2 and 3, two types of amino alkyl radical can be generated. Radicals of type $>NCHCH_2OH$ are more effective initiators than $CH_2N<$.

Characterization of DuPont Photopolymers in Infrared Light for Free-Space Optical Interconnects. Zhou, H.J.; Morozov, V.; Neff, J. (Optoelectronic Computing Systems Center University of Colorado, Boulder, CO 80309-0525, USA). Appl. Opt. 1995 (Pub. 1995), 34 (32), 7457–9 (Eng.). DuPont photopolymer as a potential holog. material for an optical interconnect system was studied. The optimized conditions for an optical interconnect system was studied. The optimized conditions of recording plane-wave holograms with ~ 99% effective diffraction efficiency for IR reconstruction were obtained by testing different DuPont photopolymers and different copying parameters. The scattering ratios of the holograms recorded with DuPont photopolymers HRF600-10, HRF600-20, and HRF600-38 were measured and compared.

6.33 1996

Digital Imaging Using IR Induced Tack and Toning. Anon. (UK). Res. Discl. 1996, 385, 298–299 (No. 38526) (Eng.). Digital proofing medium is described which can be used for digital color proofing systems of both the surprint and overlay types. The medium provides imagewise IR-induced transfer of a tack from a film coating to a receptor sheet. The transferred image areas are subsequently toned. IR induces chem. reaction in the hexaarylimidazole dimer/1,4-dihydropyridine deriv. system, where the reaction products plasticize acrylic polymer-based coating to photoinduce transferable tack.

Magnetic Field and Polymer Matrix Effects on Photo-Chemical Reactions of Hexaaryl-Biimidazole in Solid Polymer Matrixes. Morita, Hiroshi; Kanazawa, Kazuhiro; Hashimoto, Katsuhiko; Tsubame, Tetsuya (Graduate School Sci. Technol., Chiba Univ., Chiba, Japan 263). J. Photopolym. Sci. Technol. 1996, 9 (1), 65–71 (Eng.). Upon exposure to UV light, bis[2-(o-chlorophenyl)-4,5-diphenylimidazole] (o-Cl-HABI) in solid polymer matrixes such as bromo- and chloromethylated polystyrene (BCMS) and chloromethylated polystyrene (CMS) generates 2-(o-chlorophenyl)-4,5-diphenylimidazolyl radical which rapidly abstracts a hydrogen atom from the polymer to produce polymer radicals which initiate crosslinking reaction of the polymer films. Efficiency of crosslink formation and relative efficiency in producing the polymer radicals were evaluated from the measurements of the gel fraction of solid films and fluorescence intensity of the imidazole. Both the efficiencies are higher in BCMS than in CMS, suggesting that a high sensitivity of crosslink formation is mainly due to high efficiency in producing the polymer radicals. By the application of a magnetic field the efficiency of crosslink formation of BCMS/o-Cl-HABI decreases slightly.

6.34 1997

Laser-Flash Photolysis in High-Speed Photopolymer Coating Layers Containing Carbonyl-Biscoumarin Dyes and 2,2′-Bis(2-Chlorophenyl)-4,4′,5,5′-Tetra-Phenyl-1,1′-Bi-1*H*-Imidazole.

Urano, Toshiyuki; Nagasaka, Hideki; Shimizu, Shigeki; Ito, Ffimto; Shimizu, Makoto; Takahara, Shigeru; Yamaoka, Tsuguo (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan 227). Bull. Chem. Soc. Jpn. 1997, 70 (7), 1659–1664 (Eng.), Chemical Society Japan. The sensitization mechanisms of keto-coumarin dyes with a radical generating reagent (10,10′-carbonyl-bis[1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]benzopyrano[6,7,8-11]-quinolizin-11-one) (KCD-J), 3,3′-carbonylbis[7-(diethylamino)-2H-1-benzopyran-2-one] (KCD-DA) with 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1H-imidazole (BI), in a poly(Me methacrylate) (PMMA) film have been investigated by laser-flash photolysis using a total reflection cell. The triplet decay time of the dyes in a PMMA film was quenched by BI with a k_qs of 1.3 and 0.60×10^5 mol dm^{-3} s^{-1} for KCD-J and KCD-DA. The fluorescence and initial absorption for KCD-DA were not quenched by BI in a PMM film. The fluorescence was quenched at a quenching distance of 10.0 Å, and the initial triplet absorption was quenched for KCD-J in a PMMA film. These results show that a MO-static sensitization from the triplet to BI is the predominant process in a photoinitiation system contg. KCD-DA, and that both static sensitization from the singlet excited state to BI and non-static sensitization the triplet to BI exist in a photoinitiation system contg. KCD-J.

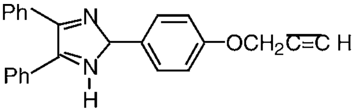
Kinetic Study of Long Wavelength Light Photopolymerization Initiated by Cyanine Dye and Hexaarylbiimidazole. Lidong, Li; Yongyuan, Yang; Wei, Xu; Weidong, Yang; Ping, Chen; Cunlin, Mang (Inst. of Photogra. Chem., the Chinese Academy of Sciences, Beijing, Peop. Rep. China 100101). J. Photopolym. Sci. Technol. 1997, 10 (2), 347–352 (Eng.), Technical Association of Photopolymers, Japan. The long-wavelength sensitive photoinitiating system composed of 3-n-propylsulfonic acid-2-[5-3-n-propylsulfonic acid triethylamine-2-benzothiazolinylidene)-1,3-pentadienyl-benzoxazolium inner salt (SP-36), 2-chlorohexaarylbiimidazole (o-Cl-HABI) and 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA), which acted as sensitizer, initiator and hydrogen-donor resp., can be used to initiate the polymn. of Me methacrylate (MMA). The kinetic study was carried out in trichloromethane soln. at 30°C by using dilatometer. The relation between the polymn. rate and the concns. of SP-36, o-Cl-HABI, IVITA and IAMA was studied. The kinetic formula was deduced: $R_p = K[\mathrm{SP\text{-}36}]^{0.45}\,[\mathrm{HABI}]^{0.40}\,[\mathrm{MTA}]^{0.24}\,[\mathrm{MMA}]^{1.0}$. The photopolymer system can record stable hologram under helium–neon laser.

Determination of Formal Potentials and Anion Radical Lifetimes for Hexaarylbiimidazole Derivatives. Oliver, Edward W.; Evans, Dennis H. (Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, USA). J. Electroanal. Chem. 1997, 432 (1–2), 145–151 (Eng.), Elsevier. The redn. of three hexaarylbiimidazole (HABI or L_2) derivs. was studied in acetonitrile by cyclic voltammetry. The redn. of o-Cl-HABI was previously shown to occur by an ECE process. The radical anion initially formed in the 1st electron transfer (L_2-) undergoes a fast cleavage reaction to produce the triaryl-imidazole anion ($L-$) and the radical (L•), the latter of which is reduced at the electrode to produce a 2nd anion. The two other HABI derivs. studied in this study show similar behavior. Homogeneous redox catalysis was used to det. the formal potential (E_1^0) for the L_2/L_2-couple for each of the three HABIs and the rate const. of the cleavage react for o-Cl-HABI ($k_f = (5.6 \pm 1.0) \times 10^6$ s^{-1}). The values of E_1^0 are -1.85 ± 0.01 V vs. the ferrocene/ferrocenium formal potential for o-Cl-HABI and TCTM-HABI (tetrachlorotetramethoxyhexaphenylbiimidazole), and -2.01 V for o-EtO-HABI. Cyclic voltammetry was also used to det. the formal potential for the L/L$-$ couple, E, O, and the rate const., k_{dim}, for dimerization of the imidazolyl radicals. The results for E_2^0 are -0.15, -0.27 and -0.15 V vs. ferrocene and k_{dim} is 1.1×10^4, 4.5×10^3 and 4.2×10^3 M^{-1} s^{-1} for o-Cl-HABI, o-EtO-HABI and TCTM-HABI, resp.

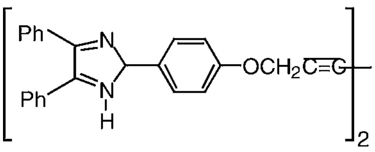
Synthesis of 4,5-Bisaryl-2-(2,5-dimethylthiophen-3-yl)imidazoles and their Dimers. Bajinquan; Han, Xiao Chun; Wang, Yong Mei; Meng, Ji Ben (Dep. Chem., Nankai Univ., Tianjin, Peop. Rep. China 300071). Chin. Chem. Lett. 1997, 8 (12), 1031–1032 (Eng.), Chinese Chemical Society. 4,5-Diphenyl-, 4,5-bis(4-methylphenyl)-, and 4,5-bis(4-methoxyphenyl)-2-(2,5-dimethylthio-phen-3-yl)imidazoles were synthesized. Oxidn. of the obtained imidazoles with potassium ferricyanide in water–alc. soln. of alkali gave the corresponding dimers.

Synthesis and Photochromism of Dimers of 4,5-Diaryl-2-(2,5-dimethylthiophen-3-yl)imidazolyl. Bai, Jin-Quan; Han, Xiao-Chun; Wang, Yong-Mei; Meng, Ji-Ben (Department of Chemistry, Nankai University, Tianjin, Peop. Rep. China 300071). Chin. J. Chem. 1997, 15 (6), 553–555 (Eng.), Science Press. 4,5-Di-Ph, 4,5-di-(4-methylphenyl), and 4,5-di(4-methoxyphenyl)-2-(2,5-dimethylthiophen-3-yl)imidazoles I (Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$) were synthesized. Oxidn. of the obtained imidazoles with potassium ferricyanide in water–alc. soln. of alkali gave the corresponding dimers II. The structures were characterized by IR, ^1H NMR, mass spectroscopy, and elemental anal. The dimers showed photo-chromism in soln. on irradn.

Free Radicals. XXV. Triarylimidazolyl Radicals Containing Triple Bonds in the Side Chain. Pryanichichnikova, M.K.; Tikhonova, L.G. (Ogarev Mordovian State University, Saransk, Russia 430000). *Russ. J. Org. Chem.* 1997, 33 (9), 1311–1314 (Eng.), MAIK Nauka/ Interperiodica Publishing. 2,4,5-Triarylimidazoles cpmtg. mono- and diacetylene residues in the para position of the benzene ring at C2 (I and II)



I



II

were synthesized. Oxidn. of these compds. yielded corresponding radicals which were isolated as dimers. The rate consts. of dissocn. of the dimers were detd., and the ability of triarylimidazoles and their dimers to solid-phase polymn. was studied.

Synthesis of 1,4′-Linked Oligoimidazoles and Similar Compounds. Suwinski, Jerzy; Wagner, Pawel (Pol.). Zesz. Nauk. Politech. Slask., Chem. 1997, (135), 73–80 (Pol.), Wydawnictwo Politechniki Slaskiej. Anrorc type reaction of 1,4-dinitroimidazole with 4-amino-arylimidazoles (prepd. by redn. of 1-aryl-4-nitroimidazoles) afforded derivs. of 1,4′-biimidazole and triimidazole. In similar manner 1,3-bis(4′-nitro-l′-imidazolyl)benzenes were prepd.

6.35 1998

Kinetic Study of Visible Light Photosensitive Polymerization Initiation of Methyl Methacrylate. Li, Lidong; Yang, Yongyuan; Zhao, Chunying; Xu, Wei; Chen, Ping; Zhang, Cunlin (Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, Peop. Rep. China 100101). Ganguang Kexue Yu Guang Huaxue 1998, 16 (l) 1–7 (Ch.), Kexue Chubanshe. The long-wavelength (633 nm) sensitive photoinitiating system composed of 1,3,3-trimethyl-2[5-(1,3,3-trimethyl-2-indolylidene)-1,3-pentadienyl]-indoliumiodide (NK-529), 2-chlorohexaarylbiimidazole (o-Cl-HABI) and hydrogen donor, 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA) can be used to initiate the polymn. of Me methacrylate (MMA). The kinetic study was carried out in chloroform soln. of Me methacrylate (MMA). The kinetic study was carried out in chloroform soln. at 30°C by dilatometry. The relationship between polymn. rate and the concn. of NK-529, o-Cl-HABI-MTA and MMA was studied. As the result shows, the kinetic formulation was deduced: $R_p = K[\text{NK-529}]^{0.51}[\text{HABI}]^{0.41}[\text{MTA}]^{0.36}[\text{MMA}]^{1.0}$. The photopolymer system can record stable hologram under 633 nm He–Ne laser radiation.

Double-Amplified Photoinitiator Systems. Urano, Toshiyuki; Ito, Hideki; Takahama, Keiji; Yamaoka, Tsuguo (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan 227). Rad. Tech ’98 North Am. UV/EB Conf. Proc. 1998, 734–745 (Eng.). RadTech’98 International North America: Northbrook, Ill. Photoinitiation processes for photopolymer coating layers have been investigated with respect to quenching rates by a laser flash photolysis using total reflection cell as well as to decompn.-quantum yield of sensitizer dyes and radical-generating reagents by a gel permeative chromatog. anal. (GPC); the sensitizer dye, 2-[p-(diethylamino)styryl]naphtho[1,2-d]thiazole (DNT), and the radical-generating reagent, 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-lH-imidazole (BI). Strong fluorescence and no transient absorption were obtd. at excitation of 355 nm laser pulse, and the fluorescence was statically quenched with a quenching distance, R = 11 Å. The high-quantum. yield of decompn. (O) were obtained as O (DNT) = 2.5 and O (BI) = 9.3 for DNT and BI in the presence of acrylate monomers, trimethylolpropane triacrylate (TMPTA) at 488 nm exposure of 3 mJ-cm^2 required to form photohardened image, though no decompn. of DNT and BI were detected in the absence of TMPTA. The results imply that the photoinitiator system accelerated photopolymn. of the acrylate monomers not only by the efficient-static-dye sensitization but also by chain decompn. of DNT and BI.

Photopolymer Materials for Holography. Cunlin, Zhang; Jia, Zhao; Jingsuo, He; Lidong, Li; Yongyuan, Yang (Dep. of Physics, Capital Normal University, Beijing, Peop. Rep. China 100037). J. Photopolym. Sci. Technol. 1998, 11 (l), 85–88 (Eng.), Technical Association of Photopolymers, Japan. The photopolymer holog. recording material is composed of a monomer, a binder, a photoinitiator system that contains a sensitizer, a initiator and a hydrogen donor. The photopolymer materials is sensitive to red light (633 run), the effective exposure sensitivity of the photopolymer plate can be increased by adding the third beam to expose the photopolymer plate simultaneously during the initial holog. exposure. Mechanisms of photoinitiating polymn. and hologram formation are discussed. More than 80% of reflection grafting diffraction efficiency can be obtained. The holog. gratings have a good phys. and chem. stability under ambient conditions.

Pyrolysis and Photolysis of 1-Aroylamino-4,5-Diaryl-1,2,3-Triazoles: Generation and Thermal Transformations of 4,5-Diaryl-1,2,3-Triazolyl Radicals. Hadjiantoniou-Maroulis, C.P.; Charalambopoulos, A.Ph.; Maroulis, A.J. (Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece GR-54006). J. Heterocycl. Chem. 1998, 35 (4), 891–894 (Eng.), Hetero Corporation. The pyrolysis of 1-aroylamino-4,5-diphenyl-1,2,3-triazoles yields, presumably via the 4,5-diphenyl-1,2,3-triazolyl radical, 2,3-diphenyl-2H-azirine and 2-aryl-4,5-diphenylimidazoles as the major products. Products. Upon irradn. 1-benzoylamino-4,5-diphenyl-triazole gives 4,5-diphenyl-1(2)H-1,2,3-triazolyl radical, together with benzamide and 1,2-dibenzoylhydrazine. The latter products result from the benzoyl-amino radical by hydrogen atom abstraction and dimerization resp.

Syntheses and Properties of Coordination Complexes of Imidazole Types. Mao, Qing; Lin, Zhamu (School Pharmacy, West China University Medical Sciences, Chengdu, Sichuan, Peop. Rep. China 610066). Sichuan Shifan Daxue Xuebao, Zirun Kexueban 1998, 21 (4), 436–440 (Ch.), Sichuan Shifan Daxue. The authors have reported three types of coordination complexes of imidazole with Cu, Co and Ni which were synthesized from imidazole, biimidazole and transition metal acetate. Their properties were systematically characterized by TGDK IR, ^{60}Co-γ irradn., XPS and EPR.

Photopolymerization of MMA Initiated by Cyanine Dye and Hexaarylbiimidazole. Zhao, Chunying; Yang, Yongyuan; Li, Lidong; Xu, Wei; Feng, Shujing (Institute of Photographic Chemistry, The Chinese Academy of Sciences, Beijing, Peop. Rep. China 100101). Chin. J. Polym. Sci. 1998, 16 (4), 310–315 (Eng.), Science Press. The photoinitiating system composed of 1-ethyl-3′-Me thiacyanine bromide (C-I), 2-chlorohexaarylbiimidazole (o-Cl-HABI) and 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA), which act as sensitizer, initiator and hydrogen-donor resp., can be used to initiate the polymn. of Me methacrylate (MMA). The kinetic study was carried out in trichloromethane soln. at 30° by using dilatometry. The relation between the polym. rate and the concns. of C-1, o-Cl-HABI, MTA and MMA was studied.

Photoinitiating Systems and Photopolymer Materials for Holography. Zhang, Cunlin; Zhao, Jia; He, Jingsuo; Li, Lidong; Yang, Yongyuan (Department of Physics, Capital Normal University, Beijing, Peop. Rep. China 100037). Proc. SPIE—Int. Soc. Opt. Eng. 1998, 3559 (Holographic Displays and Optical Elements 11), 81–87 (Eng.), SPIE—The International Society for Optical Engineering. In this paper, the kinetics of photosensitive initiating polymn. and photopolymer holog. recording materials were studied. Four sensitizers that could be sensitive to He–Ne (632.8 nm) laser were synthesized and chosen for the study: (1) NK 529 (2) NK 3960 (3) (MCD) (4) ECD. The long-wavelength sensitive photoinitiating system are composed of one of the four compds. above, 2-chlorohexaarylbiimidazole (o-Cl-HABI) and 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA), which acted as sensitizer, initiator and hydrogen-donor resp. The kinetic study was carried out by using dilatometer, we found the relationships between the rate of polymn. and the concn. of each component. We believe that the photopolymn. was initiated by free radicals which were produced by the electron transfer between the sensitizer and the initiator in the excited state. Comparing the monomer conversion of these four systems, we found: MCD > ECD > NK 529 > NK 3960. We chose the system (MCD-HABI-MTA) as a photoinitiating system of photopolymer holog. materials. The holog. material was composed of the above photoinitiating system, a binder, a mono- or multifunctional monomer, and other additives. Adding the third beam to expose the photopolymer plate simultaneously during the initial holog. exposure can increase the effective exposure sensitivity of the photopolymer plate. Mechanisms of photoinitiating polymn. and hologram formation are discussed. More than 80% of reflection grating diffraction efficiency can be obtained. The holog. gratings have a good phys. and chem. stability under ambient conditions.

Laser Flash Photolysis in High-Speed Photopolymer Coating Layers: Elucidation of Radicals Generated from Coumarin Dye-Sensitized Photoinitiator Systems. Hino, Etsuko; Urano, Toshiyuki; Ito, Hiroto; Shimizu, Makoto; Yamaoka, Tsuguo (Research Center, Mitsubishi Chemical Corporation, Aobaku, Yokohama, Japan 227). Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 1998, 315, 337–342 (Eng.), Gordon & Breach Science Publishers. Radical generation from photoinitiation systems contg. a carbonylbiscoumarin dye with a radical-generating reagent, 3,3′-carbonylbis[7-(diethylamino)-2H-l-benzopyran-2-one] (KCD-DA), with 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1H-imidazole, (BI) in a poly(Me methacrylate) (PMMA) film were investigated by laser flash photolysis using a total reflection cell. Imidazolyl radical (Im•) was predominantly generated from carbonyl-biscoumarin triplet-sensitized decompn. of BI, the quantum yield, Ø of Im• at an infinite concn. of BI was measured, Ø = 0.5–1.4. The high quantum yield implies an efficient KCD-DA triplet-sensitized photoinitiation. system contg. BI.

Electrochemical Determination of Mechanistic, Thermodynamic and Kinetic Properties for Hexaarylbiimidazole Derivatives and N-F Type Fluorinating Reagents. Oliver, Edward Walter. Univ. of Delaware, Newark, DE, USA. Avail. UIVII, Order No. DA9906866. (1998), 107 pp. From: Diss. Abstr.

Laser Flash Photolysis in High-Speed Photopolymer Coating Layers; Elucidation of Radicals Generated from Coumarin Dye-Sensitized Photoinitiator Systems. Urano, Toshiyuki; Hino, Etsuko; Ito, Hiroto; Shimizu, Makato; Yamaoka, Tsuguo (Research Centre, Mitsubishi Chemical Corporation, Yokohama, Japan 227). Imaging Sci. J. 1998, 46 (3/4), 103–106 (Eng.). Royal Photographic Society of Great Britain. Radical generation from photoinitiation system containing a carbonylbiscoumarin dye, 3,3′-carbonylbis(7-(diethylamino)-2H-1-benzopyran-2-one) (KCD-DA), with a radical generating reagent, 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1H-imidazole (BI) in a poly(Me methacrylate) film were investigated by laser flash photolysis using a total reflection cell. The imidazolyl radical (Im•) was predominantly generated from KCD-DA triplet-sensitized decompn. of BI, where the quantum yield $Ø_{inf}{}^{o}$ of Im• at an infinite concn. If BI was measured as $Ø_{inf}{}^{o} = 0.5–1.4$, the high quantum yield $Ø_{im}{}^{o}$ implies an efficient KCD-DA triplet-sensitized photoinitiation system contg. BI. [1707-68-2].

6.36 1999

Photopolymerization Mechanisms of Acrylates in Poly(Methyl Methacrylate) Films. Urano, Toshiyuki; Ito, Hideki; Takahama, Keiji; Yamaoka, Tsuguo (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan 227). Polym. Adv. Technol. 1999, 10 (4), 201–205 (Eng.), John Wiley & Sons Ltd. Photoinitiation processes for photopolymer coating layers were investigated with respect to quenching rates by a laser flash photolysis using a total reflection cell, as well as to the decompn.-quantum yield of a sensitizer dye and a radical-generating reagent by a gel permeative chromatog. anal. (GPC); the sensitizer dye, 2-[p-(diethyl-amino)styryl]naphtho[1,2-d]-thiazole (DNT) and the radical-generating reagent, 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1H-imidazole (BI). From expts. using flash photolysis, strong fluorescence was obsd. At excitation of 355 nm laser pulse, though no transient absorption was obsd. The fluorescence was statically quenched by BI with a quenching distance, R = 11 Å. From the expts. using GPC, the high-quantum yield of decompn. Ø was obtained as Ø (DNT) = 3 and Ø (BI) = 9 for DNT and BI in the presence of acrylate monomers, trimethylol-propane triacrylate (TMPTA), at 488 nm exposure of 3.36 mJ/cm which was required to form a photo-hardened image, however no decompn. of DNT and BI was detected in the absence of TMPTA. The results imply that the photoinitiator system undergoes efficient static-dye sensitization and efficient polymn. of the acrylate monomers accompanied with the chain decompn. of DNT and BI.

Sensitizer Dyes and Sensitization Mechanisms in Photopolymer Coating Layer II. Urano, Toshiyuki; Ishikawa, Masayo; Sato, Yuko; Itoh, Hiroki (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan). J. Photopolym. Sci. Technol. (1999), 12 (5), 711–716. Quenching of imidazoyl radical (Im•) produced in 2-[p-(diethyl-amino)styryl]naphtho[1,2-d]thiazole (NAS) sensitized photolysis of 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1H-imidazole (BI) in PMMA film in the presence of 2-mercapto-benzothiazole (MBT) was studied by laser flash photolysis using a total reflection cell. It was obsd. that MBT acted as an accelerator increasing the initial concn. of Im• by slowing down the back electron-transfer from BI anion to NASA cation, and also quenched Im• radical by hydrogen transfer.

Quenching of Radicals Formed in a Photopolymer Layer by an Acrylate Monomer. Urano, T.; Ishikawa, M.; Itoh, H. (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan 227). Imaging Sci. J. (1999), 470, 121–125 (Eng.), Royal Photographic Society of Great Britain. The quenching of imidazoyl radicals (Im) in photoinitiator systems consisting of an aminostyryl dye and a radical generating reagent by acrylate monomers in poly(Me methacrylate) (PMMA) films was investigated by laser flash photolysis using a total reflection cell. In addn., the quenching of Im by oxygen in the presence and absence of poly(vinyl alc.) (PVA) overlayer as an oxygen barrier was discussed. [1707-68-2].

6.37 2000

Photolysis of Hexaarylbiimidazole Sensitized by Dyes and Application in Photopolymerization of Methyl Methacrylate. Gao, Fang; Xu, Jin-Qi; Song, Xiao-You; Li, Li-Dong; Yang, Yong-Yuan; Feng, Shu-Jing (Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, Peop. Rep. China). Chin. J. Chem. (2000), 18 (3), 280–285. Kinetic studies on the near-UV photo-initiating polymn. of Me methacrylate (MMA) sensitized by dye/hexaarylbiimidazole systems were carried out. When exposed to high-pressure Hg lamp (filtered by Pyrex glass), dye/hexaarylbiimidazole the system undergoes quick electron transfer and free radicals are produced. Mercaptans (RSH), as H donor, can improve the polymn. efficiency of MMA. Comparisons of influence of different dyes and different RSH on the conversion of MMA photo-polymn. were carried out. Excellent results were obtained in photoimaging studies, e.g. a min. exposure energy of the photosensitive systems of 8 mJ/cm^2 can be reached and the resoln. of presensitized printing plate was $\sim 10\ \mu$m.

Microwave-Assisted Synthesis of Substituted Imidazoles on a Solid Support Under Solvent-Free Conditions. Usyatinsky, A.Y.; Khmelnitsky, Y.L. (EnzyMed Division, Albany Molecular Research Inc., Iowa City, IA 52242, USA). Tetrahedron Lett. (2000), 41 (26), 5031–5034 (Eng.), Elsevier Science Ltd. The solvent-free microwave-assisted synthesis of 2,4,5-substituted and 1,2,4,5-substituted imidazoles is reported. Imidazoles were obtained as a result of the condensation of 1,2-diarylethane-dienones with an aldehyde and an amine using acidic alumina impregnated with ammonium acetate as the solid support.

On the Ability of Coumarin Derivatives to Interact with Photoinitiators. Allonas, X.; Fouassier, J.P.; Kaji, M.; Miyasaka, M. Departement de Photochimie Generale, UMR No. 7525, Ecole Nationale

Superieure de Chimie, Mulhouse, Fr. J. Photopolym. Sci. Technol. (2000), 13 (2), 237–242 (Eng.). The interactions of excited states of a coumarin or a ketocoumarin photosensitizer with a bisimidazole deriv., mercaptobenzoxazole photoinitiators, and titanocene were studied by laser absorption spectroscopy and by photocond. The redox potential of the compds. was measured and used in calcn. of the free enthalpy change for a possible electron transfer reaction. The coumarin forms radicals through an electron transfer reaction, while the ketocoumarin undergoes an energy transfer reaction with bisimidazole and a hydrogen abstraction reaction with a benzoxazole deriv. Thus, coumarin or ketocoumarin/free radical initiator combinations are suitable as initiators of radical polymn. reactions, esp. those applicable to laser imaging. [1707-68-2].

Photoinitiation Mechanisms in Photopolymer Layer. Urano, Toshiyuki; Tsurutani, Yasuyuki; Ishikawa, Masayo; Itoh, Hiroki (Research Center, Mitsubishi Chemical Corporation, Yokohama, Japan). J. Photopolym. Sci. Technol. (2000), 13 (1), 83–88 (Eng.). Quenching of imidazoyl radicals (Im•) in photo-initiator systems comprising an aminostyryl dye and a radical generating reagent by acrylate monomers in a poly(Me methacrylate) (PMMA) film was investigated. This process was also studied by a laser flash photolysis using a total reflection cell, as well as quenching of Im by oxygens in the presence and absence of poly(vinyl alc.) (PVA)-overlayer as an oxygen barrier. [1707-68-2].

In Situ Observation of Molecular Swapping in a Crystal by X-Ray Analysis. Kawano, Masaki; Sano, Tomokatsu; Abe, Jiro; Ohashi, Yuji. CREST, Japan Science and Technology Corporation, Tokyo, 12), 1372-13730366-7022. Journal written in English. Abstract X-ray diffraction anal. elucidated that a pair of hexaarylbiimidazoles was transformed to a complex composed of two lophyl radicals and a piezo-dimer on irradn. at low temps. The piezo-dimer, the existence of which has been assumed spectroscopically as an unstable isomer, was produced via mol. swapping of two photoinduced lophyl radicals with drastic conformational change. The black crystal reverted to the original structure on warming to 250.

Synchrotron Radiation Structure Analyses of the Light-Induced Radical Pair of a Hexaarylbiimidazolyl Derivative. Origin of the Spin-Multiplicity Change. Kawano, Masaki; Ozawa, Yoshiki; Matsubara, Koutatsu; Imabayashi, Hidekazu; Mitsumi, Minoru; Toriumi, Koshiro; Ohashi, Yuji. CREST, Japan Science and Technology Corporation, Japan. Chemistry Letters 2000 (11), 1130–1131 (Eng.), Chemical Society of Japan. In situ synchrotron radiation structure analyses of a light-induced radical pair from 2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole were performed by using an X-ray vacuum camera at 23–70 K at the BL02B1 station of Spring-8. The combined results of X-ray anal. with theor. calcn., IR, and UV-vis spectroscopy reveal that a slight conformational change of the radical pair causes the drastic spin-multiplicity change during 2–140 K.

6.38 2001

Study of Dye-Sensitized Systems for Photoimaging. Gao, Fang; Zhao, Chun-Ying; Yang, Yong-Yuan; Li, Li-Dong. Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, Peop. Rep. China. Chin. J. Polym. Sci. (2001), 19 (l), 79–83. Journal written in English. o-Chlorohexaarylbiimidazole (o-Cl-HABI) can be sensitized efficiently by cyanine dyes, the cyclopentanone- and cyclohexanone dyes, when exposed to xenon lamp (use filter cut $\lambda \leqslant 400$ nm). The photoreaction between the photoinitiator and the dyes was completed through an electron-transfer process. Excellent results have been obtained in photoimaging studies, e.g., the resoln. of the image can reach 7 nm. The influence of the content of the dyes and the heat after the exposure on the resoln. of the image was investigated.

EPR and Density Functional Studies of Light-induced Radical Pairs in a Single Crystal of a Hexaarylbiimidazolyl Derivative. Abe, Jiro; Sano, Tomokatsu; Kawano, Masaki; Ohashi, Yuji; Matsushita, Michio M.; Iyoda, Tomokazu. Department of Photo-Optical Engineering, Faculty of Engineering, Tokyo Institute of Polytechnics, Kanagawa, Japan. Angew. Chem., Int. Ed. (2001), 40 (3), 580–582 (Eng.). The intermol. exchange coupling for the light-induced radical pair in a crystal of

2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole has been detd. The coupling const. 2J was evaluated by calcg. the spin-projected energy difference between the singlet and the triplet states. The study shows that DFT methods can provide an accurate description even for the through-space coupling in radical pairs.

Two and Three Component Photoinitiating Systems Based on Coumarin Derivatives. Allonas, X.; Fouassier, J.P.; Kaji, M.; Miyasaka, M.; Hidaka, T. Departement de Photochimie Generale, UMR No. 7525, Ecole Nationale Superieure de Chimie, Mulhouse, Fr. Polymer (2001), 42 (18), 7627–7634 (Eng.). Several coumarin or ketocoumarin/additives combinations (bisimidazole deriv., mercapto-benzoxazole, titanocene, oxime ester) can initiate quite efficiently radical polymn. The interactions between the excited states of coumarins or a ketocoumarin and various additives have also been studied by laser absorption spectroscopy, time resolved fluorescence and photocond.; the redox potentials of these different compds. have been measured and allowed the calcn. of free enthalpy variations for a possible electron transfer reaction. The whole results explain the interaction mechanism and show that the coumarins are able to form radicals through an electron transfer reaction with the different additives whereas the ketocoumarin leads to an energy transfer with bisimidazole and to an hydrogen abstraction with the benzoxazole deriv.

Three-Component Radical Photoinitiating Systems—The Effect of the Accelerator. Suzuki, Shota; Urano, Toshiyuki; Miyagawa, Nobukazu; Takahara, Shigeru; Yamaoka, Tsuguo. Department of Information and Image Science, Faculty of Engineering, Chiba University, Chiba, Japan. J. Photopolym. Sci. Technol. (2001), 14 (2), 259–262 (Eng.). The effect of an accelerator was studied on photo-polymn. initiator system contg. 2-[p-(diethylamino)styryl]naphtho[1,2-d]thiazole as sensitizer (NAS), 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-lH-imidazole (131) as radical generating reagent. The sensitivity and efficiency of N-phenylglycine accelerator was compared with this of 2-mercapto-benzothiazole (MBT). Quenching of bimol. reaction in PMMA film was studied by flash photolysis from transient absorption spectra of NAS and 131 and NAS and NPG in PMMA films. Rate of quenching of photo-produced imidazolyl radical by NPG was detd. as 5.7×10^3 mol^{-1} dm^3 s^1. For photopolymer sensitivity detn. cyclohexane soln. contg. poly(methacrylic acid–benzyl methacrylate), pentaerythritol triacrylate, NAS, 131 and accelerator was coated on glass- or oxidized Al plate, pre-baked, imagewise exposed and developed with tetramethyl-ammonium hydroxide. The sensitivity of the photopolymer including NPG was 1.9 times higher than that of NPG-free system. It is suggested that NPG affects adhesion between the photopolymer coating layer and the aluminum substrate plate.

6.39 2002

Hexaarylbisimidazoles and Ketocyanine Dyes as Effective Electron Transfer Photoinitiating Systems. Bendyk, Malgorzata; Jedrzejewska, Beata; Paczkowski, Jerzy; Linden, Lars-Ake. Fac. of Chem. Technol. and Eng., Univ. of Technol. and Agriculture, Bydgoszcz, Pol. Polimery (Warsaw, Poland) (2002), 47 (9), 654–656 (Eng.). Four different hexaarylbisimidazoles (HABIs) and 5 ketocyanine dyes (JAWs) have been synthesized. Chem. structures and basic spectroscopic properties of JAWs obtained have been characterized. Free energy changes (DGel) of the process of electron transfer between HABIs and JAWs tested have been exptl. detd. for 20 pairs of HABI + JAW. The dependence of the rate of 1,1,1-tri(acryloxymethyl)propane photopolymn., initiated with HABI + JAW systems in the presence of mercaptobenzoxazole, on the DGel value and on the radiation wavelength (488 nm and 355 nm or 365 nm) has been detd. It was found that chem. structures of HABI and JAW do not affect considerably the rate of polymn.

6.40 2003

Excited State Processes on a Four-Component Photosensitive System Based on a Bisimidazole Derivative. Allonas, X.; Fouassier, J.P.; Kaji, M.; Murakami, Y. Departement de Photochimie

Generale, Ecole Nationale Superieure de Chimie de Mulhouse, Mulhouse, Fr. Photochemical & Photobiological Sciences 2003, 2 (3), 224–229 (Eng.). Royal Society of Chemistry. The four component system consisting of bis[2-(o-chlorophenyl)-4,5-diphenyl-imidazole] (Cl-HABI), N,N′-bis(diethylamino)benzophenone (EAB), N-phenylglycine (NPG) and an iodonium salt (BIP-T) can be used for the photo-initiation of radical polymn. reactions. The excited state processes involved are reported and all the transient species, including the triplet state and ketyl radical of EAB as well as the lophyl radical, are characterized. Rate consts. of interaction between the different partners in the four component system are detd. Redox potentials of the different compds. are evaluated enabling the free energies for electron transfer reactions to be calcd. An overall scheme for the evolution of the excited states and a general discussion on the role played by the different components in photoinitiating polymn. are then provided.

Synthesis and Photochromism of Hexaarylbisimidazoles. Yang, Wei-Hua; Xiao, Guo-Min; Kong, Xiang-Xiang. Department of Chemistry and Chemical Engineering, Southeast University, Nanjing, Peop. Rep. China. Yingyong Huaxue (2003), 20 (4), 406–408. Journal written in Chinese. Two hexaarylbisimidazoles were prepd. from benzyl, arylacetates and ammonium acetate after cyclization and oxidn. Their structures were identified by IR spectra and elemental anal. The photochromic properties of the hexaarylbisimidazoles were studied. The absorption spectra of hexaarylbisimidazole in solvents were measured. The decoloration kinetics of the bisimidazoles in dark circumstance was found to be followed through the second order reaction.

Two-Photon Polymerization of Gratings by Interference of a Femtosecond Laser Pulse. Guo, Hengchang; Jiang, Hongbing; Luo, Le; Wu, Chengyin; Guo, Hongcang; Wang, Xi; Yang, Hong; Gong, Qihuang; Wu, Feipeng; Wang, Tao; Shi, Mengquan. State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing, Peop. Rep. China. Chemical Physics Letters 2003, 374 (3, 4), 381–384 (Eng.). Elsevier Science B.V. Two-photon polymn., initiated by 2,7-bis[[4-(dimethylamino)-phenyl]methylene]-cycloheptanone and 1,1′,2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetra-phenyl-bisimidazole, was employed to fabricate refractive index-modulated holog. gratings by the interference of a femtosecond laser pulse at wavelength of 810 nm. The diffraction efficiency of the grating was up to 57% and the refractive index modulation reached 4.3×10^{-3} after thermal fixation with the film thickness of 40 nm. And dependence of the diffraction efficiency and refractive modulation on laser pulse energy was also investigated.

Photochemistry and Polymerization Efficiency of Bis-Imidazole Based Photoinitiator Systems. Allonas, Xavier; Obeid, Houssam; Fouassier, Jean-Pierre; Kaji, Makoto; Ichihashi, Yasuhisa; Murakami, Yasuharu. Departement de Photochimie Generale, UMR No. 7525, Ecole Nationale Superieure de Chimie, Mulhouse, Fr. Journal of Photo-polymer Science and Technology (2003), 16 (1), 123–128. Photopolymn. efficiency of an acrylate formulation (Ebecryl 605) under light irradn. at 365 nm has been evaluated by using RTFTIR. The role of various multicomponent photoinitiating systems based on bisimidazole derivs., in the presence or not of an aminobenzophenone, N-phenylglycine and several iodonium salt derivs. has been emphasized. Excited state processes in these two-, three- or four-component systems have been investigated through time resolved laser spectroscopy. The different photophys. processes and photochem. reactions involved are defined and the role of each partner is discussed: this helps to explain the high performance of the three- and four-component photoinitiating systems.

7

THE CHEMISTRY OF HEXAARYLBIIMIDAZOLES

Two publications, entitled "Some Properties of Triarylimidazolyl Radicals and Their Dimers" and "Some Reactions of Triarylimidazolyl Free Radicals" by L.A. Cescon, G.R. Coraor, R. Dessauer, E.F. Silversmith, A.S. Deutsch, H.L. Jackson, A. Maclachlan, K. Marcali, E.M. Potrafke, R.E. Read, and E.J. Urban [1] described several novel hexaarylbiimidazoles and their reactions.

These were the first to show the broad range of chemistry that could be initiated photochemically with hexaarylbiimidazoles. The first of these reported in detail some of the properties of HABIs, and the second addressed the reactivity of different HABIs. This work involved the synthesis of over a dozen different triarylimidazoles and their oxidation to the corresponding dimers. It was thus possible to gain a better understanding of substituent effects.

This work was particularly significant as it showed the remarkable versatility in the chemistry of the 2-*o*-phenyl substituted HABIs, which have since become the preferred photooxidants and photoinitiators in a myriad of applications. For this reason, this chapter has excerpted important conclusions from these and several other DuPont publications.

Colored triarylimidazolyl free radicals **1** are formed from the thermal or photolytic dissociation of hexaarylbiimidazoles, the oxidation products of triarylimidazoles **4** [2–10]. Two hexaarylbiimidazole isomers have been reported [11]. In solution, the more stable **2** is produced at room temperature and **3** is formed below $-20°$. Interconversion of **2** and **3** involves **1**. Structures were inferred from infrared data [11].

Dimer **2** is referred to by some authors as the photochromic dimer and **3** as the thermochromic dimer. The kinetics of radical recombination have been reported to be second order in radical concentration [4,5]. Longer reaction times reveal deviation from second-order kinetics. Wilks and Willis reported 3/2 order which, after several half-lives, changed to first-order kinetics in radical disappearance [12].

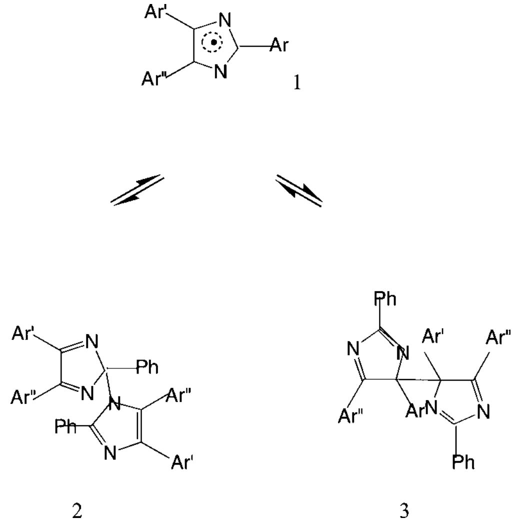
The authors prepared several novel hexaarylbiimidazoles, particularly a group bearing ortho substituents in the aromatic rings, and report here the effect of substitution on the rate of radical disappearance and on spectra of radicals and dimers.

7.1 RESULTS AND DISCUSSION

All hexaarylbiimidazoles studied, including those with ortho substituents on aromatic rings, were readily prepared in good yields.

Substitution on **2** resulted in little spectral change in the ultraviolet (6 nm in $\lambda_{\max}$ and less than a factor of two in $\varepsilon_{\max}$). See Table 7.1. Spectra of **1**, on the other hand, were more sensitive to structural changes (80 nm in $\lambda_{\max}$ and a factor of seven in extinction coefficients). These results are consistent with the assumption that the radicals are more nearly planar than

Table 7.1. Spectral properties and rate constants of the dimerization of some substituted triphenylimidazolyl radicals in benzene at 27 ± 1°



No.	Substituents			In methanol				Dimerization at 27°C	
	Ar	Ar′	Ar″	λ_{max} (nm)	$\varepsilon \times 10^{-4}$ ($l\,mol^{-1}$)	λ_{max} (nm)	$\varepsilon \times 10^{-4}$ ($l\,mol^{-1}$)	Benzene	
								$10^3 k/\varepsilon$	$k^{b,d}$
a	H	H	H			550	3.28	7.7	25.2
b	4-MeO	H	H	263	3.09	610	6.9	1.5	10.3
c	2,4-DiMeO	H	H	262	2.99	620	8.13	13.7	111
d	2-Cl	H	H	265	2.79	540	2.8	122	342
e	4-Cl	H	H	267	2.74	570	4.49	6.8	30.5
f	4-Br	H	H	265	2.89	560	3.9	6	23.4
g	4-NO_2	H	H			530	1.38	6.2	8.56
h	4-CN	H	H	264		560	2.19	10	21.9
I	3-Cl	H	H	265	2.78	550	2.9	16.2	47
j	3-NO_2	H	H	265	3.92	540	1.14	12.8	14.6
k	2-Br	H	H	265	2.69	560	4.07	123	501
l	2,4,6-TriMe	H	H			590	5.1	16.7	85.2

parent dimers. Absorption maxima correlated roughly with electron-releasing ability of substituents, e.g., λ_{max} p-OCH_3 > p-Br > p-NO_2 [13].

All dimers also could be converted into their less stable isomers **3** by irradiating a solution below −20° as previously reported by White and Sonnenberg [11]. If the **2** position in Ar was unsubstituted, **3** could be obtained which contained very little **2**, by evaporating the solvent under vacuum or by adding a nonsolvent; however, only very crude **3** was obtained with biimidazole having groups in the **2** position in Ar. A third dimer, first discovered by Reitz [14,15], was observed for all dimers studied, it could be detected by cooling a solution of **2** to −85° and irradiating for 10–15 min. Radical color disappeared after irradiation was stopped. (Reitz reported concomitant ESR signal loss.)

When this solution was slowly warmed to room temperature, the following changes occurred. At about −40° radical color (and ESR signal according to Reitz) reappeared. The solution once again became colorless on standing at about −35°. Further warming above

−20° caused dissociation of dimer **3** to radical with final loss of color as the temperature reached about 12°. Dimer **2** was the predominant product at the end.

Dimer **3** was identified in this experiment by its instability in solution at room temperature and by its UV spectrum. (The $\lambda_{\max}$ of **3** are about 10 nm higher than of **2**.) The structure of the third dimer was not determined. The important fact is that all dimers behaved the same way, at about the same conditions.

Dissociation constants of **2** have been reported to be higher for dimers with electron donating substituents in the para positions of the phenyl rings [15]. We found that these groups in ortho positions resulted qualitatively in very different properties. Any ortho substituent in Ar decreased dissociation. Thus, a benzene solution of the stable dimer of 2-(2-chlorophenyl)-4,5-diphenylimidazolyl radical **2d** exhibited no radical absorption spectrum below 80°, whereas the 4-chloro compound **2e** was partially dissociated in solution at room temperature. Ortho substituents in Ar' and Ar'' affected the equilibrium quite modestly but appeared to have the opposite effect, that is, increased dissociation. Qualitatively, meta substituents had little effect on the equilibrium of dissociation.

The wide variation in thermal stability of dimers and (where ortho groups are present in Ar) the high reactivity encountered at temperatures where dissociation was readily observable discouraged our measuring equilibria or thermal dissociation kinetics. Photodissociation was complete at the end of a 5-μsec flash with no evidence for short-lived intermediates.

Radical disappearance, however, was readily followed spectrally. Benzene solutions at 27 ± 1° were irradiated and absorbance, A, at $\lambda_{\max}$ was determined at measured time intervals. A graphic method was utilized to obtain rate constants. Linear plots of $1/A$ vs. t were obtained until A was about half of A_0, when deviations from a second-order plot became apparent. The slopes of the linear first half-life was taken as equal to $k/\varepsilon l$ in cm sec^{-1} ($l = 1$ cm) from which the rate constants, k, were obtained. The values of k/ε and k are in Table 7.1.

Our presentation of results in terms of second-order rate constants fitted to initial rates during about one half-life does not imply knowledge of the detailed mechanism of radical disappearance. We observed, as did Wilks and Willis, that 3/2 order plots are linear for longer reaction times, but that these too deviate from linearity as well as vary in slope with A, and with the presence of sensibly inert additives. This information convinces us that the detailed mechanism of radical disappearance will remain to be understood until all reaction components can be measured quantitatively as reaction proceeds. We are attempting to develop such techniques.

At this time we are concerned with the effect of structure on radical dimerization and assume only that a common mechanism prevails for all. The low-temperature dimerization experiment, in which all compounds behaved comparably under similar conditions supports this assumption.

A method was devised to determine extinction coefficients of radicals. A flash photolysis unit with filters to confine irradiation to a spectral region where only biimidazoles absorbed was utilized to generate radicals whose initial absorbance was recorded photographically from an oscilloscope. In the same cell another solution was then photolyzed as above. This second solution contained an identical concentration of biimidazole to the first plus leuco Crystal Violet dye, tris-(4-dimethylamino-phenyl) methane, and toluenesulfonic acid. The absorbance of dye produced by oxidation of leuco dye by was observed at an unobstructed wavelength. The extinction of the dye at this wavelength in this medium was determined experimentally. The stoichiometry of radical attack on dye was and the quantum yield of this reaction under

Table 7.2. Dimerization of 2,4,5-triphenylimidazolyl radical at 27°

Solvent	$10^3 k/\varepsilon$ (cm s^{-1})
Benzene	25.2
Anisole	24.6
Benzonitrile	21.0
tert-Butylbenzene	43.2
1,2-Dimethoxybenzene	28.2
Nitrobenzene	31.8

these conditions had been previously determined experimentally by Kellogg and Kooser to be unity [17] (that is, one dye molecule is formed per biimidazole dissociated or per two radicals). Calculation of initial radical concentration corresponding to dye produced allowed calculation of radical extinction coefficient in the usual fashion from observed absorbance.

Our value for ε of 3280 cm^{-1} for **2a** in benzene–methanol compares with Wilks and Willis value 4150 cm^{-1} in dioxane–water and 3900 in benzene–pyridine. We consider these values in agreement.

The disparity in rates required use of different experimental techniques for different solvents. Radical absorbance was followed with a spectrometer when benzene was solvent, whereas a flash photolysis unit was employed in the methanol-containing solvent runs. In the latter, a photograph was made of the oscilloscopic trace of radical transmittance vs. time.

Radical extinction coefficients were measured in 50 : 50 vol. benzene–methanol and, in one case, in methanol as well. It proved impossible to determine extinction coefficients by this method in benzene, the preferred solvent for kinetic runs, because of reagent insolubility. Rate constants in benzene are, therefore, equal to those reported multiplied by the experimentally unattainable ratio, $\varepsilon_{\text{benzene}}/\varepsilon_{\text{benzene–methanol}}$. The ratio is assumed to be relatively constant for the radicals studied. The method is the best compromise which would allow all rates to be measured by a common method.

The rate constants obtained by Cescon et al. agreed reasonably well with those of Reitz [14], determined by EPR in toluene at 26°. The rate constant for disappearance of **1a**, 25.2, compares with second-order values approximated from Hayashi's data of 3.3 at 19° and 7.4 at 23° and from Wilks and Willis' data of between 7 and 18, depending on **2a** concentration.

The solvent exerts a profound influence; dimerization is 30-fold faster in methanol than in benzene. The degree of rate enhancement by methanol is disturbingly large. Efforts to characterize photolysis products other than dimer after prolonged periods of irradiation of methanol solutions showed a variety of products in trace amounts insufficient to characterize by liquid chromatography and inseparable by other techniques. Second-order plots showed the same deviations as were found in benzene. Rate studies were attempted in other solvents in the hope of shedding some light on medium effect. Unfortunately, a combination of problems precluded measurement of extinction coefficients in most of these. The k/ε values of dimerization of **1a** in various solvents are listed in Table 7.2.

A substituent in the ortho position of Ar but not of Ar′ or Ar″ unmistakably enhances the rate of radical combination. Thus, the 2-*o*-chlorophenyl compound **1d** (Table 7.1) dimerized seven and ten times as fast as its meta and para isomers **1i,** and **1e**, respectively, 30 times as fast as the isomer with an ortho chloro group in Ar′ (**1n**), and an order of magnitude faster

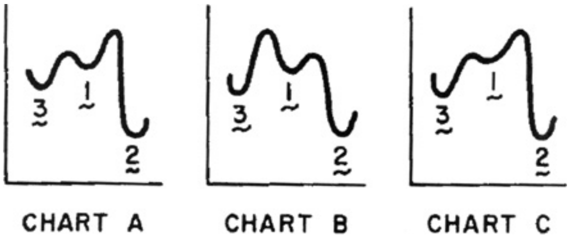


Figure 7.1.

than the analog having ortho chloro groups in Ar′ and Ar″ (**1o**). Bromo-substituted radicals followed a similar trend, the ortho isomer **1k** being 50-fold faster than the para isomer **1f**; the methoxy compounds **1b** and **1c** behaved similarly. The largest rate constant of dimerization was shown by **1m**.

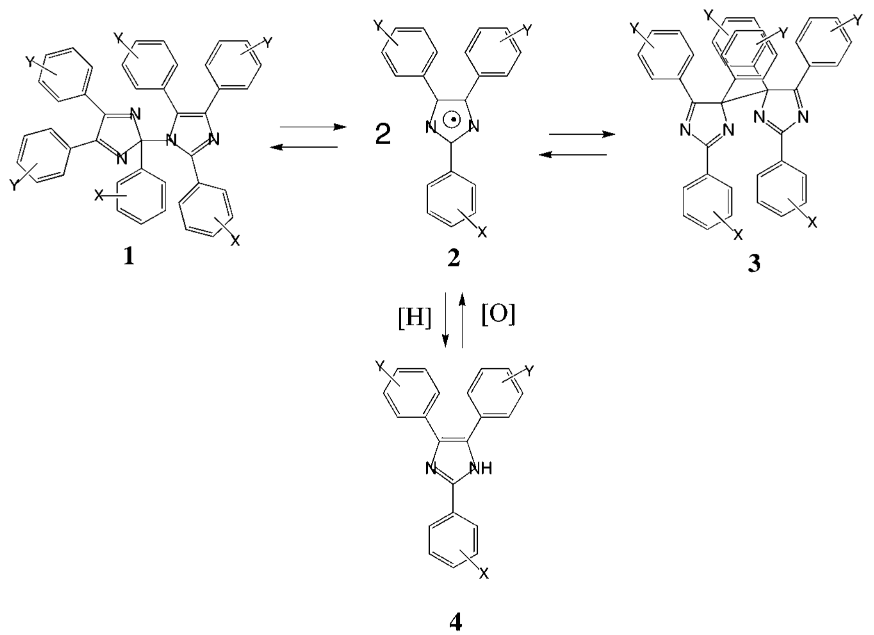
The influence on rate by meta and para substituents was not great. Compare **1a** with **1b**, **1g**, **1h**, **1i**, and **1j**. Groups which are either strongly electron donating or attracting appear to retard the rate by a small factor.

From the equilibrium constants of Baumgärtel and Zimmerman [16] obtained in toluene at 25° and our rate constants for association, the rate constants of dissociation are calculated to be about 4.4×10^{-5} and 2.6×10^{-4} $\sec^{-1}$ for **2a** and **2b**, respectively.

The unusual aspect of these data is that the most hindered dimers, namely, those having ortho groups in Ar, form fastest. The effect is clearly steric since all groups have a similar influence. The results are consistent with two hypotheses. Ortho substituents in Ar result in (a) a different product, at least initially, or (b) a lower transition state of **2**, due to destabilization of **1**.

Hypothesis a implies, for example, that hexaarylbiimidazoles without substituents in Ar would be represented by the energy diagram in Chart A, due to White and Sonnenberg [11] whereas those with ortho substituents on Ar would be represented by that in Chart B (Fig. 7.1). The similar low temperature behavior of all radicals, that is, their dimerization to the same isomers at similar temperatures, argues against this hypothesis. The products at the completion of kinetic runs did not differ observably among radicals studied. Hypothesis a, furthermore, would imply that ortho substitution in Ar somehow stabilizes that transition state which involves coupling closest to the hindrance. No precedent for this was found in the literature.

Hypothesis b allows the unsubstituted biimidazole system still to be represented by Chart A. The diagram for biimidazoles with ortho groups in Ar can be depicted by Chart C (Fig. 7.1). Radical destabilization is to be expected from steric hindrance of ring coplanarity. X-ray crystallography has shown that crystalline dimer **2k** has no two rings which are coplanar [18]. Models of the radical, however, show that unsubstituted Ar can achieve coplanarity with the heterocyclic nucleus. They also show that ortho substitution in Ar does greatly interfere with rotation to achieve ring coplanarity of Ar and the imidazole nucleus. Models further reveal that Ar′ and Ar″ cannot simultaneously be coplanar with the imidazole ring and strongly suggest that individually this may also be impossible. Because neither radical nor dimer gains appreciable resonance stabilization from Ar′ and Ar″, kinetics anequilibria of reactions of radicals or dimers should not be greatly effected by ortho substituents on these rings. A further test of ring coplanarity should be found in spectral data. The high sensitivity of radical spectra, both $\lambda_{\max}$ and ε, to substituents contrasts markedly with the biimidazoles



a, X = H, Y = H
b. X = 2-Cl, Y = H
c. X = 4-MeO, Y = H
d. X = 2-Br, Y = H

Scheme 7.1.

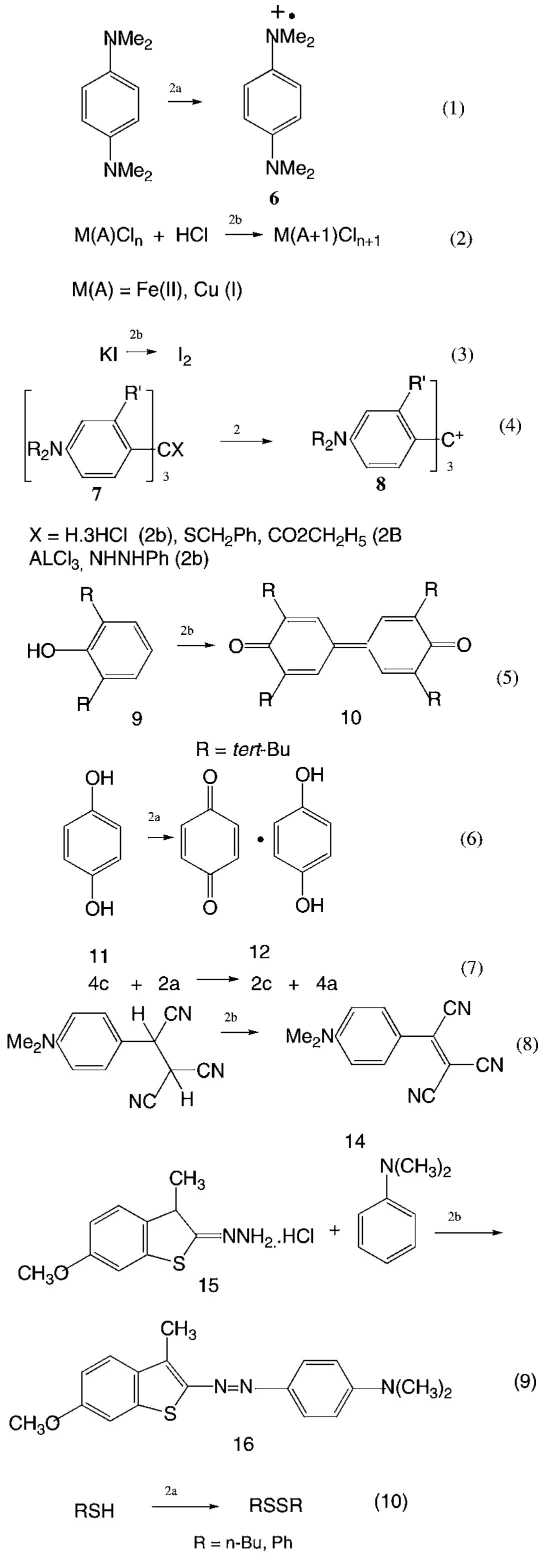
(Table 7.1). Parallel observations in the biphenyl series have been related to ring coplanarity [19].

The formation of triarylimidazolyl free radicals **2** from the thermal or photolytic dissociation of hexaarylbiimidazoles **1** has been reported [2,3,7,9,10]. These radicals are known to dimerize to regenerate a hexaarylbiimidazole, usually one of the two favored isomers **1** or **3** (Scheme 7.1) [3,7,9]. They are also known to react with nitric oxide to give N-nitrosotriarylimidazoles [2] and to react with hydrogen peroxide to give 4-hydroperoxytriarylimidazoles [10].

Further exploration of triarylimidazolyl radical chemistry was undertaken. Two types of oxidations by **2** were studied: abstraction of electrons and of hydrogen atoms. Both reactions normally yield triarylimidazole **4** as the reduction product, the proton being obtained from the solvent if necessary. Results are summarized in Scheme 7.2. Examples of representative reactions are the subject of mechanistic studies reported in subsequent papers [15,17,22–24].

Radicals **2** do not react with aromatic hydrocarbons, aliphatic alcohols, oxygen, or vinyl monomers at rates which compete detectably with dimerization or the oxidation reactions studied. Thus, benzene and methanol could be used as solvents under conditions employed without observing side products due to their presence. Reactions proceeded equally well with or without degassing. When radicals **2a** or **2b** were produced photolytically in neat monomers such as ethyl acrylate, acrylonitrile, or pentaerythritol triacrylate, no polymerization could be detected.

The reactivity of photolytically and thermally produced **2** was identical. Hence, in the reactions studied, only the ground state **2** is presumed to be involved.


NMe2
NMe2
2a
+•
NMe2
NMe2
6
(1)
M(A)Cln + HCl
2b
M(A+1)Cln+1
(2)
M(A) = Fe(II), Cu (I)
KI
2b
I2
(3)
R'
R2N
CX
3
7
2
R'
R2N
C+
3
8
(4)
X = H.3HCl (2b), SCH2Ph, CO2CH2H5 (2B
ALCl3, NHNHPh (2b)
R
HO
R
9
2b
R
R
O
O
R
R
10
(5)
R = tert-Bu
OH
OH
2a
O
O
OH
OH
(6)
11
12
(7)
4c + 2a
2c + 4a
Me2N
H
CN
CN
NC
H
2b
Me2N
CN
CN
NC
(8)
14
CH3
CH3O
S
NNH2.HCl
15
+
N(CH3)2
2b
CH3
CH3O
S
N=N
N(CH3)2
16
(9)
RSH
2a
RSSR
(10)
R = n-Bu, Ph

Scheme 7.2.

Table 7.3. Preparation of different hexaarylbiimidazoles

No.	Substituents			Yield (%)	M.p. (°C)	Formula	Reg. No.
	Ar	Ar′	Ar″				
a	H	H	H	88	200–201	$C_{42}H_{30}N_4$	7189-41-5
b	4-MeO	H	H	85	127–128	$C_{44}H_{34}N_4O_2$	29898-55-3
c	2,4-DiMeO	H	H	91	120–121	$C_{46}H_{38}N_4O_2$	29898-56-4
d	2-Cl	H	H	89	202–203	$C_{44}H_{34}N_4Cl_2$	7189-82-4
e	4-Cl	H	H	85	210.5–212	$C_{44}H_{34}N_4Cl_2$	7189-80-2
f	4-Br	H	H	82	210–211	$C_{44}H_{34}N_4Br_2$	29936-66-1
g	4-NO_2	H	H	85	—	$C_{42}H_{28}N_6O_4$	29898-58-6
h	4-CN	H	H	70	~162–168	$C_{44}H_{28}N_4$	29843-51-4
I	3-Cl	H	H	81	167.5–168.5	$C_{44}H_{34}N_4Cl_2$	77189-78-8
j	3-NO_2	H	H	74	~150	$C_{42}H_{28}N_6O_4$	29898-60-0
k	2-Br	H	H	90	190–191	$C_{44}H_{34}N_4Br_2$	29843-52-5
l	2,4,6-TriMe	H	H	78	195–203	$C_{48}H_{42}N_4$	29898-61-1
m	2,4-DiCl	H	H	95	—	$C_{42}H_{26}N_4Cl_4$	7189-83-5
n	H	H	2-Cl	43	~190	$C_{42}H_{28}N_4Cl_2$	29898-63-3
o	H	2-Cl	2-Cl	94	~210	$C_{42}H_{26}N_4Cl_4$	29898-64-4

Reactions (1)–(4) (Scheme 7.2) involve as the first step electron abstraction by **2** which is two to three orders of magnitude faster than dimerization of **2** [1,15,24].

The inability of **2** to initiate vinyl polymerization is not due to an energetic deficiency since the intermediate products (radicals or radical ions) formed in reactions (1) and (4) do initiate polymerization. Thus, if a mixture of N,N′-dimethylaniline, a biimidazole, and a monomer such as pentaerythritol triacrylate is photolyzed, a hard polymer is formed. If the N,N-dimethylaniline is omitted, no polymerization occurs, no monomer double bond loss is evident from the infrared spectrum, and radical dimerization is observed at a rate normal for inert solvents.

The failure of **2** to initiate polymerization may result from steric or resonance factors; however, justification for neither is evident. However, other delocalized radicals, which contain nitrogen atoms, especially when hindered, do not initiate polymerization and sometimes inhibit it [23].

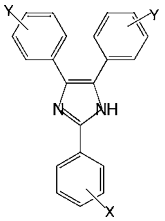
Reaction (4) involves stoichiometrically 1 mol of leucodye salt, 1 mol of biimidazole, and 1 equiv of acid. Maclachlan and Reim [17] found the mechanism to be

$$\begin{aligned} \mathbf{1} &\rightarrow \mathbf{2} \\ \mathbf{7} + \mathbf{2} &\rightarrow \mathbf{4} + \mathbf{7}^{\bullet +} \\ \mathbf{7}^{\bullet +} &\rightleftharpoons \mathrm{H}^{+} + \mathbf{7}^{\bullet} \\ \mathbf{7}^{\bullet} + \mathbf{7}^{\bullet +} &\rightarrow \mathbf{8} + \mathbf{7} \end{aligned}$$

where $\mathbf{7}^{\bullet +}$ and $\mathbf{7}^{\bullet}$ are the intermediate radical ion and radical, respectively, of the triarylmethane leuco dye **7**. With proper choice of components and conditions, this reaction can give unit quantum yield of dye even in the presence of oxygen [18].

R.L. Cohen [19] examined the effect of substitution on the rate of disappearance of **2** in reaction (4). His selection of compounds was designed to emphasize steric variations in **2**. A plot of Cohen's rate constants vs. $-E_{p/2}$ values for various imidazole–imidazolyl radical

Table 7.4. Cyclic voltammetric oxidation-reduction of triarylimidazoles in acetonitrile solutions



X	Y	Reg. No.	$-E_p$ (V vs. SCE)	$-E_{p/2}$ (V vs. SCE)	log K (step 1) reaction
H	H	484-47-9	0.923	0.808	6.08
2-Cl	H	1707-67-1	0.994	0.891	7.45
2-F	H	1740-26-7	1.024	0.904	7.13
2-Br	H	1740-25-6	1.036	0.931	7.5
2-Me	H	13730-60-4	0.889	0.774	6.15
2-NO_2	H	29864-19-5	1.088	0.963	7.63
2-MeO	H	1965-19-1	0.899	0.862	6.2
H	4-MeO	7044-99-7	0.738	0.668	4.41
H	2-MeO	29864-28-4	0.898	0.718	5.4

redox couples (Table 7.1) (Fig. 7.1) is linear. The linear relationship of $E_{p/2}$ and σ^+ values is shown by Table 7.2 and Fig. 7.2. Rate differences in reaction (4), which result from substituents X are thus strongly influenced by electron delocalization.

Rate constants of reaction (4) with variously substituted leuco dyes have been found by Cohen [20] to correlate with σ. Delocalization effects were specifically excluded in the leuco dyes employed in that study. Reaction (1) actually is an exact model of the first step in reaction (4) with the added degree of freedom that substituents para to the dimethylamino group can be varied to include those capable of strong delocalization effects. This reaction has been studied kinetically with various para substituents, and rate constants were found to correlate with σ^+ [21].

Reactions (6)–(10), formally, involve hydrogen atom abstraction. The lower rate constant observed by Maclachlan et al., when O-deuterated phenols were used instead of normal phenols, was consistent with a rate-determining hydrogen atom abstraction in reaction (6) [21]. Reactions (7)–(10) have not been studied mechanistically as yet; all are sufficiently fast to preclude observable radical dimerization. Rate constants of reactions (5) and (6) (with variously substituted phenols and hydroquinones) were found to be several orders of magnitude greater than that for radical dimerization.

Because visible spectra of radicals **2** vary considerably, reaction (7) can serve as a convenient method for determining the relative oxidation potential of different radicals. For example, reddish purple **2a** (formed by adding to the reaction imidazole **4c** to a blue radical **2c**). Colorless imidazole **4a** was the other product.

Redox potentials, $-E_{p/2}$, of imidazole–radical systems provide a quantitative ranking of the oxidizing ability of different radicals. Some $-E_{p/2}$ values determined by cyclic voltammetry appear in Tables 7.4 and 7.5.

A number of additional reactions were carried out on a crude scouting basis to test the generality of this oxidation technique. Thus, irradiation of a 1 : 4 dimethylformamide–methanol

Table 7.5. Oxidation potentials of some triarylimidazoles in acetonitrile solvent

X	Registry No.	$-E_p$ (V vs. SCE)	$-E_{p/2}$ (V vs. SCE)	σ^a	$\sigma^{\pm a}$
H		0.923	0.808	0	0
4-MeO	1728-95-6	0.716	0.641	−0.27	−0.78
2-Cl	29898-73-5	0.918	0.778	0.37	0.37
4-Cl	5496-32-2	0.978	0.978	0.23	0.11
3-Br	29913-29-9	1.038	0.878	0.39	0.39
4-Br	5406-33-3	0.981	0.856	0.27	0.15
4-I	20036-60-5	0.974	0.768	0.30	0.13
3-F	29913-31-3	0.990	0.84	0.34	0.35
4-F	2284-96-0	0.031	0.836	0.06	−0.07
4-Me	5496-31-1	0.850	0.765	−0.17	−0.31
3-NO	5496-38-8	1.236	0.986	0.71	0.66
4-NO_2	.496-39-9	0.969	3.919	0.78	0.78
4-CN	29898-72-4	1.121	0.936	0.66	0.66
3,4-Benzo[5]	13866-85-8	0.882	0.787	0.48	−0.13
4-Me_2N	1728-97-8	0 461	0.376	−0.83	−1.7

[a] C.D. Ritchie and W.F. Sager, Progr. Phys. Org. Chem. 2, 334 (1964).
[b] That is, "$C_6H_4 \cdot X$" = β-naphthyl.

solution of *N*,*N*-diethyl-*p*-phenylenediamine, thenoylacetonitrile, and **1b** gave a magenta-colored product as expected for the "oxidative coupling" product, 2-(4-diethylaminophenylimino)-3-thenylpropionitrile. Similarly, irradiation of a solution of *N*,*N*-dimethyl-*p*-phenylenediamine, phenol, and **1d** gave a blue color typical of 4-(*N*,*N*-dimethylaminophenylimino)cyclohexadienone. Also, irradiation of a benzene solution of phenothiazine and **1d** gave the blue-green color of oxidized phenothiazine; similarly, 10-propionyl-3,7-bis(dimethylamino)-phenothiazine and **1b** in acetone produce methylene blue. In each case, products were identified by comparison with known dye spectra. If the biimidazole was omitted from the above mixtures, no color developed.

It is thus obvious that radicals **2** can serve as highly selective oxidizing agents. When generated from biimidazoles photochemically, a convenient and versatile means is provided for carrying out photoinduced oxidations with high quantum yield without the problem of triplet quenching by oxygen.

It is probably true that all reactions studied involve electron abstraction or hydrogen abstraction. However, formally, a wide variety of organic oxidation reactions are represented: O—H, N—H, S—H, and C—H bond cleavage (reactions (6), (7), (8), and (10)), oxidative coupling (reactions (5), (9), and (10)), and electron abstraction (reactions (1)–(4)).

Subsequent papers, were directed at obtaining a better understanding of the HABI/leuco dye chemistry.

> Thus flash photolysis of a substituted hexaarylbiimidazole and reactions of the imidazolyl radical [25] was employed to study the rate of reaction of 2-(o-chlorophenyl)-4,5-diphenylimidazolyl radical with additives in various solvents. Evidence based on measured rate constants, including kinetic deuterium isotope effects, prove that the rate-determining step in the reaction $L^{\bullet +}$ aromatic amine is an electron exchange reaction at the amino nitrogen, while in the reaction $L^{\bullet +}$ hydroquinone the rate-determining step is hydrogen abstraction.

The biimidazole-sensitized photooxidation of leuco triphenylmethane dyes [15], specifically of tris(2-methyl-4-diethylaminophenyl) methane by photogenerated 2-(o-chlorophenyl)-4,5-diphenylimidazolyl radical (L•) was studied by flash photolysis. An electron-exchange reaction involving L• occurs at an unprotonated amino nitrogen of the leuco dye and is responsible for the first oxidation step. Subsequent reactions do not involve the L• radical and depend only on the structure of the leuco dye and environmental effects. The influence of pH on both the course and rate of the dye-forming reaction was investigated.

Substituent effects on the reactivity of triarylimidazolyl free radicals toward tris(2-methyl-4-diethylaminophenyl)methane [22] were also investigated. The effect of aryl substituents on the reactivity of substituted triarylimidazolyl free radicals, photolytically generated from their corresponding dimers, in an electron-exchange reaction with an aminotriphenylmethane substrate was studied by flash photolysis. The reaction rate was retarded by electron-donating substituents and enhanced by electron withdrawing groups on the imidazolyl radical. Bulky substituents, ortho to the imidazole ring, also increased the reactivity. These results are consistent with the previously proposed mechanism for the reaction.

7.2 RADICAL LIFE

Certain HABIs have remarkably prolonged free radical life. As part of an investigation of the improved performance of TCTM-HABI vs. CDM-HABI and o-Cl-HABI, visual colors of the radical, as well as ESR measurements showed that TCTM-HABI formed extremely stable free radicals.

From U.S. 4,252,887: It is known that imidazolyl radicals exhibit unique signals when examined in an ESR spectrometer; diminution of the signals indicates disappearance of the radical to give the starting dimer. It is further known that many biimidazole compounds on photolysis give rise to colored free radicals. In the absence of exciting radiation, these radicals recombine to give the starting dimer. This dimerization process may be speeded up by heat or increased plasticization of the medium. Techniques for measuring absorption spectra of the radicals or colorimetric measurements of films or treated papers may thus be employed to make comparisons in the lifetime of imidazolyl radicals.

The following examples illustrate the increased radical lifetime of radicals formed from certain imidazolyl dimers.

7.2.1 Electron spin resonance (ESR) measurements

(A) Solutions of 0.01 molarity in methylene chloride are made with o-Cl-HABI and TCTM-HABI. These were inserted in 3.0 mm (ID) Pyrex™ tubes inside the cavity of a Bruker R™ BR420 ESR spectrometer, and are exposed to several flashes with an electronic flashgun (Exposure Source 3 of Table 7). The signal generated by the radical was recorded over a period of time, and disappeared completely after 200 seconds for the control. Signal strength of one-third the original was detected after more than 2000 seconds for TCTM-HABI, a lifetime of over 10 times greater in solution for the radicals derived from TCM-HABI.

(B) Films were prepared by coating a lacquer containing 0.96 g cellulose acetate butyrate described in the photosensitive compositions of 0.15 g of different hexaphenylbiimidazoles, and 8.0 g methylene chloride onto a polyethylene terephthalate film using a 032 coating bar. The film weight was approximately 0.056 g/dm^2. A film made with TCTM-HABI, was inserted in a 4.0 mm (ID) Pyrex™ tube, and was exposed for several minutes with ultraviolet light. The sample was placed in the cavity of the above-described ESR instrument, and the signal is recorded. After 66 hours the sample was scanned again. It retains 40% of the original signal strength. A similarly exposed film made with o-Cl-HABI shows a signal initially but shows no signal after 16 hours, indicating appreciably longer radical lifetime in films prepared containing the more highly substituted hexaphenylbiimidazoles. The solution (A) containing hexaphenylbiimidazole TCTM-HABI, shows a single ESR absorption 7 Gauss wide with G-factor of 2.0028. This signal is also observed in irradiated films (B) except that a slightly broader line width of 8 Gauss is found.

7.2.1.1 *Stability of radicals by optical measurements* Films were prepared as described in Example 25 (B) except that the below listed hexaphenylbiimidazole compounds were used. The films were scanned in a Cary Model 17 spectrophotometer from 700 nm to 300 nm. Samples were then irradiated with ultraviolet light from BLB lamps for 110 seconds. Exposed samples were then returned to the spectrophotometer for additional scanning over the same wavelength range. The scanning was repeated after 22 hours. Approximately the same length of time was employed in handling each sample. Scanning from 700 to 300 nm took about 4 minutes.

A wavelength was selected at which there is a maximum difference between the exposed and unexposed film sample.

Sample	Wavelength (nm)	Loss (%)
o-Cl-HABI	380	100
TCTM-HABI	400	52

These data show that the radicals from the photolysis of TCTM-HABI have longer radical life versus the controls. The differences between the controls and hexaphenylbiimidazole compounds indicate that electronic effects, arising from substituents, as well as steric factors which may be present, as shown by 4-phenyl ortho-substituted compounds of this invention influence radical life.

7.2.1.2 *Colorimetric measurements* Samples of the above films are irradiated for 90 seconds with a light source containing BLB lamps, with an irradiance of about 9 mW/cm^2. Reflectance measurements are made on the films prior to exposure, immediately after exposure, 2 hours after exposure and 67 hours later. Reflectance readings are made with the film over a black tile, using a Photomatch R™ 300 colorimeter; the readings are ΔL (lighter/darker), Δa (redder/greener) and Δb (yellower/bluer). The values for ΔE set forth Table 7.6 were derived from the square root of the sum of the squares ($\Delta L^2 + \Delta a^2 + \Delta b^2$) and gave an approximation of the overall change of color of the film sample. It was observed that the control hexaphenylbiimidazoles form relatively little color after exposure, which disappeared after 2 hours. All film samples containing the more highly substituted hexaphenylbiimidazole compounds retained color longer their longer radical life.

Table 7.6. Film sample change in ΔE values

	2 hours		67 hours	
	Before exposure	After exposure	Before exposure	After exposure
TCTM-HABI	1.5	6.2	5.1	5.1
o-Cl-HABI	1.1	1.9	1.1	0

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8

THE DEVELOPMENT OF DYLUX® INSTANT ACCESS PHOTOSENSITIVE PRODUCTS

8.1 INTRODUCTION

DYLUX® 503 proof paper became the standard medium for analog monochrome proofing in a relatively short time. It was introduced to the market at the National Printers and Lithographers Show in Chicago in 1969, and had a steady growth until the early 2000s, when digital printing and other proofing approaches, e.g., ink jet, caused erosion of the market. Nevertheless, for over 30 years a product conceived in the 1960s was a dominant factor in the market.

A historical/technical treatment of the development of DYLUX® 503 proof paper shows that there were a number of miss-steps or diversions, which, while enriching the technology, also seem to have been wasteful, in retrospect. This entire development was undertaken by chemists who had no experience in imaging technology; this development was also a significant educational experience.

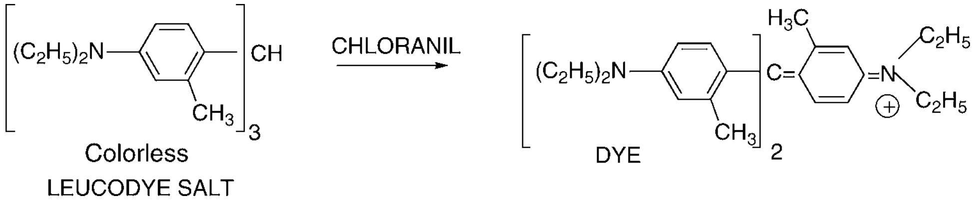
No one associated with this development at the outset had any real idea as to where it would lead. There was an intuitive feeling that the technology was interesting and that it would likely be good for something, whatever that might be. Initially the chemists working on this program were handicapped by a lack of understanding of the then rapidly expanding imaging market, and later they were handicapped by the lack of enthusiasm of the Photo Products Department for this technology and a lack of support in the development of markets until it was firmly established that the printing community was enthusiastic about a two-sided coated proof paper that could be imaged without processing.

However, the development of DYLUX® proof paper, and the associated HABI chemistry was essential to DuPont's successful photopolymer products, which depended on the unique stability and versatility of HABIs. Had the DYLUX® program been terminated before it was a commercial success, the essential o-chloro-HABIs would not have been available for subsequent products.

DYLUX® products were developed by the DuPont Company, employing research on hexaarylbiimidazoles (HABIs) started in the early 1960s by Cescon, Coraor and Dessauer. As reported elsewhere, the original impetus for work with HABIs was their photochromic behavior. The fatigue reaction of HABIs, inevitably lead to the reduction product triarylimidazole, suggesting that these compounds were excellent photo-oxidants.

8.2 SOME HISTORY OF LEUCODYE RESEARCH

Years earlier, W. Balon and O. Stallmann et al. at DuPont had investigated stable derivatives of Leuco Crystal Violet in spirit duplicating processes. The latter were a popular and a rel-



Scheme 8.1. Chemical oxidation of leucodyes.

atively inexpensive means of making duplicates when the “master” could be generated on a typewriter.

The master was composed of a waxy layer, containing dyes and a paper support. The wax layer, containing preferably triphenylmethane dyes was ruptured by the pressure of a typewriter key, and the resulting sheet was moistened with alcohol (spirit of methanol), allowing transfer of the “exposed” dye to a piece of plain paper. Crystal Violet was the preferred dye for this process because of its low cost and high tinctorial strength.

An improvement was considered. Replacement of the dye with a leucodye allowed formulation of a colorless master, which was believed to be more popular than a similar master containing dye, as it minimized problems in handling, i.e., no dye would rub off during the preparation and mounting of the master. In the proposed new product, chloranil, an oxidant was dissolved in the duplicating fluid. Color formed when this solution came in contact with the leucodye during transfer (Scheme 8.1).

The process, however, liberated hydrogen chloride, which over a period of time corroded the machinery. Why no other oxidant was selected is unclear now, some 60 years later. In any event, the project was terminated.

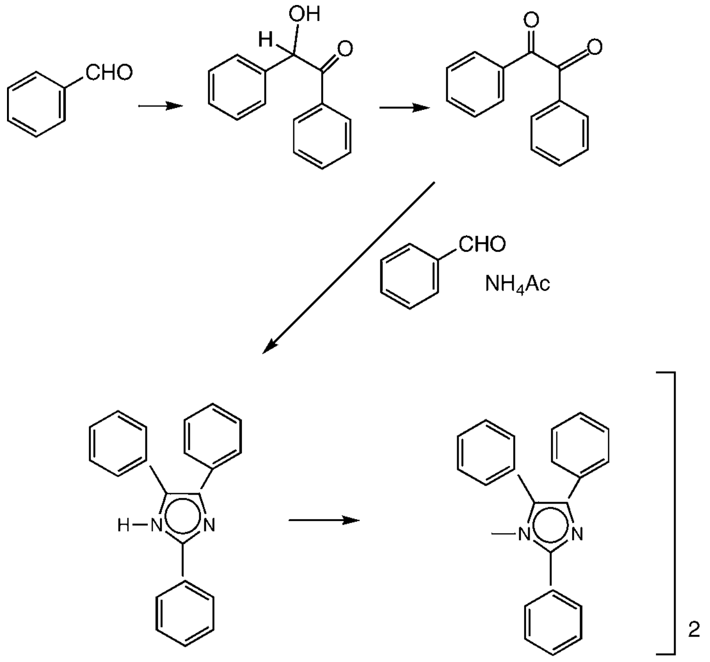
8.3 ENTER HEXAARYLBIIMIDAZOLES (HABIs)

A program to investigate various organic materials as photochromic components in automotive and architectural windows, initiated about 1958 at DuPont seriously examined hexaarylbiimidazoles (HABIs), which had been reported in the literature [see Chapter 5]. These compounds were relatively easy to synthesize, by the route indicated below (Scheme 8.2).

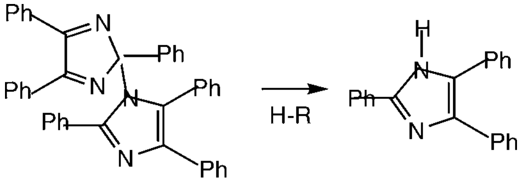
A large number of aromatic aldehydes was available commercially.

Despite a major synthetic effort to investigate structural changes, this program failed to overcome a serious limitation; the regeneration of the photochromic material in the absence of light did not offer sufficient reversibility because the radicals were excellent hydrogen abstractors, regenerating the corresponding triphenylimidazole (Scheme 8.3).

Cescon considered that a “double-barreled” triphenylimidazole derivative (Scheme 8.4) might offer some interesting possibilities for reversal. However, it turned out that oxidation of the precursor resulted in a blue colored material, presumably a quinoidal oxidation product. The question then arose whether the HABI chemistry might be adapted to a color-forming process. Dessauer located a still colorless sample of tris(*p*-diethylamino-*o*-tolyl)-methane that had been prepared earlier by W. Balon and collaborated with Cescon to oxidize it with hexaarylbiimidazole. The solution was exposed with a photographic flashgun; the photo-oxidized leucodye was an intense blue. The experiment was repeated with filter paper dipped into a solution of HABI and leucodye salt, and a cyan color produced with a flash of light.



Scheme 8.2. Synthetic route to HABI.

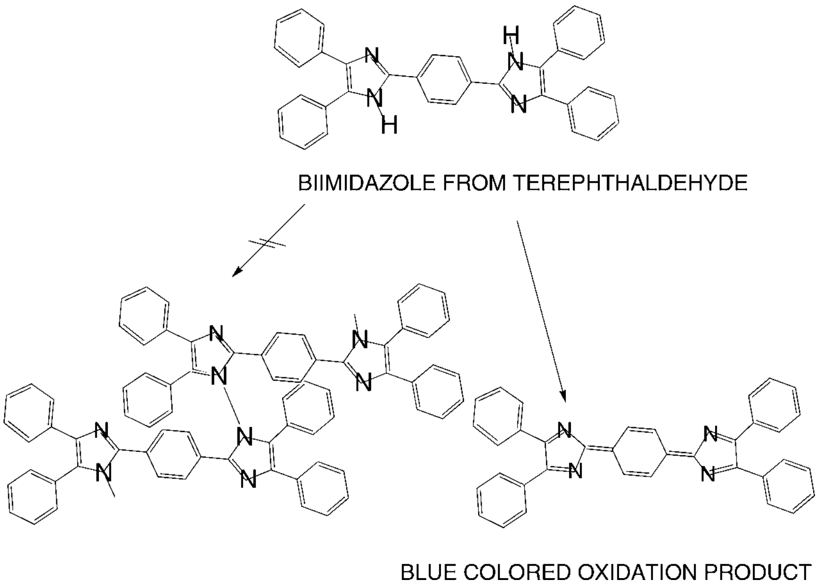


Scheme 8.3. Fatigue reaction of biimiazoles.

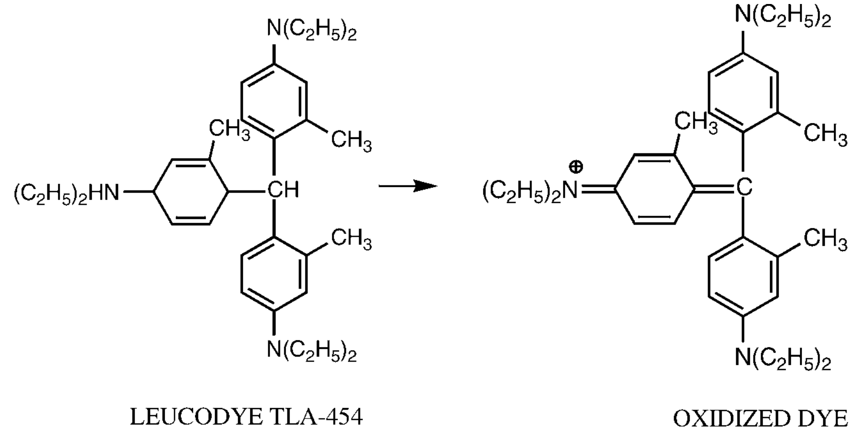
It soon was clear that the photo-oxidation of triphenylmethane leucodyes was potentially useful as a means of forming colored images with light. What was not at all clear was what one could do with images so generated. The technology initially was referred to as UVI, for ultraviolet imaging. This name persisted until late in 1968, when the term DYLUX® was coined.

U.S. 3,445,234. Leuco Dye/Hexaarylbiimidazole Image Forming Composition. Cescon, Lawrence A.; Dessauer, Rolf. E. I. du Pont de Nemours and Company. May 20, 1969 (Cl. 430/332; 430/538). Appl. May 13, 1968. An image-forming composition of (1) a dye in its leuco form, and (2) a 2,2′,4,4′,5,5′-hexaarylbiimidazole. The composition can be combined with a binder and coated upon a substrate from a solvent solution. A representative composition is tris(4-diethylamino-o-tolyl)methane trihydrochloride and 2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetraphenyl biimidazole.

Immediate concerns addressed some of the issues that were perceived to be critical for a potential commercial product, whatever it might be. In industrial research laboratories, chemistry is done for a purpose—to develop new products. So uppermost in the mind of the inventors of the HABI-photooxidation system was what one could do with it.



Scheme 8.4. Double barreled biimidazole.



Scheme 8.5. Oxidation of stable leucodye TLA-454.

It was of course apparent that while the color-formation was impressive, it was only the beginning of a new approach to printout systems. In order to develop an acceptable product, it was considered important that no wet chemistry be involved, and that the entire system had to be capable of being coated in a single pass onto paper.

The technical hurdles that had to be addressed included:

(1) Stabilization of the unimaged, i.e., uncolored areas.
(2) Was the sensitivity of the system capable of improvement?
(3) Would it be possible to generate a truly black image?
(4) The type of dye used in the initial experimentation belonged to a class of dyes that had generally poor light stability and it was felt that image stability would therefore be an issue.

(5) The stability of the unexposed material, i.e., pre-image shelf life was another concern. It was believed that the coated material should possess shelf life of over a year under normal storage conditions, i.e., without refrigeration.
(6) As many of the photochromic HABIs were also thermochromic, the formation of radicals by a thermal reaction became a possibility.

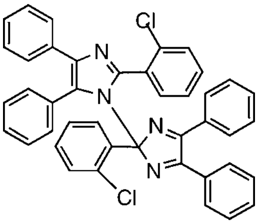
As a result of a considerable research effort these issues were resolved and several routes were identified which allowed the contrast between imaged and unimaged areas to be maintained.

8.4 INVENTION OF IMAGING AND DEACTIVATIO SYSTEMS

Several routes toward image stabilization were considered.

8.4.1 Modification of HABIs

Cescon had shown that HABIs with o-substituents in the 2-phenyl ring had improved dark stability vs. unsubstituted analogs. From synthetic work it was learned how substituents influenced the absorption spectra of HABIS. The preferred material, because of stability and ease of preparation was o-Cl-HABI.



o-ClHABI

It was anticipated that it the absorption spectrum of HABIs could be modified so that only deep ultraviolet light would cause radical formation, the unexposed areas would be room light stable. Many HABIs were synthesized but none had the desired spectra to allow this approach to be realized.

8.4.2 Desiccation

It was observed early in the program that the filter paper impregnated with the HABI/leucodye chemistry could be more easily imaged when moist. An improvement in background stability was observed when the imaged paper was desiccated over periods of time.

U.S. 3,630,736. Leuco Dye/Hexaarylbiimidazole Compositions and Processes. Lawrence A. Cescon, Rolf Dessauer. E. I. du Pont de Nemours and Company. December 28, 1971 (Cl. 430/343). Appl. June 19, 1969. Process for deactivating selected photosensitive, color-forming compositions against color formation by removing solvent from the compositions until they are substantially dry, and maintaining such dry compositions at a temperature below the activation temperature of the compositions; especially compositions comprising an admixture of selected hexaarylbiimidazoles and selected leuco dyes dispersed in a thermoplastic binder.

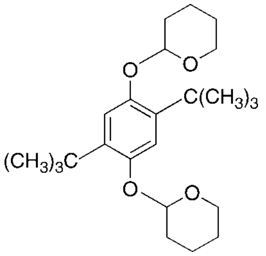
8.4.3 Chemical treatments

Stabilization of the unimaged areas was initially demonstrated by immersing filter paper, which had been treated with solutions of HABI and leucodye in ethereal solutions of hydroquinone. This was hardly a practical method, but it showed a path. Diethyl ether, as solvent was used because the conventional solvents dissolved the leucodye. Many years later (1976) it was learned that phenidone was an exceptional effective radical scavenger.

8.4.4 Thermal generation of inhibitors

Could hydroquinones be generated thermally from a precursor that was incorporated in the HABI/leucodye-recipe? Dr. Philip Manos, a chemist working on another project volunteered his services and prepared a number of hydroquinone ethers. Filter paper containing the leucodye, HABI and such ethers could be imaged, and thermally "fixed" by converting the ether to a hydroquinone.

> **U.S. 3,390,995. Light-Sensitive Composition Consisting of Organic Color-Generator, Photooxidant and Organic Thermally Activatable Reducing Agent Progenitor.** Manos, Philip (du Pont de Nemours, E. I., and Co.). July 2, 1968 (Cl. 430/337; 430/340; 430/344). Appl. April 29, 1964. This invention is directed to novel light-sensitive compositions and a unique process for deactivating them by heat so that they are no longer light-sensitive. More particularly, this invention deals with a composition consisting of (1) an organic color-generator, (2) a photo-oxidant, and (3) an organic compound capable of forming a reducing agent by heat. This novel composition quickly undergoes a color change to form a sharp image upon irradiation with a pattern of ultraviolet light. After a brief heat treatment, however, the composition is no longer light sensitive, i.e., it has become deactivated, and the image is preserved against a stable background.



Thermal inhibitor

8.4.5 Matrix modification

By this time it was realized that the treated filter papers worked better when a small amount of a plasticizer was incorporated in the recipe. Early on poly(ethylene oxide) derivatives were explored for this purpose. It was then realized that better images could be formed when the imaging materials were applied as a coating over the paper instead of being dispersed inside it. This was achieved by adding a cellulose acetate binder to the HABI/leucodye/plasticizer solution. Gradually, the components of the imaging system emerged!

Looney suggested an alternate approach to fixing! She reasoned that selection of certain binders would make it possible to restrict molecular motion at room temperature and increase it at elevated temperatures. Indeed, it was possible to formulate coatings in which the image was exposed to light, and subsequently heated to limit color formation only to the exposed areas. The extended half-life of the free radical made that possible. Alternatively, one could heat the coating and imagewise expose it simultaneously.

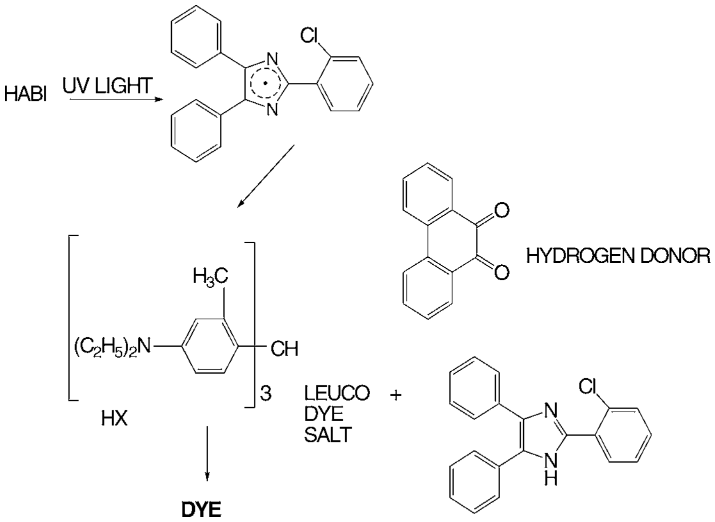
U.S. 3,615,481. Leuco Dye/Hexaarylbiimidazole Thermally Activated Imaging Process. Looney, Catharine E. (du Pont de Nemours, E. I., and Co.). October 26, 1971 (Cl. 430/335; 430/336; 430/337). Appl. May 19, 1969. Process for imaging photosensitive color-forming compositions comprising selected leuco dyes, hexaarylbiimidazoles, and, optionally, a binder, which process comprises heating said composition to a temperature at which the composition becomes sufficiently fluid to permit fluid movement of the components of the composition, but below the decomposition temperature of the composition, and subjecting the composition to photoirradiation with activating light within the ultraviolet and visible regions. Preferably the binder is a thermoplastic polymer having a glass transition temperature above room temperature but below the decomposition temperature of the composition. In the alternative, the steps of the process may be reversed, i.e., the irradiation step may be carried out first, followed by heating as described above.

8.4.6 Photogeneration of inhibitors

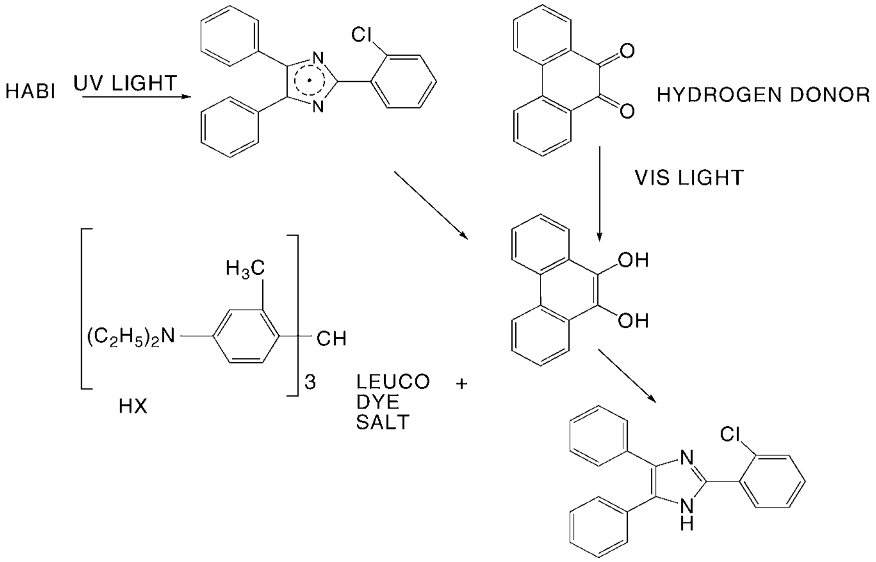
A chance meeting with Drs. Richard G. Bennett and Alexander Maclachlan, employed at the DuPont Company's Radiation Physics Laboratory, resulted in a major collaborative effort, in which the Organic Chemicals Department supported quantitative studies of this chemistry. Before long, RPL had four scientists working with the Organic Chemicals Department.

Maclachlan, a kineticist, quantified a number of relationships, and made significant measurements. He proposed a novel approach to stabilizing the imaged materials: photogeneration of a radical trap. In his earliest experiments, Maclachlan found that coatings of a solution containing a HABI, a triphenylmethane leucodye salt, a polyethylene oxide plasticizers and 9,10-phenanthrenequinone would no longer form color when exposed to visible light, while a cyan color resulted when the same coating was exposed to ultraviolet light. This offered a dry, non-thermal approach to image formation and stabilization.

Immediately upon seeing Maclachlan's demonstration of his "photofix concept" it was realized that a unique approach to non-silver imaging was possible: a single coating capable of giving either positive or negative images based on exposure sequences of two distinct wavelength bands! This is what we had been looking for, and Coraor reassigned several chemists to optimize this system. Especially important were the contributions of C. Yembrick, who



Scheme 8.6. Dye formation in HABI/leucodye/quinone system.



Scheme 8.7. Photodeactivation (fixing) in HABI/leucodye/quinone system.

investigated additives and P.S. Strilko, who sought to develop a better understanding of the light/chemistry interactions.

> **U.S. 3,390,996. Photosensitive Composition Comprising an Organic Nitrogen-Containing Color-Generator, a Photo-Oxidant and a Redox Couple.** A. Maclachlan (1968) (du Pont de Nemours, E. I., and Co.) (Cl. 430/334; 430/337; 430/340; 430/344). Appl. April 29, 1964. A composition which forms color when irradiated with light of one wavelength and becomes relatively insensitive to that light when irradiated with light of a different wavelength. The composition comprises (a) an organic nitrogen containing color-generator, such as a leuco dye, (b) a photooxidant, such as a HABI, which upon being irradiated oxidizes the color-generator to its colored form, (c) a redox couple of (1) a reductant, and (2) an oxidant which when activated by light reacts with the photo-oxidant to deactivate it. The composition can be coated on a substrate such as plastic, paper or metal.

Photolysis of HABIs as a result of UV-irradiation leads to radicals that abstract an electron from the leucodye salt, which then disproportionates to form at least one dye molecule. Visible light absorbed by the quinone converts it into a reduced derivative, which can react with the imidazolyl radical as the latter is formed. Reaction between these species is very rapid and prevents the radical from interacting with the leucodye salt. Hence, no color is formed. The quinone reduction product also interacts with the cellulosic binder, converting the initially light yellow coating to colorless. Initial studies of a preferred quinone/H-donor combination employed Carbowax. In time amine derivatives were found to be more effective.

Strilko made a thorough analysis of the relationship between different light sources and the coatings in order to optimize the fixing and imaging conditions. He contributed the following analysis of the chemistry/light interaction.

Maclachlan had shown that quinones could be photochemically exposed to visible light to generate hydroquinone-fixing agents that would prevent unwanted color formation from occurring. Following that discovery, a team of chemists set out to synthesize various quinone structures that could be tested for suitability in a product. These quinones were placed in test formulations, coated on paper, dried and exposed to visible light and then to UV light stepwise. This method employed a Xenon flash lamp of 1/1000-second duration and fabricated with a quartz glass envelope to maximize the amount of UV. Xenon lamps were selected since they are rich in both UV and visible light output. Corning Glass optical filters were used to isolate the various wavelength regions so that either the deactivation or color forming processes predominated. Exposure through the Corning 7-54 filter (colored deep purple) isolated the desired UV while blocking the blue and most of the visible light wavelengths. In the test, the Corning 0-51 filter (pale straw color), which effectively blocked UV, was placed over the coated paper during the first exposure to generate the hydroquinone. Then the same area was exposed to UV light using the Corning 7-54 filter. First the density of the color was checked against a standard to verify that the test compound was not interfering with the basic color forming reaction. Then the density of color formed in the block exposed first to visible light and then to UV was compared to assess the effectiveness of the fixing agent. While this method was quick and simple; it proved to be too quick and too simple. There were some serious drawbacks to this approach.

The type of light source and the costly Corning filters, which were used, bore little resemblance to what could be employed in any type of practical system. Additionally when the level of quinone was sufficiently large to prevent color formation in this test, more often than not, it diminished the color forming capability. By this test method, all the quinone had to be converted to hydroquinone to show it to be an effective fixing agent. The duration of the Xenon flash didn't allow for additional photochemical changes to take place. But the best way to prevent unwanted color formation in the background areas proved to be one that consumed all of the HABI. The best way to do that was shown to utilize a combination of fixing agents and light wavelengths so that some controlled amount of UV was included with the visible light. It is what one person called the leaky filter concept. The concept was to generate hydroquinone and triarylimidazolyl radicals at the same time. The rate of reaction of the triarylimidazolyl radicals is several orders of magnitude faster with the hydroquinone than with the leucodyes. When the hydroquinone reacts with the triarylimidazolyl radicals, it is converted back to the initial quinone. Basically the quinone is being continuously recycled while the hexaarylbiimidazole is converted into an inactive molecule. The slower rates of exposure to these fixing wavelengths permit this recycling to occur. This approach also permitted using lower quantities of fixing agent(s) in the formulations. The type of light source used for exposure dictates imaging wavelengths of light.

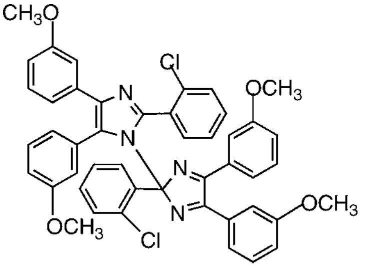
Further, the emitted wavelengths could be modified by the use of filters as well as anything else that might be in the path of light. For contact printing applications the light might be mercury or mercury/metal additive lamps or other arc lamps commonly used in the printing industry, or a series of fluorescent lamps configured in a bank. Filtering of that light to get the desired wavelengths is critical for light sources that are rich in both visible and UV light. In the case of fluorescent lamps, there are commercially available black light blue lamps, which effectively blocked the deactivating wavelengths. Contacts with many manufacturers of glass and optical glass ultimately uncovered a deep purple glass made for decorative stained glass markets that proved to be a perfectly useable filter for the imaging chemistry. It was inexpensive and available in large sheets. While not of optical quality, the distance between this filter and the paper being exposed is sufficiently large that any optical imperfections in the glass are inconsequential.

As the work continued it was shown that some of the earliest candidate quinones which were either relatively easily available or could be manufactured inexpensively ultimately became the components of choice. Thus the use of the more costly and esoteric molecules was avoided. Pyrenequinone, as the mixed 3,6- and 3,8-isomers, has a low quantum yield photochemically, but spectrally provides some desired filtering of the near UV and blue components of many light sources. 9,10-Phenanthrenequinone has a much higher quantum yield, but spectrally overlaps too closely with the imaging chemistry. When used by itself, it imparts slow imaging speeds and reduced optical density of the images. The combination of both of these quinones behaves in ways not initially anticipated in that formulations based on the mixture can give rise to coatings that are slowly deactivated under normal room light conditions. Specialized phosphors emitting strongly in the blue region were investigated which give faster deactivation, but these have been little used. More esoteric light sources were investigated including cathode ray tubes with UV emitting phosphors and UV transmitting fiber optic faceplates. These were shown to effectively image HABI/leucodye compositions but the relative slow imaging speeds made use of this approach impractical. In most instances, the half-life of the phosphor was too short given the energy requirement to generate good density images quickly; additionally these tubes were expensive to manufacture.

8.4.7 A new HABI is required

The group of chemists that addressed these issues was primarily experienced in synthetic chemistry, a field that was strongly encouraged in graduate schools in the 1950s. It was realized that some physical chemistry was required to address the problems of sensitivity, performance and optimization.

Analysis of the spectra of the HABI and quinone initiators predicted that better images would result if a HABI could be employed that showed more absorption in the 360 nm region, where 9,10-phenanthrenequinone had little absorption. R.L. Cohen was given this task. He identified CDM-HABI as a possible candidate. The substitution of a meta-methoxy functions on the 4- and 5-phenyl rings shifted the spectrum so as to separate the quinone and HABI peaks further apart.



CDM-HABI

U.S. 3,390,994. Photographic Triarylmethane Dye Process. Cescon, Lawrence A. (du Pont de Nemours, E. I., and Co.). July 2, 1968 (Cl. 430/334; 430/337; 430/343). Appl. February 17, 1966. A composition which forms an intense color when irradiated with light of one wavelength and becomes rapidly insensitive to that light when irradiated with light of a different wavelength. The composition comprises (a) an acid salt of a leuco aminotriarylmethane, (b) a hexaarylbiimidazole, (c) a redox couple of (1) pyrenequinone or phenanthrenequinone and (2) a lower alkyl ester of nitrilotriacetic acid or nitrilotripropionic acid. The composition can be coated from solution on a substrate such as plastic, paper or metal.

U.S. 3,579,342. Leuco Triarylmethane/Hexaarylbiimidazole Color Forming System Containing a Deactivator. Strilko, Peter S. (du Pont de Nemours, E. I., and Co.). May 18, 1971 (Cl. 430/340; 430/538); (G 03c). Appl. June 27, 1968; 11 pp. A photoimagable and photodeactivatable composition of (A) A salt of a leuco triarylmethane and a salt-forming acid; (B) A hexaarylbiimidazole which absorbs principally in the ultraviolet region and is a photooxidant for the salt of the leuco triarylmethane present in an amount of from about 1 to 2 moles per mole of said salt of the leuco triarylmethane; (C) l,6-pyrenequinone or 1,8-pyrenequinone or both, present in an amount of from about .04 to .4 mole per mole of hexaarylbiimidazole; (D) A visible light-absorbing carbonyl compound selected from 9,10-phenanthrenequinone, perinaphthenone, or 4-methoxy-l,2-naphthoquinone; present in an amount of from about .05 to 2 moles per mole of hexaarylbiimidazole; and (E) An ether containing at least one oxymethylene group wherein the methylene bears at least one hydrogen; present in an amount providing from about 50 to 500 oxymethylene groups per mole of the combined quinone components (C) and (D).

U.S. 3,666,466. Deactivating Dual Response Photosensitive Compositions with Visible and Ultraviolet Light. Strilko, Peter S. (du Pont de Nemours, E. I., and Co.). May 30, 1972 (Cl. 430/333; 430/337). Appl. November 26, 1969. Method for deactivating a photosensitive composition, which composition is characterized by forming color on irradiation with ultraviolet light and being deactivated against color formation on irradiation with light of longer wavelengths, e.g., visible light radiation. The method comprises exposing the surface of the photosensitive composition to be deactivated to both ultraviolet and visible light radiation, with the intensity of the ultraviolet radiation being an amount up to the maximum amount said surface of the composition can absorb without undergoing substantial color formation, the intensity of the visible light radiation being effective for deactivation, whereby the resistance of the composition to color formation on subsequent exposure to ultraviolet light is either increased or the time required to achieve a particular degree of such resistance is decreased.

8.4.8 Other components

Better hydrogen donors were sought to allow more effective deactivation, better hydrogen donors, including 3,3,3-trinitrilopropionic acid, triethanolamine triacetate and dibenzylaminoethanol acetate were identified.

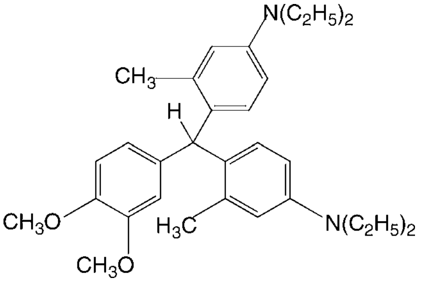
U.S. 3,658,543. Dual-Response Photosensitive Compositions Containing an Acyl Ester of Triethanolamine. Gerlach, Howard G., Jr.; Looney, Catharine E. (du Pont de Nemours, E. I., and Co.). April 5, 1972 (Cl. 430/343; 430/524; 430/531; 430/538). Appl. 99,512, December 18, 1970, 15 pp. Improved photosensitive compositions comprising A. an acid salt of a leuco aminotriarylmethane such as tris(4-N,N-diethylamino-o-tolyl)methane; B. a hexaarylbiimidazole such as a 2,2′-bis(o-chloro-phenyl)-4,4′,5,5′-tetraphenylbiimidazole; and C. a redox couple containing (1) as an oxidant a polynuclear quinone absorbing principally in the 400–550 nm region such as 1,6-pyrenequinone, and (2) as a reductant an acyl ester of triethanolamine such as triethanolamine triacetate optionally mixed with a lower alkyl ester of a nitrilotrialkanoic acid such as 3,3′,3″-nitrilotripropionic acid, trimethyl ester are effective color forming compositions useful in a variety of applications. The need for an effective plasticizer system was solved by the addition of sulfonamides and ethoxylated phenol derivatives.

The choice of acids, plasticizers and binders continued and the coatings continued to improve in performance.

U.S. 3,658,542. Dual-Response Photosensitive Compositions Containing an Alkylbenzenesulfonic Acid and an Arene Sulfonamide. Henry, Cyrus P., Jr.; Jeffrey, John R. (du Pont de Nemours, E. I., and Co.). April 25, 1972 (Cl. 430/343; 430/524; 430/531; 430/538). Appl. 99 511, December 18, 1970, 13 pp. Improved photosensitive compositions comprising A. an acid salt of a leuco aminotriarylmethane such as tris(4-N,N-diethylamino-o-tolyl)methane; B. a hexaarylbiimidazole such as a 2,2′-bis(o-chloro-phenyl)-4,4′,5,5-tetraphenylbiimidazole; and C. a redox couple containing (1) as an oxidant a polynuclear quinone absorbing principally in the 400–550 nm region such as 1,6-pyrenequinone and (2) as a reductant an acyl ester of triethanolamine such as triethanolamine triacetate, a lower alkyl ester of a nitnilotrialkanoic acid such as 3,3′,3″-nitrilotripropionic acid, trimethyl ester or their mixtures: are obtained with the use of an alkylbenzenesulfonic acid to form the salt of the triarylmethane and an alkyl arene-sulfonamide plasticizer. The improved compositions are effective color forming compositions useful in a variety of applications.

8.4.9 Leucodyes

The group of scientists working in this field grew slowly from three to four and more; soon it was joined by a consultant, Dr. Catherine Looney, a spectroscopist, who had worked on triphenylmethane dyes during her graduate research program. She, Cescon and Dessauer developed a series of novel triphenylmethane leucodyes, which gave near-black colors on photooxidation. Of these, most effective was LB8, the blue-black forming leucodye bis(4-diethylamino-*o*-tolyl)(3,4-diethylaminophenyl)methane.



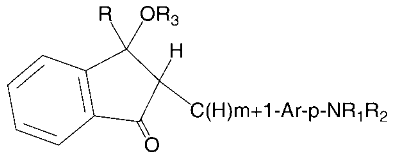
LB-8 leucodye

A goal to develop a color-forming chain reaction was not achieved. The photosensitivity of the system could not be increased significantly, but the major applications for this technology did not require increased imaging speed. In time, black images were made with different mixtures of leucodyes, involving structural modifications of the triphenylmethane leucodye.

U.S. 3,423,427. Selectively Substituted Methane Leucodyes. Lawrence A. Cescon, Rolf Dessauer and Catharine Elizabeth Looney. E. I. du Pont de Nemours and Company. January 21, 1969 (Cl. 549/74; 8/400; 8/444; 8/657; 106/14.5; 106/31.2; 106/31.21; 106/31.43). Appl. June 16, 1963. Leuco bis[4-disubstituted amino-2-ethyl (or fluoro or methyl) phenyl]-2-thienyl (or 2-furyl, 3,4-methylene-di-oxyphenyl, 2-methoxy-4-(C_1 to C_8) alkoxyphenyl) methanes, methanols, or cyanomethanes, leuco salts thereof; and dyes formed by the oxidation of the leuco dyes or their salts. The dyes are gray-to-black and of high tinctorial strength, making them useful as graphic art inks or pigment dyes. The leuco forms are useful in conjunction with photooxidants in imaging systems by conversion to the dye form when the oxidant is photolyzed. The leuco cyanomethanes can be converted to the dye form by direct photolysis and fixed with cyanuric derivatives or arylsulfonic acids. The leuco dyes are storage-stable, resisting air or heat-induced oxidation. They are prepared by conventional procedures.

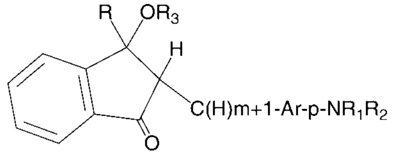
U.S. 3,449,379. Triphenylmethane Derivatives. Lawrence A. Cescon, Rolf Dessauer and Catharine Elizabeth Looney. E. I. du Pont de Nemours and Company. June 10, 1969 (Cl. 552/103; 8/657; 8/919; 430/338; 430/344; 552/100; 552/109; 552/110; 552/111; 552/113). Appl. June 26, 1963. This invention is directed to novel selected triphenylmethanes and the dyes obtained there from by oxidation. More particularly, this invention deals with triphenylmethane derivatives which are valuable because, taken singly, they are capable of forming, by simple oxidation processes, useful gray to black dyes hitherto unavailable.

U.S. 3,992,450. 2,3-Disubstituted-1-Indanones. Neumer; John Fred. E. I. Du Pont de Nemours and Company, November 16, 1976 (564/315; 430/338; 430/559; 560/22; 560/28; 560/32; 560/107; 560/163; 560/252; 564/56). Appl. April 30, 1971. Compounds of the general formula:



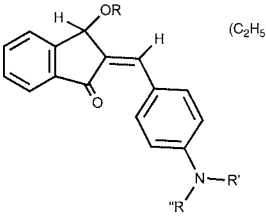
where m = 1, the formula represents a colorless leuco compound; where m = 0, the formula represents the yellow dye derivative of the leuco. These compounds are particularly useful in photosensitive compositions.

U.S. 4,078,934. Photosensitive, Image-Forming Composition Containing a Leuco 2,3-Disubstituted-1-Indanone and a Photooxidant. Neumer, John Fred (E. I. Du Pont de Nemours and Company), March 14, 1978 (Cl. 430/343; 430/338; 430/375; 430/542). Appl. May 18, 1976. Leuco dye compositions containing a compound of the formula:

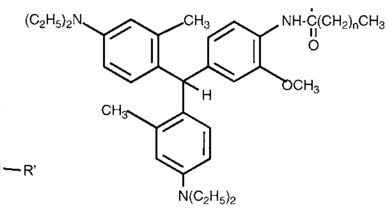


wherein m = 0 or 1: Ar is an arylene or lower alkyl substituted arylene radical; R_1 and R_2, which may be the same or different, are lower alkyl or hydroxyalkyl groups.

Preferred black compositions were formulated with the below leucodyes: The light stability of the dyes formed during the process was adequate for many applications, and in the dark, was excellent; images that are over 40 years old have survived under dark storage conditions.



Yellow Leucodye



Purple Leucodye

Many related triphenylmethane leucodyes were synthesized and similarly photooxidized. A gamut of colors was observed spanning the range from green to purple. Other classes of leucodyes were investigated and found to lend themselves to the photo-oxidation process.

Other dye classes were found to be usefully oxidized by HABIs, included: (1) aminotriarylmethanes, (2) aminoxanthenes, (3) aminothioxanthenes, (4) amino-9,10-dihydroacridines, (5) aminophenoxazines, (6) aminophenothiazines, (7) aminodihydrophenazines, (8) aminodiphenylmethanes (i) leuco indamines, (9) aminohydrocinnamic acids (cyanoethanes, leuco methines), (10) hydrazines, (11) leuco indigoid dyes, (12) amino-2,3-dihydroanthraquinones, (13) tetrahalo-*p*,*p*′-biphenols, (14) 2(*p*-hydroxyphenyl)-4,5-diphenylimidazoles, and (15) phenethylanilines.

8.4.10 Binders

A number of binder systems were investigated and cellulosic esters were found to be acceptable. By proper combinations of several, a system was developed that could be coated at relatively high coating speeds. A limitation of cellulose acetate butyrate, e.g., was that resultant coatings were somewhat humididy sensitive. This subsequently caused some customer dissatisfaction, as high image densities were not attainable in very dry environments. Several of the proposed applications necessitated that pencil or ink writing would be possible on the imaged sheet. The cellulosic ester binders presented too smooth a surface to permit this. The addition of silica in the form of Syloids™ overcame these problems.

8.4.11 Substrates

Pre-image shelf life was improved slowly by a better understanding of the principal reactions and side-reactions. In time, it was learned how to design a system that could be coated on commercial paper at high speeds. This involved an extensive search for a "neutral" paper, i.e., one that did not participate in the chemistry of the coatings.

High-holdout, i.e., prevention of penetration of the coating chemistry into the paper substrate was found important; this was achieved when paper was properly formulated and calendered. As it was desirable to produce coatings on both sides of the sheet, paper with the right optical opacity and transmissivity was required. Additionally, of course, the cost of the paper had to be considered. Heavier paper stock yields a more attractive product, but is proportionately more expensive.

Efforts were continued to produce coatings on paper. It was found that there was a lot about paper that the group did not know. Terms such as holdout, porosity, uniformity, and paper neutrality were unfamiliar. It was of course realized that a paper which permitted the imaging materials to be anchored on top was desired, but there still had to be sufficient interaction between paper and coating to keep the latter from peeling off too easily. Wicking of paper, i.e., the selective absorption of some of the components of the imaging chemistry was found to destroy imaging properties over time. Paper is not "neutral", depending on how it is manufactured. In the UVI system, with carefully balanced chemistry, a change in acidity of the substrate could significantly alter the performance of the coated product. Such changes often assert themselves over a period of time, leading to reduced shelf life. Paper uniformity is another issue. Paper is manufactured in large quantities at high speeds, and it becomes commercially unfeasible to have small lots made for a low volume application. Thus it became necessary to study and evaluate a large number of papers from different manufacturers; in time a paper identified as 32HG from Schweitzer Bros (later Kimberly Clark) offered the best overall performance. Solvent coatings of paper webs must be dried prior to being rolled up. As such coatings are frequently thermally sensitive (HABIs are thermochromic!) they must not be dried excessively to prevent thermal discoloration or degradation. To prevent coatings from sticking to the underside, a fluorotelomer stearate. was included in the mix.

This paper was relatively lightweight, could be folded easily and had adequate uniformity. It reflected some ultraviolet light during exposures, and thus over-exposure of the coated paper product resulted in fuzzy images. By comparison, the competitive Fotoproof™ paper was coated on a UV-absorbing sheet, which gave much sharper images.

U.S. 3,672,933. Preparation of Photosensitive Coated Papers by Single Pass Per Side. Marvin F. Lieberman, E. I. du Pont de Nemours and Company. June 28, 1972 (Cl. 430/502; 430/935). Appl.

October 30, 1970. Photosensitive papers, such as proofing paper, imageable on both sides are produced by (a) first coating one side with a composition comprising a volatile organic solvent and a film-forming g polymeric binder, and photosensitive ingredients, followed by drying to evaporate the solvent at a controlled rate, thereby forming a film, then (b) coating the second side with the same composition in a single coating application, and drying under the comparable conditions to the first side. Careful control of the coating conditions, drying steps, volatile organic solvents, polymeric binders, photosensitive compositions and paper substrates yield blister-free, two-side coated photosensitive papers.

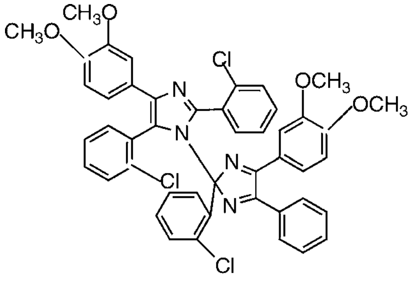
U.S. 3,674,534. Preparation of Papers Coated on Both Sides with Photosensitive Composition. Connair, Michael John (du Pont de Nemours, E. I, and Co.). July 4, 1972 (Cl. 117-34; B 44d). Appl. January 30, 1970; 4 pp. Blister-free photosensitive paper is obtained by coating opaque paper (<10 mil thick) on both sides with a photosensitive compn. contg. for example a leuco dye, a photooxidant, a film-forming binder such as poly(vinyl alc.), and a volatile org. solvent boiling between 55 and 85°. The paper is coated 1st on 1 side with this compn. in an amt. sufficient to provide a dry film coating of 6–15 lb/3000 ft^2. Of paper, dried by evapg. the solvent at a rate to prevent blister formation, and coated on the other side with the same amt. of photosensitive compn. but in multiple stages of coating and drying such that in each stage 10–60% of the total wt. is applied.

Inevitably, there was the desire to produce a film product, embodying the characteristics of the photo-fix paper. Coatings on MYLAR® polyester film were produced. Here an anchoring sub-coat was required.

8.4.12 New HABIs

Also, most importantly, the understanding of the HABI chemistry allowed selection of the preferred structural modifications to give the best spectral sensitivity, preimage shelf life and imaging speed. Thus, for example, the initial HABI was replaced by others over several iterations.

A goal was to replace the rather expensive CDM-HABI, which required an expensive starting material (*m*-methoxybenzaldehyde) with a lower cost photooxidant. After the DYLUX® Venture moved to Photo Products Department, there were few incentives at Orchem to develop new HABIs. Still, Dessauer asked one of his technicians to synthesize some HABIs based on low cost starting materials. Surprisingly, none of the earlier DuPont work had utilized unsymmetrical benzoins, which could be made by starting with two different aromatic aldehydes. Dessauer also sought to gain some spectral shift of the resulting HABIs, by having electron donating and electron withdrawing functions in the 4- and 5-phenyl rings, respectively. Not only was the anticipated result obtained, but also it was found that the resulting HABIs could be patented. Formulation studies showed that TCTM-HABI could be used at lower concentrations than CDM-HABI, and because it required relatively inexpensive starting aldehydes (*o*-chlorobenzaldehyde and veratraldehyde) it was a far less costly material. Replacement of CDM-HABI effected a saving of over $1,000,00 per year.



TCTM-HABI

Table 8.1. Ingredients of DYLUX® 503B

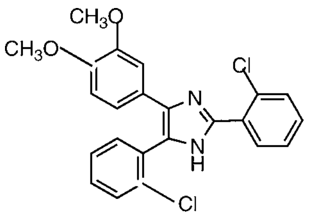
Ingredient	Weight %
Acetone (solvent)	72.000
Isopropanol (solvent)	8.000
Dodecylbenzenesulfonic acid (proton acid)	0.727
Tris(*p*-diethylamino-*o*-tolyl)methane (leuco cyan dye)	0.275
N-Ethyl-*p*-toluenesulfonamide (solid plasticizer)	2.890
o-Phenylphenol condensate with average of ~2.25 mols ethyleneoxide (plasticizer)	2.385
Triphenylimidazolyl dimer (TCTM-HABI) (one of compounds 1 to 10, Table 6)	0.434
Mixture of ~83% 1,6- and ~17% 1,8-pyrenequinones (oxidant)	0.004
9,10-Phenanthrenequinone (oxidant)	0.139
Triethanolamine triacetate (hydrogen donor)	2.013
Anti-blocking agent	0.020
Silica gel of 9 micron	0.606
Cellulose acetate butyrate (~27% butyryl)	10.507
Total	100.000

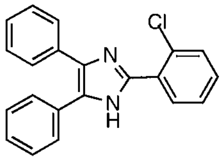
The radical formed on photolysis had greatly increased half-life and thus could more effectively oxidize the leucodyes.

> **U.S. 4,252,887. Dimers Derived from Unsymmetrical 2,4,5-Triphenylimidazole Compounds as Photoinitiators.** Dessauer, Rolf, E. I. du Pont de Nemours and Company. February 24, 1981 (Cl. 430/281.1; 430/283.1; 430/287.1; 430/288.1; 430/915; 430/917; 430/920; 522/16; 522/26; 522/79; 522/83; 522/89). Appl. August 14, 1979. Photoimaging compositions comprising (A) 2,4,5-triphenylimidazolyl dimer having selected substituents on the 2, 4 and 5 phenyl rings and an extinction coefficient determined in methylene chloride at 10^{-5} to 10^{-3} mol/liter at 350 nm of at least 4000 liters/mol-cm and at 400 nm of at least 250 liters/mol-cm; and at least one of (B1) leuco dye or (B2) addition polymerizable ethylenically unsaturated monomeric compound. The new imaging compositions are useful in preparing dual response photoimaging products such as proofing papers, printout paper, overlay films and photopolymerizable elements. Improved imaging speed is achieved at equal concentration levels when compared with conventional 2,4,5-triphenylimidazolyl dimer.

At this stage, the coating recipe of a typical DYLUX® coating solution contained the following ingredients shown in Table 8.1.

T.M. Sheets at Towanda sought to improve the economics of the coated product, and achieved success by co-oxidizing the triarylimidazoles from which TCTM-HABI and o-Cl-HABI are manufactured. Surprisingly, the mixture showed improved photofixing capability.





TCDM-HABI is formed by co-oxidation of the above triarylimidazoles.

U.S. 4,622,286. Photoimaging Composition Containing Admixture of Leuco Dye and 2,4,5-Triphenylimidazolyl Dimer. Sheets; Thomas M. E. I du Pont de Nemours and Company. November 11, 1986 (Cl. 430/343; 430/332; 430/337; 430/340; 430/344). Appl. September 16, 1985. Photoimaging composition comprising an admixture of leuco dye, and at least one 2,4,5-triphenylimidazolyl dimer prepared by an oxidative coupling reaction, a reaction product, 2,2′,5-tris-(o-chlorophenyl)-4-(3,4-dimethoxyphenyl)-4′,5′-diphenylbiimidazole, being present in an amount of 0.01 to 90.0% by weight based on the weight of solids in the composition. The composition when coated on a support is useful for prepress proofing.

8.4.13 Imaging characteristics

Figure 8.1 illustrates the dual-response capability of DYLUX® the negative with UV-light leads to color formation; subsequent exposure to visible light fixes the background without affecting the image. This is “negative-working”. When the imagewise exposure is made through the negative with visible light, and a subsequent flooding exposure with UV light causes color in unexposed areas. This is “positive working”.

In the North American market, the negative imaging mode is preferred. Image-formation with a single exposure was what customers wanted. Some, but not all ran a subsequent fixing exposure.

The spectral changes that occur after exposures are depicted in Fig. 8.2. The plot of the various spectra[1] of the DYLUX® composition follows: equal size paper samples were exposed and then dissolved in equal amounts of solvents. The plot depicts: changes as result of different exposure conditions.

(1) Sample that had not been exposed at all, show some absorption at 450 nm, derived from the HABI and quinone absorption peaks

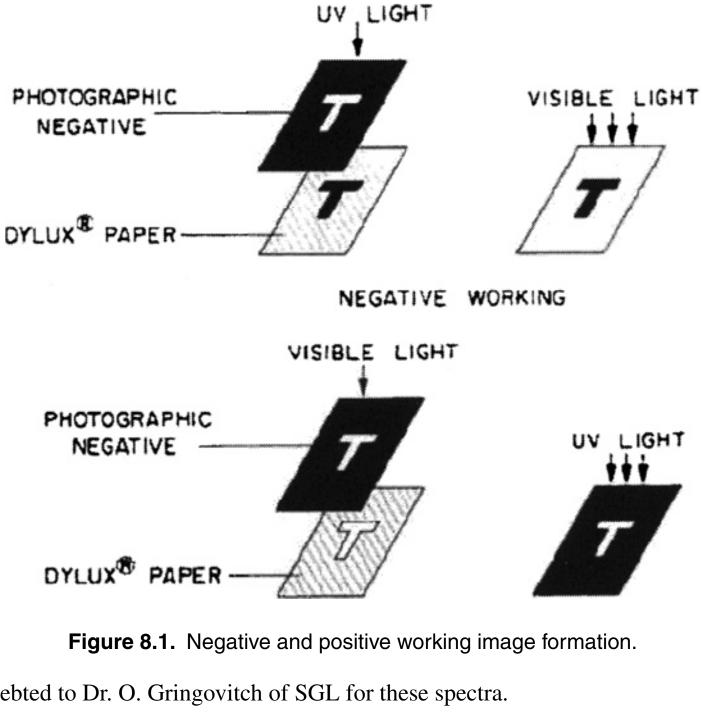


Figure 8.1. Negative and positive working image formation.

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[1] The author is indebted to Dr. O. Gringovitch of SGL for these spectra.

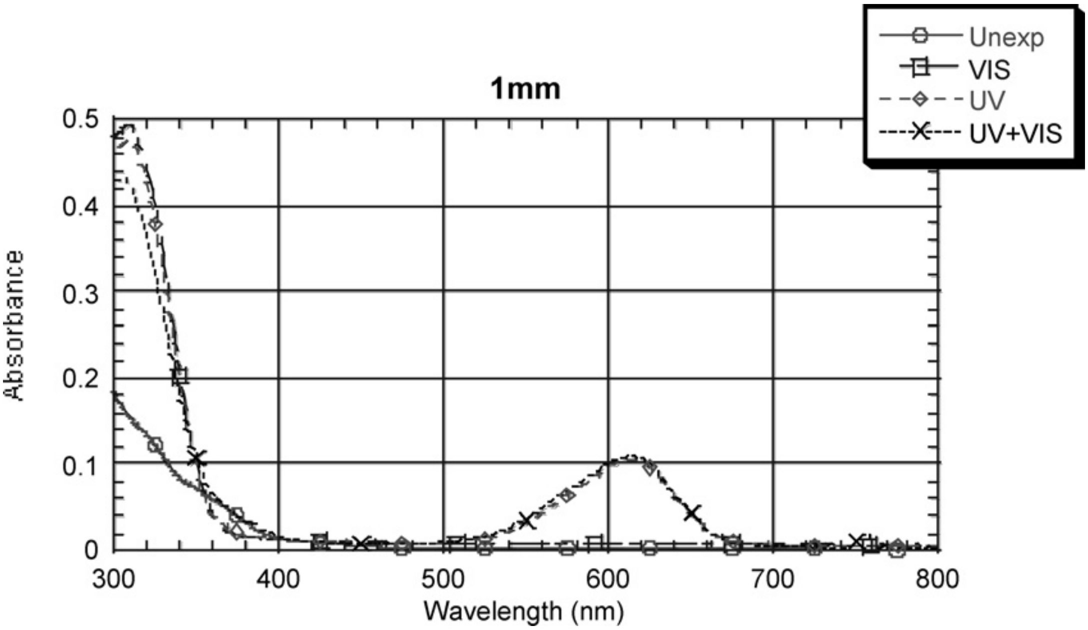


Figure 8.2. Spectral changes in DYLUX 503 proof paper.

(2) Sample that had been exposed to visible light only showing absorption in the 300-to 350 nm region, presumable from imidazoles formed during he exposure
(3) Sample exposed to ultraviolet light again shows an increase of the imidazole peak, but a new peak around 630 nm, due to dye formation; sample had a slightly greenish tinge, resulting from combination of dye and phenanthrenequinone peaks
(4) Sample exposed to ultraviolet light followed by visible light exposure was less green than (3) because the quinone components had been removed.

Most importantly, the applications for this novel printout technology were developed by dwelling on the strengths of the system, without overdue attention to its limitations. Market studies showed that the overwhelming desire for rapid formation of printout from lithographic negatives in a low light-level environment, without processing overcame many perceived objections, such as a cyan color, image dye migration over an extended period of time, relatively poor long-term image stability in daylight, etc.

8.4.14 A higher speed system

This work was done in the Organic Chemicals Department (Orchem), a part of the DuPont Company that was concerned with dye chemistry, but not with imaging technologies. That was the province of the Photo Products Department, which had research laboratories in Parlin, NJ and Rochester, NY.

Efforts were made to interest these in this technology, but no great enthusiasms were generated. The scientists at Orchem knew little of photopolymerization, which was then a strong buzzword, because the Parlin R&D Lab was interested in developing new products based on this core technology. It was suggested that perhaps these novel compounds would be useful as photopolymerization initiators, to compete with anthraquinone derivatives, aromatic ketones, e.g., benzophenone, or radical precursors such as benzoin methyl ether. Some crude experiments were performed, but the simple addition of HABIs to acrylate or methacrylate monomers failed to generate polymeric materials. Years later it was realized that a coinitator was required, but that is another story.

There is an inevitable desire of photochemists to achieve higher speed systems, and one afternoon in spring of 1964, Cescon, Cohen and Dessauer discussed alternate approaches toward this goal. It had been established that plasticization of the matrix was required to achieve color formation—so why not use a plasticizer that contained acrylate functionalities, and effect polymerization in a separate exposure, perhaps at higher wavelengths? Cescon and Cohen prepared coatings using purified polyacrylates and the then conventional photoinitiators. A photofix via photopolymerization worked! Cescon and Cohen then repeated the experiment without the conventional photopolymerization initiators, and the system still formed color at high intensity illumination, but not at low intensity, This was an early demonstration that HABIs could function as photopolymerization initiators. This system is described in detail elsewhere U.S. 3,615,454 (Chapter 9).

The new system was called "RF"-chemistry, for "rigidification fixing" as we hardened the matrix so as to prevent the molecular migration required for color-formation.

This system required coating on a film substrate, and a coversheet. At that time, the idea of coating a film sandwich was believed to be difficult, though in time that was no challenge at all. It was found that this system could be sensitized to effect changes at longer wavelengths. The increase in speed offered possibilities of projection printing, high speed film duplication, and imaging with low intensity light sources, such as cathode ray tubes. It was a new concept of imaging. Our management, who already had been concerned about the expense of developing the dual response quinone-based photofix systems, was unenthusiastic about still another extended research program. The "RF"-system never made it to the market, but it was the basis of many photopolymer products manufactured by DuPont, such as RISTON® Photoresists, CROMALIN® and CROMACHECK® proofing products, etc.

8.5 THE ROAD TO THE MARKET

Photosensitive materials are generally sold as coated products, and this immediately poses a problem in market development. In order to produce coated products economically, it is necessary to use coating machines, which frequently coat a 3 to 5 foot wide web at speeds greater than100 feet per minute. Hence in one hour, more than 38,000 square feet of material are produced. Setting up a coater for a run may take several hours, as does the cleanup thereafter. Thus, to justify the economics of coating, it almost becomes mandatory to think of products that consume large volumes of coated materials. For this reason, even small variations in recipes are not looked on favorably by coating managers, who consider every variation a new product.

During the early days of this program, there was little experience in the economics of coating. As markets began to appear, test materials could be produced on small coaters, operating 10 to 12″ wide webs at speeds to 30 ft/minute, but these had a limited relationship to production equipment and conditions.

Coating itself is an art, and coating light-sensitive materials is further complicated by the need to operate in subdued light, and also to guard against adverse thermal effects, as many photosensitive materials are also heat-sensitive. Substrate uniformity and variations in coating equipment require careful quality control.

Market development of course requires materials that work with a customer's equipment and frequently, different customers have different equipment. Hence. The coated product to be manufactured is frequently a compromise between a variety of factors.

Until coated products are produced on a large scale, one can only estimate the ultimate cost and performance. Encouraging potential customers to build or modify equipment when there is uncertainty about cost, performance, long-term pre-image shelf life, and long-term commitment to produce the product is a challenge.

DuPont fortunately had a good reputation among would-be customers, and hence, there was a willingness to try materials that had not been commercialized. Still, it was not always easy.

8.5.1 Identifying markets for printout systems

The greatest challenge in the development of the HABI based technology was to persuade management to support activities in new business areas. There was not too much doubt that we had some interesting novel technology when we identified HABIs as photooxidants and later photoinitiators. In that sense, DuPont management was generous in supporting the program. Where things became difficult was that getting a new product to the market is a risky business, and a costly one at that. The structure of the DuPont Company was both a help and a hindrance. One could easily obtain access to the R&D staff of other companies, who simply then considered DuPont an innovative company, and who were delighted to learn about new technologies. On the other hand, the internal marketing efforts were generally thwarted by the conservatism and risk-aversion of most middle managers. There were exceptions. Dr. Philip Wingate, who was General Manager and Vice President of Photo Products, was supportive, up to a point. However, his Director of Research and several of the latter's group were as antagonistic as could be.

Somewhere in the 1960s, my then Manager, Dr. Howard L. Smith suggested that I undertake a broad assignment entitled "NEW DYE USES". This was to identify new product areas or new materials for coloration; it was never defined. It gave me an opportunity to visit DuPont customers, who frequently were delighted to have a PhD chemist interested in their problems. Smith supported me with ample technicians, and I could frequently produce small quantities of novel materials for customers of the Dyes Division. Thus, I participated in a joint program on the coloration of aluminum with ALCOA, coloration of polyethylene with the Plastics Department, etc. I found this activity stimulating. I was also privileged to be a member of a team of DuPont scientists who were invited to spend a week at Meredith Publishing, publisher of "Better Homes and Gardens", to learn how a publishing house worked. Meredith had a policy then to let scientists learn about the printing industry, with the expectation that they might develop products that would make for better technology in their field. Other companies, e.g., Hallmark was also generous in opening their business to scientists.

When the photochromism program began to look like it might lead to commercial products, I was selected to investigate applications. We did not wish to compromise our patent position; it was necessary to undertake most marketing efforts inside DuPont. There were then many business areas that could make use of colored additives, and I had ample opportunities to visit many company laboratories. Inevitably, I met scientists who were interested in our unique materials. Even though no markets were found for the HABI/leucodye chemistry for several years, the management supported an effort that reached as many as 25 chemists and engineers for the period up to 1965.

8.5.2 Duplication (1962–1964)

Prior to the development of electrophotography, it was rather difficult to make copies of documents. However, relatively low cost technology was available for duplicating information when one could control the master. The preferred methods were mimeography and spirit duplication.

A mimeograph machine is a mechanical duplicator that produces copies by pressing ink onto paper through openings cut in a special stencil made of a strong paper saturated or coated with wax. Text is written or typed directly onto the stencil. Illustrations are drawn directly on the stencil with a stylus. A mimeograph machine works as follows:

- Special mimeograph or duplicator ink is applied as appropriate to the particular machine.
- Paper to be printed is placed in the paper tray.
- A prepared stencil is wrapped tautly and smoothly around the cylinder and secured at one or both ends, depending on the machine.
- As the cylinder is rotated, a pressure roller inside the machine presses paper against the cylinder.
- The roller forces the ink through the openings that were cut in the stencil onto the paper.

"Ditto" or spirit duplication machines transferred images onto a slick paper from a waxy coating containing dyes. One wrote or typed on the front page, and the image was transferred from the backside with solvent on a blank sheet.

Both these processes employed dyes, and the principal component was the relatively low cost Crystal Violet. The Organic Chemicals Department was the largest U.S. manufacturer of this dye. The initial concept for the use of the HABI chemistry was to develop duplication applications that would fit into this market. Thus the transparency generated on the mimeograph sheet was sufficient to have the latter act as a stencil through which ultraviolet light passed and imaged the photosensitive paper. This seemed clearly an application that fit into the Department's business. An attempt was made to produce a machine that had a UV-transparent glass cylinder that would permit effective imaging.

However, the timing of this coincided with the introduction of the Xerox 914 Copier, which almost instantly dominated that copier/duplication field.

8.5.3 Foot imaging/silhouette patterns (1962–1963)

It is likely that any development will have its distractions, and sometimes there is hope that a far-fetched idea may turn into a winner. In 1962, when our group was struggling to find applications, another DuPont department's management sought to obtain our assistance in perfecting a system for measuring shoe sizes!

In the early 1960s, DuPont developed a synthetic leather-like material, a poromer, named CORFAM®, which was to be a preferred material to replace shoe leather. CORFAM® shoes had many attractive qualities, but a serious detriment. Unlike leather shoes, that expanded with wear, the dimensions of CORFAM® shoes never changed! Customers inevitably buy shoes knowing that a tight fit initially will ultimately be a comfortable fit. As CORFAM® shoes did not change, they always remained as tight as when they were purchased. It seemed therefore of interest to develop some technology by which foot sizes and shoes could be connected, and a possible way was to obtain silhouettes of a customers feet, and use this information in selecting the shoe size.

A major study was to be conducted at the New York World's Fair of 1964/1965 and the then UVI paper was considered as a medium for recording foot silhouettes. To record the foot silhouette, the would-be customer was to step onto a sheet of photosensitive paper, and several fluorescent lights would rapidly form blue patterns on the paper to show the foot's outline. This would have consumed several million square feet of photosensitive paper, and on top, would have given the photosensitive paper a good exposure to many people, some of whom would surely come up with other ideas for this material! Even though the exploration of the concept went quite far, it never reached the World's Fair. However, some time in the late 1960s, an independent inventor approached DuPont with much the same idea. By that time, however, our focus was on electronic imaging, and so the photosensitive paper for silhouette imaging never went any further.

8.5.4 Optical printing (1963–1970)

8.5.4.1 *Printing via lenticular plate optics* Nevertheless, to keep this technology alive, the Organic Chemicals Department considered areas in which the Photo Products Department was not active. An early interaction, initiated by the Company's Development Department with a group of consultants from Data Communications Inc. (DCI) suggested that optical printing would offer some unique opportunities.

At that time (1963), electrophotographic printing and ink jet printing had not advanced to any significant levels, and the concept of printing with lasers or high intensity light appeared attractive. The consultants offered to develop an optical printer in which lenticular lens optics would modulate a high intensity ultraviolet light beam, with a goal of printing as many as 30 characters/second. This would exceed the speed of the then used impact Teletype™ printers, with a potentially quiet machine. Sometime in 1965 DCI did indeed deliver a machine that met many of the early goals, but DuPont elected to visit a number of potential users to interest them in the concept of optical printing onto a light sensitive medium. No data relating cost of consumables to performance was then available. The intended users were not interested. After the fiasco of being unable to sell optical printing via the DCI printer to some 20 companies, the UVI-program was severely reduced—only five chemists remained.

8.5.4.2 *Printing via magneto-optics* In 1969 an alternate approach to optical printing was considered: imaging a photosensitive material through a light transparent uniformly magnetized magnetic medium, on which image patterns had been generated with a ferromagnetic toner.

> **U.S. 3,604,326. Method and apparatus for Magnetic-Optical Printing.** James, II, Edward W.; Vassiliou, Eustathios. E. I. Du Pont de Nemours and Company, September 14, 1971 (Cl. 430/396; 346/21; 396/556; 430/31; 430/5). Appl. December 19, 1969. A method and apparatus for magnetic-optical printing employing a light-transparent uniformly magnetized magnetic medium upon which characters to be printed are first imaged magnetically and then delineated by optical masking using ferromagnetic toner, after which the characters are photographically recorded.

This approach never reached commercialization.

8.5.5 Electronic imaging (1966–1970)

A suggestion originating in the DuPont Company's Treasurer's Department in late 1965 resuscitated the program before it was terminated. By chance, someone heard that the Organic

Chemicals Department was developing a chemical solution that could be applied to a wide variety of substrates, and would contain all the components required to form images. Other technologies required heat, toners, washing, ammonia, etc. The UVI system did not—it was self-contained. It was suggested that a coating applied to an envelope might be imaged by electronically generated signals, as with a laser or cathode ray tube. This might allow high speed printing onto stuffed envelopes as a start. Charles Ford, an engineer who was familiar with the UVI technology was given several samples and tested these at Litton's Electron Tube Division with quartz-fiber optics equipped cathode ray tubes, which contained ultraviolet emitting phosphors. Ford found indeed that under some conditions, images could be generated without further processing.

At this time, interest in novel printing technologies was rampant. Gen. David Sarnoff, the president of RCA had proposed that in time, television sets would be employed to produce newspapers in the home. Naturally, if this market did develop, there would be an enormous opportunity for consumables. Before long, the UVI-program was again expanded, and then actually became one of some 30-odd Ventures, in which DuPont sought to exploit novel technologies.

8.5.6 The UVI-Venture (1966–1971)

The Venture Concept, which was favored between 1966 and 1971 was based on the idea of having small independent groups of scientists, engineers, marketers and manufacturing staff develop businesses independent of the sponsoring Departments, although these would exert financial controls. The overall success/failure of the various ventures was to be supervised by a dedicated group in the Company's Development Department. The ultimate arbiter of all this was a sophisticated computer program that would evaluate chances of success, competitive thrusts, cost to develop a strong marketing position, etc. Naturally, to make such assessments required extensive support from the Ventures, and in time, somewhere between 6 and 10 people in the UVI-Venture concentrated their effort on this.

I became the first member of the Venture's marketing division. The Venture Manger, Leon F. DuMont had ample experience in selling FREON®, an activity which apparently involved treating would-be customers to good meals, golf matches, and the like. It was an approach that did not work in the imaging field. One of our first visits to generate interest in our technology at IBM in San Jose was rudely received. We lacked data that would allow would-be customers to assess how our technology would be of use to them. A physicist, Dr. Paul Vance was then assigned to make measurements and make some order out of the samples that were prepared by the research group. We had brochures printed, which allowed us to define the limits of our technology.

Inevitably, what excited people was that one could produce colored patterns with a flash of light. Hence, a powerful flashgun was part of our travel kit. Of course, those skilled in the art of imaging were more interested in more realistic imaging devices, and before long, a diazo exposure unit also accompanied us on our travels. Here we could image our coated papers at quite good throughput speeds. The venture was created to explore consumables for electronic imaging, and thus some demonstration of our capabilities to use a CRT tube as the imaging engine was called for. Because of the relatively low photographic sensitivity of our coatings, this was very difficult.

In retrospect, the ventures were not particularly successful. When DuPont's business had a downturn in the 1970s, the sponsoring departments reduced their support, and focused their resources on existing businesses. Additionally, the entrepreneurial attitudes that were required simply did not exist at DuPont. There was no Steve Jobs or Bill Gates who wanted to run a risky business inside DuPont. The UVI-Venture at one point attracted Dr. William S. Wartell, a remarkably effective leader as head of the marketing group, but regrettably his service and impact were short-lived.

The UVI-Venture was organized with research, marketing and manufacturing divisions. The Venture Manager sought to organize an effective team, but the group was handicapped by the lack of definition as to what “electronic imaging” really was. It was soon evident, that the technology available could not be used to produce images unless specialized CRTs, with expensive UV-emitting phosphors, quartz fiber optics faceplates and sophisticated electronics were employed.

The technical problem was primarily lack of photosensitivity. Effective imaging required power that simply reduced phosphor life. Designing circuitry, which would increase the exposure period between CRTs and media, helped some, but still proved inadequate. Additionally, the only effective imaging was achieved with coatings that contained no deactivation capability.

8.5.7 The UVI movie (1967)

I suggested to the Venture management that a professional movie be made to demonstrate the various aspects of our system. They reluctantly agreed to make a short film, with the able assistance of the Company’s movie photographer, Fran Ryan. It was an eye opening experience. First of all, it is difficult to make a movie about light sensitive materials. Secondly, professional Kodachrome film, which was used, requires an enormous amount of illumination, and we could only shoot our film between midnight and 5 a.m., when the power demands at our Experimental Station Laboratory were low. The film was a success; I had to watch it over 700 times in the years following its first showing. It was even shown to Mr. Douglas Shearer, the technical director of MGM, who at that time was interested in new media for motion pictures. Shearer said that our movie was quite good but they could have used their Special Effects group to produce a similar work. Now my travel kit included a 16 mm movie projector, but at least, I was rid of the diazo exposure unit. An additional benefit of the movie was that the photographed scenes showed that things worked quite reliably. This was not always the case with life demonstrations!

8.5.8 Large wall screen displays (1967–1970)

One application in which the proposed electronic imaging came close to became a real opportunity was in the field of large wall-screen displays.

8.5.8.1 *Project Apollo* During our 1967 visit to General Electric, where we described our materials, I met Max Kerr, a senior scientist who was involved in GE’s participation in Project Apollo, a NASA program aimed at scientific exploration of the Moon. He requested materials, which had instant accessibility for large displays. Kerr and I worked together for another year, and in March 1968 I delivered some of our higher speed photopolymer materials (RF), which were imaged successfully on their CRT based imaging system. Nevertheless, nothing ever developed beyond that.

8.5.8.2 *Boeing display* Boeing Corp. had developed a communication system with Wright-Patterson AFB, in which a UV-emitting CRT would image a vesicular film (KALVAR™), which was then thermally developed. Within a few seconds, this image could be projected on a large screen using conventional optics. This satisfied a perceived need for large displays, which could be easily up-dated. When the Boeing group, learned about the UVI chemistry, they invited us to make a presentation, which was done in June 1967. They conceived an approach, which was superior to the KALVAR™-dependent system as follows.

They designed their system (Fig. 8.3) around a photosensitive coating, which could be imaged with ultraviolet light, transmitted through a UV-transmissive fiber optics faceplate of a UV-phosphor emitting cathode ray tube. On top of the faceplate was a dichroic mirror, from which the image could be projected with visible light that had the UV-component removed with optical filters.

Thus it was not necessary to deactivate the film. The imaging system was improved by pre-printing through a series of negatives certain features, such as maps, outlines of tables, etc. The variable information, e.g., flight trajectories, etc., could be formed with the cathode ray tube. In time, the system was expanded so that through clever optics, three colored projection beams were made to converge in different colors, so that the actual projected image was fully colored. This work was supported by U.S. Air Force funds, and was considered a singular achievement. Regrettably, after Boeing demonstrated the system to the Air Force, it was terminated, as it was in the nature of a feasibility study.

The UVI Marketing group tried to identify other related applications, e.g., airport displays, etc., but could not fund these sufficiently to develop commercial interest.

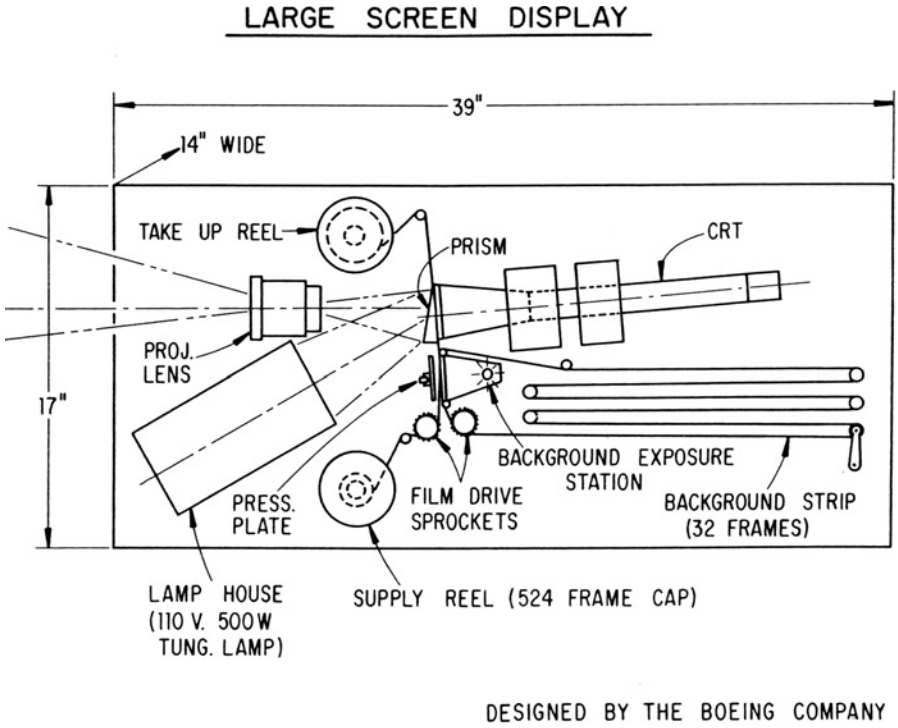


Figure 8.3. Boeing display.

8.5.9 Point of sales opportunity (1966–1969)

The forays into the potential optical printing market became known throughout the imaging community, and several applications appeared. The Litton Advanced Data System, located in Beverly Hill, CA, had contracts to develop electronically generated tickets for entertainment events as well as for transportation purposes. Some collaboration to develop tickets in which graphics could be pre-printed via contact exposures, with variable information to be printed from electronically generated sources was undertaken. Litton looked to DuPont for support, but it was decided that DuPont lacked the resources to do so. Inherently, DuPont looked at itself as a consumable supplier, rather than a system operator. This inevitably resulted in potential customers seeking other materials to solve their problems.

The Monroe Division of Litton Industries, which made cash registers and mechanical calculators, identified a potential application in the point of sales field. They had developed magnetic coatings that could be machine-read, and wanted to generate man-readable information over this. They requested a thin paper coating with a photosensitive layer that could be laminated over a magnetically active coating. Efforts were made to supply this, and a sandwich structure was fabricated which fulfilled their requirements; a successful test was conducted in a Louisville, KY Sears Department store.

Discussions as to the cost of the photosensitive coatings between DuPont and Litton Monroe resulted in their examining alternate ways of generating the man-readable images. Litton had originally assumed that impact printing would adversely affect the images embedded in the magnetic coating. When this was found not be the case, the photosensitive coating approach was discarded. Years later, the UVI-technology was again considered for Universal Product Code label printing.

An interesting note! By the time the Litton Monroe–DuPont program was at its height, the name DYLUX® had been selected for the instant access imaging technology. In order properly to register a trade name then it was necessary for the named goods to be shipped across a state line. The author traveled from Delaware to East Orange, NJ in a private automobile and hand delivered a roll of DYLUX® photosensitive paper to Litton. This made the name legal!

8.5.10 DYLUX® instant access imaging materials (1967)

A name was needed for our offering. One afternoon, our marketing manager Irene D. May, E.W. James, an engineering consultant and I were finished early with our customer visits, and sat at a motel bar in Laguna Beach, CA. I suggested that we use the time to think up some names for our proposed product while we were drinking Mai-Tais.

There were a few rules for naming products in those days. The name had to be novel, it should not directly describe the product or its features, and it should be easy to pronounce. I came up with the name DYLUX®, based on the idea of making dyes with light. We all liked it. May suggested we have a contest in the Venture group for a name, but in the meantime, did a search for the term DYLUX® among trade names. When nothing showed up, he generously suggested that I had worked so hard on this that I should be permitted to give it a name. So, the trade name DYLUX® was to identify DuPont's Instant Access Imaging Materials. Objection to the name came from the German light bulb manufacturer, Osram, who made a lamp that was marketed under the name Bilux™. We ignored them.

DuPont attached a descriptors to identify trade names, and for DYLUX® it was to be "Instant Access Imaging Materials". By the year 2000 the name DYLUX® had become so identified with proofing products, that a paper base, manufactured for ink-jet proofing systems by DuPont was also given this trade name.

8.5.11 Toys and Mattel (1968–1969)

It occurred to us that Mattel could be interested in a toy based on a photosensitive paper, and we made contact to visit them. With the help of the enormous income from the Barbie Doll, Mattel developed cutting-edge toys with the help of master electronic engineer Jack Ryan. Mattel was recognized as the first toy company to take full advantage of modern technology in the Sixties.

The reception was extremely positive; Jack Ryan, director of research and development, and creator of the Barbie Doll invited me to stay on his estate for a week and showed great enthusiasm for the technology we presented; he considered it a creative challenge to conceive a toy that could use sunlight as an imaging source. Mattel assigned several engineers to design toys based on DYLUX® materials. The program progressed nicely until our Venture manager paid a visit to Mattel. His first question dealt with what the prospective volumes of a photosensitive paper might be over the next five years. Mattel countered that toys generally have short life times, and that predicting volumes for over three years would not make much sense. Thereupon DuPont decided that the toy business was not a good fit for our technology.

8.5.12 Microfilm applications (1965–1971)

In the early 1960s, many people in the imaging community considered microfilm to be a potentially huge opportunity for information storage. Magnetic media or optical media, fully accepted in the year 2005 were not available. Microfilm images were obtained by conventional photographic means, employing special high-resolution silver films.

8.5.12.1 *Microfilm duplication* Images on silver-based films could be duplicated either onto other silver films, or on diazo or vesicular media. The diazo films were relatively inexpensive but were believed to lack archival quality. Vesicular films on the other hand did not contain any dye-images, and thus were believed to be archivally stable. The microfilm industry at the time also promoted the use of microfiche, on which a micro-images were positioned on a 6″ × 4″ sheet of film. DuPont, as a supplier of MYLAR polyester film enjoyed significant sales of this for microfilm duplication products.

All the above media required some form of development, either chemical or thermal. This made it difficult to design simple equipment. The industry was looking for ways of replicating images in non-laboratory environments, for example libraries or offices.

We considered that the lack of wet or thermal processing would make DYLUX® materials eminently suitable for microfilm and microfiche duplication. Some devices, such as a duplicator manufactured for Kalvar™ films by Canon Inc. worked well with or coated film materials. Canon subsequently established a close relationship with DuPont to produce dedicated equipment. A small California company, Marks Systems, which had been successful in building film duplicators for Kodak products, invited us jointly to develop film-duplicating technology.

In the end, this was a market in which DuPont's Photo Products Department should have participated, but after some preliminary efforts, the decision was made to ignore he field. That of course killed any opportunities for DYLUX products in this area.

8.5.12.2 *Microfilm blowback* Enlargement on coated papers was termed "blowback". Up to this time, this was done with silver based paper products that required development. 3M

Co. offered their DrySilver™ product to this market. Like all silver-based materials, it had to be handled in the dark. Photographically microfilmed copies of engineering drawings were frequently positioned in the window of an aperture card, making it possible to machine-search these. Electrophotography had not advanced sufficiently in 1965 to suggest that it would be a preferred method. A small English engineering company, CAPS LTD, had developed a microfilm projector, which with UV optics was able to produce enlarged images onto diazo paper. Commercially available diazo paper was positive working, i.e., the image had identical light and dark areas as the photographic negative that was projected. The market objected to images in which light lines were on a dark background and preferred a negative working duplicating medium. The UVI-papers tested by CAPS worked in the desired negative mode. CAPS showed considerable interest in promoting the use of DYLUX® materials, but as these were not optimized for this application, and no selling price was disclosed, the collaboration came to naught.

DYLUX® proofpaper and certain modifications of it could be used to make enlargement of microimages in a positive mode. Thus, when the film image was projected with visible light, the areas so struck were "deactivated". The paper could be exposed with ultraviolet light as the visible light formed the image; those areas, which received only ultraviolet exposure, turned color. This system worked remarkably well, but no significant research effort was made to increase the gamma of the photosensitive coatings, and not sufficient contrast was achieved. The simple, dry, one-step approach was of potential interest to two equipment manufacturers, Canon Inc. and MacDonnell Douglas, who built prototype exposure units.

> **U.S. 3,661,461. Co-Irradiation System for Producing Positive Images.** Dessauer, Rolf. E. I. Du Pont de Nemours and Company, May 9, 1972 (Cl. 355/37; 250/475.2; 355/43; 355/67; 355/71; 355/77; 355/80; 430/39). Appl. November 26, 1969. Method for producing positive images by irradiating photoimagable and photodeactivatable compositions which are characterized by forming color on irradiation with light in a first wavelength range and by being deactivated against color formation on irradiation with light in a different second wavelength range. The method comprises simultaneously exposing such composition disposed as an image-capture surface to radiations in both wavelength ranges, with 1. the deactivating radiation being applied pattern wise according to the desired image to be captured, 2. the color-forming radiation being applied over the entire surface to be imaged, and 3. the intensities and the relative intensities of the two radiations being such that I. the deactivating radiation is itself effective for deactivation and Ii. the color-forming radiation is itself effective to cause color formation in other than the co-struck areas but is ineffective in the presence of the deactivating radiation in the co-struck areas to cause substantial color formation. The composition used is a mixture of A. color forming components which are responsive to said first wavelength range and thereby produce a first photo-induced oxidation-reduction reaction, and B. deactivating components which are responsive to said second wavelength range and thereby produce a deactivating agent by a second oxidation-reduction reaction, said deactivating agent thus produced being a stronger reducing agent than the reductant member of the color-forming components and thereby preventing the color-forming reaction when the composition is subsequently exposed to the first wavelength range.

8.6 AT LONG LAST—GRAPHIC ARTS (1968)

By good fortune, William S. Wartell, became marketing manager in early 1969. He had considerable experience in marketing, though not with photochemical materials. He succeeded in getting Photo Products' marketing group to allow us to visit several graphic arts customers. We were allowed to show our prospective proof paper. An able electrician, Harold Wilbur was assigned to the venture to rebuild small commercial contact printers, and with these one could easily demonstrate the capability of DYLUX® proof paper of generating proofs without processing.

At that time, DuPont sold through distributors and the function of the salesmen known, as Technical Representatives (TR) was primarily to assuage customers when things had gone wrong with their products. Occasionally, research people, who were trying to identify the customer's needs, accompanied them. DeCampi, who had joined the group in 1968 after attending the Harvard Business School and I worked up presentations, which demonstrated the advantages of using DuPont's proof paper. DuMont allowed us to entertain customers and TRs generously, and the result obviously was that the DYLUX® presentations were popular with everyone.

Except of course the Photo Products R&D management, who because they had no experience in this field, considered our efforts a distraction. Inevitably, we had to state that we were dealing with experimental products, for which no commitment to manufacture had been made. This is not a good way to get customers to modify equipment or commit to extensive evaluations!

In April 1969, I was asked to make a visit to a U.S. Air Force Photographic Laboratory located in St. Louis, MO. Unfortunately, the group to be visited canceled our invitation, and the TR who was to take me there suggested we might as well visit a couple of graphic arts accounts. The first one was referred to as a "yellow-box account"; Eastman Kodak, who packaged their offerings in yellow boxes, manufactured almost all graphic arts products purchased there. The TR suggested to the plant manager that we wanted to get his opinion of our proposed proof paper offering. This gentleman was quite outspoken; he said that his opinion of DuPont was not particularly high, and if we could not see what a potential winner we had, we must be blind. Then he took the TR and the author out to lunch; a reversal of the normal process where we tried to invite potential customers.

That afternoon, we visited another printing account. The manager apologized for having so little time for us; he was "up to his eyeballs in work". The author asked if he would one minute of time, to plug in the small contact printer, and make a proof in 20 sec. That broke the ice. Suddenly he had all afternoon for us, and asked if he could borrow the contact printer and some paper for a demonstration at a printers' club that evening. The following morning he urged us to encourage DuPont to get the product into the market as soon as possible; everyone saw advantages of making proofs on DYLUX®. I called Wartell from the airport and told him that our current version of DYLUX® 503 was good enough to get to the market, and he agreed; that afternoon the Venture decided to start manufacturing proof paper at a custom coater. Of course, there still was no sales organization and Photo Products Department was still undecided whether they wanted to sell an inexpensive paper product.

8.6.1 Competitors can be helpful! (1969)

I had attended many meetings of the Society of Photographic Scientists and Engineers (SPSE) and even presented papers. My presentation at the 1969 Boston Symposium on Unconventional Imaging Materials, describing the capabilities of our yet to be commercialized system attracted much interest, including a lengthyà including a lengthy conversation with several marketing people from Agfa-Gevaert, the German/Belgian photographic company.

They were curious why DuPont had not commercialized DYLUX® paper. I pointed out the reluctance of our sister department, Photo Products, to enter the proofing market. They then asked if perhaps Agfa-Gevaert might market this proof paper, if DuPont did not want to. I suggested they write a letter to that effect. This letter came soon after my visit to St. Louis, and precipitated a bit of a crisis. Photo Products Management had to make a decision, and finally, they agreed to consider DYLUX® as part of their product line. At long last, there was commercialization!

8.6.2 The market wants DYLUX® proofpaper! (1969)

Mike Connair of the manufacturing group had developed coating technology that allowed the coating of paper on both sides. This turned out to be another great plus for DYLUX® technology. The two-sided coated paper ultimately took most of the market share. As a matter of fact, DYLUX® 503 paper for the proofing market had all the attributes that one could want for evaluating the quality of lithograph negatives, making imposition proofs

As experience in the market increased, it was realized that we had invented a product that met many marketing needs that had not been anticipated. It was a most unusual situation.

The success of DYLUX® proofpaper could be attributed to these characteristics:

1. Function. The DYLUX® instant image proofing system produces dry, instant image blueline proofs without processing. The proofing papers give single- and two-sided proofs used for editing pages, customer approval and quality checks. It can be handled in subdued light, and there is no need for processing, assuring good dimensional stability.
2. Exposure modes. Either negative or positive images could be formed with the same material. When imaged in a negative mode, the ability to add-on information to an exposed sheet by a subsequent exposure permitted sequential positioning of alphanumeric as well as pictorial information. The ability to form images of different densities by double burns allowed the printer to simulate different colors in the actual print. Here one might expose a portion of the proof to a density of 1.2, while another might be exposed to a density of 0.8, by reducing the exposure time. This would give a clearly distinct difference, and was found useful in indicating that different colored printing inks would be used in different areas.
3. Images. Negative images were formed in a single step. The photo-deactivation was only necessary if the imaged proof was to be handled in daylight. The cyan-color, which was thought to be less attractive than black actually offered advantages—the user knew he was dealing with a proof, and could mark it up with a black or colored pencil. A near black image was subsequently available from another product, DYLUX® 535. As the DYLUX® images possessed a fairly low gamma of around 0.7, it was possible to produce attractive prints from continuous tone negatives. When the proof was handled in room light it eventually “fixed” itself.
4. Materials. Two-side coated papers, which could be imaged without a processing step allowed the second negative to be lined up against the image on the reverse side – the paper was sufficient translucent to allow the cyan color to peek through it. This allowed the printer easily to produce signatures (large sheets printed with four or a multiple of four pages that when folded become sections of the book). The foldability of the paper was also important, in order easily to prepare signatures. The paper was relatively

lightweight, which made shipping of proofs less expensive. A coating similar to that of DYLUX® 503B was supplied on a film base a s DYLUX® 608A Registration Master film, which was employed on layout tables for stripping color positives or negatives.

5. Cost. The paper was priced to reflect value-in-use, and customers soon realized that the labor-saving achieved by obviating the need for processing allowed greater productivity. At the time of its introduction in 1969, the single-sided paper was priced at $0.07/sq. ft.
6. Equipment. Exposure with most graphic arts light sources gave inadequate image density, because the sources contained too much visible light. When the exposure source was made with an assembly of black-lite blue fluorescent lamps, the image density was excellent. It was found that a relatively inexpensive cobalt glass, obtained from the Kokomo Opalescent Glass Co., passed enough UV, and absorbed visible light, so as to prevent premature deactivation and could be inserted between many light sources and lithographic negatives.

The volume of DYLUX® proof paper consumed was related to the available exposure sources, and as these penetrated the graphic arts market, the consumption of paper grew also. Actually, there was not a single quarter between 1969, when DYLUX® 503 was introduced at the National Association of Printers and Lithographer's show, and the late 1990s, when the volume sold did not exceed the previous quarter.

8.7 PRINTOUT PAPER FOR DUPONT 'aca' AUTOMATIC CLINICAL ANALYZER (1969–1979)

By that time, another DYLUX® product began to be commercialized. In the early 1970s, DuPont marketed a novel machine, designed automatically to analyze various body fluids. Here a fluid, e.g., urine was introduced into a small plastic pouch, containing pods that could be made to release various chemicals that would permit a spectrophotometric analysis. Dr. Donald R. Johnson, one of the guiding spirits of this program knew about DYLUX® from personal contacts with the author, and conceived a novel approach to transmitting analytical data.

A small (3″ × 5″) translucent plastic card (matted polyester film), onto which pencil writing could enter data such as patient name, date, location, etc. were thus recorded. The card traveled though the machine with the plastic pouch and after analysis was completed, the plastic card entered an imaging station, in which a contact exposure onto a DYLUX®-type paper was made. The substrate here was a perforated "chart-paper" material.

The machine contained a mechanical printer, which recorded the analysis data on the unexposed area. This approach resolved a serious problem in the medical analysis field; the transmittal and accurate transcription of information. This application consumed considerable amounts of light-sensitive paper. Originally the images were cyan, but as the xerographic printers of the period had difficulty coping cyan images, a blue-black leucodye was subsequently incorporated in the recipe. For many years, the "aca" paper represented a lucrative market.

In the mid 1980s, alternate technologies were employed for printout, and the market for this application vanished. A number of users considered this type of image transfer to be an asset, as it eliminated any error in data transmittal. Unfortunately, DuPont never pursued related applications, which surely must have been there.

8.8 MARKETING TO THE MILITARY (1967–1970)

8.8.1 Reconnaissance film duplication

There were opportunities to receive funding from the military for research. DuPont maintained an office in Washington, DC to facilitate contacts. We were told that there was a need for quick contact copies of aerial reconnaissance films, so that photo interpreters could rapidly make duplicates, while studying the roll of film that was supplied. As the original was a "negative", a print on a DYLUX® film would yield the desired "positive". Beale AFB, at Marysville, CA, was one of the centers for reconnaissance activities connected with the Viet Nam war and encouraged this development at DuPont. The U.S. Air Force had funded considerable research at Photohorizons, which had not resulted in any acceptable products. The Air Force also requested that we assist Photohorizons but DuPont declined because their technology involved handling unstable toxic components.

The U.S. Navy Photo Lab in Washington, DC had a more ambitious agenda: they sought a product that would allow copying photographic color film onto a non-silver medium. We considered that the RF-film, which could be sensitized to achieve polymerization at different wavelengths, offered a possible route to this, but it would require a fairly expensive R&D program.

8.8.2 Aerial mapstrip annotation

During the 1960 and 1970, pilots used colored map strips in projection devices to orient themselves in flight. There was a need to annotate these maps, so as to update them with recent information.

This could be solved, for example by applying a DYLUX® photosensitive coating to an imaged Kodachrome™ film, and then image it by contact or by a projection minification.

8.8.3 Conclusion

The goal was to solicit funding from the military for these programs, and to prevent such funds to going to possible competitors. It involved many contacts with military personnel, who were supportive of our programs. When the DYLUX® Venture was transferred to the Photo Products Department, those that had been involved in this effort remained at Orchem, and the Photo Products R&D management decided that they did not want to be involved in government programs. This then terminated all contacts and opportunities in this area.

8.9 W.H. BRADY AND THE KALOGRAPH (1967–1970)

The W.H. Brady Co., of Milwaukee, WI, a premier sign and label manufacturer showed interest in photoprinting labels, and manufactured a device, in which characters and symbols could be exposed one character at a time. This machine, called Kalograph™, was a compact label maker measuring about 10″ × 10″ × 9″ that was designed to contact-print on a label substrate, which consisted of a transparent or colored polyester substrate with adhesive backing. The photosensitive coating was a DYLUX® type composition.

Regrettably, the Kalograph™ device never became a big seller. It was probably too expensive to compete with pressure-generated labels, like the inexpensive and popular Dymo™ label maker.

Brady engineers obtained patents for the Kalograph™ and the exposure system.

> **U.S. 3,698,296. Actinic Label-Making Tool.** Heuser, Elliott G.; Muttera, Jr., William H. W. H. Brady Co. October 17, 1972 (Cl. 396/559; 250/461.1; 347/224; 396/556; 400/118.2; 400/134.5). Appl. September 29, 1969. A label-making tool utilizing an ultraviolet light system and including: a supply of tape material having an ultraviolet-imaging coating, means to incrementally advance the tape material past an exposure station, rotatable type means for selectively positioning a character at the exposure station, and ultraviolet light means adapted to emit u.v. light to produce an image of the character positioned at the exposure station in the ultraviolet-imaging coating of the tape material.

DuPont showed great reluctance to sell DYLUX® solution, as it was feared that this might be used to develop competitive proofing products. Brady was the only company that was able to buy a DYLUX® solution. Their coated product was sold in cartridges. The labels were attractive, and to improve the light stability, Brady manufactured and sold a solution containing wet-fix chemistry. This was supplied in little applicators, similar to those used for applying liquid shoe-polish. The pricing of the machine was a challenge. At the initial price of $300 it was too expensive for many prospective users.

8.10 AFTER THE VENTURE (1971)

In late 1970, the Venture was officially transferred to the Photo Products Department. That is, about half the staff was shifted. Several of the more experienced hands like John De Campi and the author were not moved; they had antagonized too many of the Photo Products R&D management in the process of their successful marketing efforts. Dr. Robert Upson, the director of research did not appreciate research programs that he did not conceive, and A.B. Cohen, an assistant research director, who had become the company's champion of photopolymer technology felt that anything that did not involve photopolymerization was an unnecessary diversion in the path of developing new products. Regrettably, this almost put an end to further research on photo-oxidation of leucodyes, syntheses of new HABIs and exploration of new materials.

In time, the author was able to persuade the Organic Chemicals Department to continue investigating HABI/leucodye chemistry for other applications.

8.11 PHOTODECORATION (1972)

A chance meeting with a designer, Bob Ellefson, who had worked on CORFAM® resulted in an exploration of the technology for decorative purposes. Ellefson pointed out that the ability to print quality patterns on leather-substitutes and leather-splits might be an attractive opportunity. Ellefson had good contacts in the footwear industry, and was able to persuade several companies, e.g., Genesco and George Neuman Co, to work with us. The goal was to print patterns of topgrain leather onto substrates that would otherwise have been less valuable. Several approaches to achieve this were demonstrated.

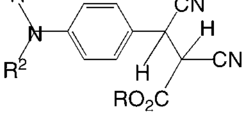
> **U.S. 3,847,608. Photodecorating Sheet Material with Matched Colored Designs.** Dessauer, Rolf and Ellefson, John R. E. I. Du Pont de Nemours and Company. Filed November 12, 1974 (Cl.

> 430/352; 002/243.1; 430/351; 430/394; 430/538). Appl. August 8, 1972. A process for color decorating sheet material with a design, which material will be used to form an article by assembling multiple pieces of the designed sheet material, whereby the shapes of the pieces are laid out on sheet material in closely-spaced arrangement and the pieces are then cut from the sheet material, is improved by A. either before or after cutting out the pieces, coating the sheet material with a photosensitive composition capable of generating color subsequent to exposure to activating light, B. exposing the coated shapes to activating light through a light modulating means which registers at least a portion of the desired design on the shaped piece, the piece design being one which matches with an adjacent piece in the assembled article, and C. color stabilizing the design by fixing the coating after registration of a latent design or after color has been generated. Such a process permits minimum waste of sheet material and maximum convenience in accurately matching piece designs in an assembled article.

In the 1970s, considerable work was done to develop dye transfer technology to decorate fabrics, especially polyester. We considered this approach here too. Photosensitive coatings on a release substrate could be imaged in a roll-through device at considerable speed, and the imaged layer could be stratum-transferred to the leather or similar substrate. This allowed the binder layer, e.g., a polyurethane to be transferred at the same time, resulting in improved performance of the decorated material.

> **U.S. 3,909,328. Decoration of Substrates by Thermal Transfer of Photosensitive, Thermoplastic Dye-Imaged Film.** Dessauer, Rolf; Looney, Catharine. E. I. Du Pont de Nemours and Company. September 30, 1975 (Cl. 156/219; 430/142; 430/146; 430/173). Appl. April 10, 1973. A multicolor photoimaging procedure utilizing ⩾2 dye-image forming steps followed by thermal transfer printing is described for producing decorations on suitable receptor layers. Thus, a strippable paper support was coated with a photosensitive hexaarylbiimidazole-coumarin-leuco dye compn., photoimaged, impregnated with a diazonium salt, imaged a 2nd time to form a multicolor design, contacted with a polyester-cotton blend cloth, the sandwiched assembly placed between the heated platen surfaces of a Carver press at 1000 psi and 130° for 10 sec, and the paper support stripped away to give a multicolor-design-printed cloth.

Additionally, Ellefson identified a wood finishes group in the DuPont Fabrics and Finishes Department who showed interest in using this technology to produce intricate wood patterns, e.g., inlays, on wood-like materials, such as MDF (medium density fiber board) or plywood. In these photodecorative areas, it was necessary to produce an insulating layer to prevent the phenolic components of the natural products from interfering with the imaging compositions. It was not necessary to develop photofix chemistry, because both leather and wood surfaces have multiple coatings applied during their manufacture, and it was thus possible to employ a “chemical” fix. This facilitated the dye selection, also. Combination of the proof paper dye, TLA-454 with almost any other color gave a greenish tint; substitution for this by the blue-black forming LB-8 allowed formulation of attractive brownish black, when an orange forming leucodye



LEUCO ORANGE DYE

was added. The color-forming chemicals (HABIs, leucodyes) could be applied as polyurethane or acrylic lacquers for the footwear application, and as methacrylate or similar lacquers for the furniture application. The “fix” coat contained hydroquinone derivatives as well as UV-screening agents, e.g. Cyasorb® 24 (a hydroxybenzophenone derivative), which enhanced the composite’s lightfastness. The fix coat usually contained an organometallic dye of DuPont’s CAPRACYL® line, which further enhanced the light stability. When the concept of photodecoration was shown to several furniture manufacturers in the Greensboro, NC area in 1973, there was great enthusiasm for this approach. It was anticipated that it would permit on-demand pattern formation from relatively low cost photographic negatives. It would make for attractive inlays, again via photographic negatives, without the expensive handwork then required. The issue of durability was quickly resolved when it was shown that these composites were less likely to undergo change than the natural product! Thomasville, a major furniture manufacturer installed equipment to use photosensitized plywood in the manufacture of inlay tabletops.

We appeared well on the road to success when DuPont’s upper management decided to leave the Furniture Finish industry. Regrettably, the group with which we worked was unwilling to let us offer the technology to others in the industry, and the program was terminated. Then, the Organic Chemicals Department management did not wish to support the program any longer. End of Photodecoration!

8.12 UPC OPPORTUNITY (1972–1977)

The DuPont Company’s Film Department was a strong force in the packaging field, with sales of MYLAR® polyester and cellophane films. There was a continued examination of higher-value-in-use products. The emerging program of bar coding supermarket merchandise, which lead to the UPC (Universal Product Code) was believed to be an area where DYLUX® technology might find application.

In the early 1970s, the supermarket industry decided that some level of inventory control and improved checkout would be possible if a machine-readable symbol would be incorporated in the items sold in supermarkets. After considerable scouting, a bar code symbol, to be read with a red He–Ne laser was selected to be applied to the bottom of supermarket packages, bottles, etc. This was easily doable for printed packages, e.g., cereal cartons. It was more difficult for bottled goods, as the bottom of many bottles is not flat, preventing contact printing. Several companies that sold their products in glass containers, e.g., Tropicana and PepsiCo approached us for help, and we considered the feasibility of designing novel label materials, printing techniques, etc. The challenge to develop novel label concepts, embodying photosensitive components was met by several approaches. One potentially unusual property of such labels was that they could be imaged through a transparent coversheet, which offered protection and prevented tampering with the information.

It was considered important to form a high contrast image that might be located on bottles, dark containers, and the like. Formulations that contained white pigments were formulated so that a cyan image on a white background would be formed.

> **U.S. 4,207,102. Marking Transfer Sheets and Process.** Dessauer, Rolf. E. I. Du Pont de Nemours and Company. June 10, 1980 (Cl. 430/252; 250/318; 427/553; 427/557; 430/256; 430/259; 430/494; 430/947). Appl. March 8, 1978. A marking transfer sheet comprising an imaging layer of pigment, binder and a color-forming, radiation-sensitive component on a carrier film and a process for its use comprising exposing the imaging layer to a pattern of radiation to form a mark, heating the imaging layer until adhesive, and contacting the imaging layer with a support more adherent to the imaging layer than the carrier film; and optionally separating the carrier film from the imaging layer.

U.S. 4,029,506. Universal Product Code Marking Composition Containing a Photosensitive Dye Former, a Pigment and a Binder and the Use Thereof. Dessauer, Rolf. E. I. Du Pont de Nemours and Company. June 14, 1977 (Cl. 430/332; 106/31.16; 106/31.28; 430/33). Appl. September 27, 1976. Described are a marking composition of a color-forming, radiation-sensitive component, a diffusely reflecting pigment and a binder, and a process for the use of the same comprising coating a product surface with the marking composition; exposing the coating to a pattern of radiation to form a marking; and then reading the marking with a diffuse reflectance scanning means.

U.S. 4,232,108. Marking Transfer Sheets. Dessauer, Rolf. E. I. Du Pont de Nemours and Company. November 4, 1980 (Cl. 430/259; 430/338; 430/346; 430/541). Appl. May 1, 1979. A marking transfer sheet comprising an imaging layer of pigment, binder and a color-forming, radiation-sensitive component on a carrier film and a process for its use comprising exposing the imaging layer to a pattern of radiation to form a mark, heating the imaging layer until adhesive, and contacting the imaging layer with a support more adherent to the imaging layer than the carrier film; and optionally separating the carrier film from the imaging layer.

However, a significantly greater opportunity was perceived for store printed labels. It was necessary to print labels for store-weighed goods, such as meats, fruits and vegetables, etc. Contacts were made with Hobart Manufacturing Co., the country's largest manufacturer of weighing scales. We had rationalized the size of the opportunity by assuming that the 30,000 domestic supermarkets would each print ca. 2,000,000 labels/year, or some 60,000 million. The minimum label size to be recognized by the scanners was to be 1.5 square inches; hence the opportunity for photosensitive label material was anticipated to be 60 million sq. ft.

But why use DYLUX® technology? Hobart had found impact label printers to be of little reliability and the quality of images to be marginal. When a transferr-image was made it created the need to dispose of a substrate. Thermal printing was still inadequate. Most importantly, Hobart pointed out that our volume projection was low; they anticipated the need for larger labels, and felt that our add-on imaging capability would permit them to print certain variable information, e.g., nutritional contents, critical dates, etc. in a contact mode from selected negatives or stencils. A joint R&D program was set up. The Film Department's Spruance plant, which had unused coating capacity, and a chemist and an engineer there were assigned to undertake scale up of compositions supplied by Orchem.

One requirement stated by Hobart was the need to require minimal service for the imaging device. We established contact with GTE-Sylvania, who claimed that some of their airport lighting systems possessed the requisite longevity to permit flashing of lights at a high rate for as long as a year. Before long a management decision was to incorporate the Film Department into the Plastics Department. The latter showed little interest in the UPC market, and the program was terminated in spite of early successes.

8.13 PATIENT IDENTIFICATION SYSTEM (1975)

Prof. Martin Rubin of the Georgetown University Medical School in Washington, DC noted that the printout system used in the early models of the DuPont 'aca' clinical analyzer offered a foolproof method of transferring information for medical samples. He proposed a system of supplying the patient with wrist bracelets that contained a stencil or negative, on which bar code symbols would be printed. These could then be used to uniquely identify samples taken from the patient without the possible error in transcribing information. DuPont collaborated with Rubin and sought to work with medical supply houses. This technology was too advanced for the industry at the time Rubin sought to introduce it.

U.S. 4,476,381. Patient Treatment Method. Rubin, Martin I. October 9, 1984 (Cl. 235/375; 235/385; 235/491; 283/45; 283/89; 283/900). Appl. February 24, 1982. A patient treatment method and system facilitates automated administration of the treatment of a patient, including establishing a direct linkage, at all stages of treatment, between the patient, on the one hand, and tests performed on the patient, specimens taken from the patient, and medication and services administered to the patient, on the other hand. The patient treatment method and system includes a patient identification method which provides the patient with a wrist bracelet which not only identifies the patient, but also facilitates generation, at various stages of treatment, of labels for identification of specimen containers containing specimens taken from the patient. The patient treatment method and system also includes a medication verification method and device, by means of which the identity of the patient receiving medication is validated as coinciding with the identity of the patient for whom the medication is intended. The patient treatment and method system also includes a specimen analysis system and method for testing and analyzing specimens contained in respective specimen containers sequentially moved into an aspiration position, concurrently with scanning identifying indicia on each container, as the container is moved into the aspiration position, so as to concurrently provide test data and identification data to a processor. Finally, each specimen container is provided with an extension device holding identifying indicia relating to the identity of the patient from whom the specimen was taken.

8.14 DYLUX® DFF FLEXIBLE FILTER (1976)

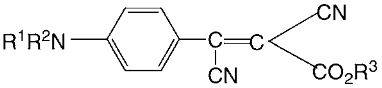
Philip Botsolas, a dedicated sales manager from Photo Products Department was asked by his management to investigate why DYLUX®, a very unique product, had not penetrated the market further. I pointed out that DYLUX® received little technical support at the Photo Products Department, as all the transferees had been reassigned and no one particularly championed this technology.

Botsolas found that one limitation was that many installed graphic arts light sources employed for proofing and plate making employed Xenon sources that contained both visible and ultraviolet light. When these were used to expose DYLUX®, the effect was that both imaging and fixing took place simultaneously, resulting in marginal optical density. DuPont had recommended installation of a cobalt glass filter assembly, made with low cost Kokomo Cobalt glass, but this entailed equipment modification.

What was needed was a flexible filter that would act to absorb visible and pass ultraviolet light. Botsolas asked whether we could not develop a film that would perform as desired. Per chance, a dye related to the leuco orange dye developed for the furniture photodecoration program possessed the desired properties. It was not commercial at that time, but in a few months we were able to scale up the preparation.

Looney calculated the composition for optimum performance. Attainable image density with the filter still fell short of the maximum attainable with BLB-fluorescent lamps, but it was markedly better. Soon after the DFF DYLUX® Flexible Filter became commercially available, sales volume of DYLUX® proof paper increased rapidly. After customers saw how well DYLUX® worked with the filter, they often installed dedicated exposure equipment.

U.S. 4,167,490. Flexible Ultraviolet Radiation Transmitting Filters. Looney, Catharine E. E. I. Du Pont de Nemours and Company. September 11, 1979 (Cl. 252/582; 252/588; 359/350; 359/885; 428/219; 428/480; 544/171; 558/395; 558/403). Appl. December 22, 1975. Flexible filters capable of transmitting radiation in the spectral range of 315 to 380 nm and absorbing radiation in the spectral range of 400 to 550 nm consist essentially of a thin flexible film, e.g., polyethylene terephthalate containing or having coated thereon a dye in a concentration of 15 to 60 mg/dm^2 and optionally, as a component of the coating, a thermoplastic organic binder, e.g., cellulose acetate butyrate, present in the coating with the dye, said dye being of the formula:



where R^1 is lower alkyl of 1 to 5 carbon atoms; R^2 and R^3, which may be the same or different, are selected from the group consisting of R^1, 2-cyanoethyl, 2-hydroxyethyl and $-CH_2CH_2O-CO-R^4$ or form a saturated 5- or 6-membered ring; R^4 is taken from the class consisting of lower alkyl of 1 to 5 carbon atoms, aryl or alkaryl of 6 to 9 carbon atoms, and aralkyl. The filters are useful in exposing dual response photosensitive materials with ultraviolet radiation sources, which contain appreciable quantities of visible radiation. The DFF served other applications; exposures of a number of photosensitive products made by competitors were reported to benefit by having a more restricted imaging spectrum.

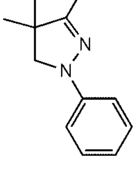
8.15 FOUR COLOR DYLUX® QUICK PRINTS (1977)

Next, Botsolas wondered why we had not made use of the dye-forming properties of our technology to develop a color-overlay system, similar to 3M's Color Keys. The latter are a simple way of providing colored foils, which may be overlaid to give some indication of the ultimate color of a composite printed image.

In spite of a considerable amount of dye research, no good magenta leucodye had ever been developed as part of the program. Emphasis had inevitably been on developing good black shades. Many of the leucodyes, which had been examined were oxidized by the quinones of the DYLUX® formulations. It then occurred to us that a film product, unlike a paper product, could easily be wet-processed without adverse effects. Many simple wet-processing devices were commercially available. Botsolas and some of his colleagues felt that if we could develop DYLUX® -like coatings that would produce separately cyan, magenta, yellow and black images, and if these could be stabilized by passing through an aqueous bath, we would have a potentially attractive overlay film product.

The leucodye TLA-454 gave a nearly perfect cyan shade; and yellow and red leucodyes based on tricyanovinyl chemistry, which had been explored 20 years earlier in DuPont's Central Research Department gave good yellow and magenta colors on oxidation. A black could be formulated by a variety of routes; mixtures of green and magenta or yellow and purple leucodyes. Compositions that are shown in Table 8.2 show the ingredients of the various DYLUX®-4C films.

Wet fixing chemistry turned out to be a bit more of a challenge. Hydroquinone and substituted hydroquinones could be employed to stabilize the exposed images, but inevitably, background color developed. A chance meeting with Ray Firmani, a photographer resulted in a solution. Firmani, who possessed limited



Phenidone (1-phenyl-3-pyrazolidinone)

Table 8.2. Color forming solutions for DYLUX®-4C films

Component	Magenta		Yellow		Cyan		Black	
	Solutes	Solution	Solutes	Solution	Solutes	Solution	Solutes	Solution
Cellulose acetate butyrate	56.26	7.83	46.2	11	71.71	13.16	61.8	16.69
2,2′-bis-(*o*-chlorophenyl)-4,4′,5,5′-tetraphenyl-biimidazole	5.47	0.76	7.21	1.71	0.65	0.12	5.99	1.62
2,2′-bis-(*o*-chlorophenyl)-4,4′-5,5′-tetrakis(*m*-methoxyphenyl)-biimidazole	4.63	0.64	5.94	1.41	0.55	0.1	5.6	1.51
Telomer B stearate	0.2	0.03	0.12	0.03	0.35	0.06	0.28	0.07
Leuco Magenta Dye	1.22	0.17					0.34	0.03
Leuco Green Dye							1.42	0.38
Leuco Yellow Dye			6.69	1.6				
Leuco Cyan Dye					0.83	0.15		
p-Toluene sulfonic acid	0.91	0.12	2.64	0.63	0.87	0.16	1.48	0.4
N-Ethyl-*p*-toluene sulfonamide	15.56	2.16					11.43	3.09
Triethanolamine triacetate	0.03	0.01						
Nonylphenoxy poly(ethyleneoxy)ethanol	15.56	2.16	30.8	7.32	25.02	4.59	11.43	3.09
Phenidone	0.16	0.02	0.04	0.1	0.02	0.01	0.23	0.06
Total solutes	100		99.64		100		100	
Propanol-2		7.8		7.8		8.17		7
Methylene chloride		78.3		68.4		73.48		66
Dry coating (g/sq. m) wt	6.99		22.49		23.98		37.25	
Image density	1.14		1.36		1.33		2.00	

Leuco Magenta is *p*-dibutylaminophenyltricyanoethane.
Leuco Cyan is tris(2-methyl-4-diethylamino-phenyl)methane.
Leuco Green is bis(2-methyl-4-diethylamino-phenyl)-(4-diethylaminophenyl) methane.
Leuco Yellow is (4-[*N*-ethyl-*N*{2-hydroxy-3-phenoxy-propyl}amino]-2-methylbenzylmalononitrile) carbanilate ester.

understanding of the HABI chemistry asked if we had considered phenidone as a possible “fixing” agent. We had not. He obtained a small sample of phenidone from a photographic supply store, and it provided the perfect deactivation component. Aqueous propanol solutions of phenidone permitted effective background stabilization.

> **U.S. 4,247,618. Photoimaging Systems with Cyclic Hydrazides.** Dessauer, Rolf; Firmani, Raymond A. (E. I. Du Pont de Nemours and Company). January 27, 1981 (Cl. 430/342; 430/33). Appl. May 11, 1979. A photosensitive system comprising in intimate admixture (1) a dye in its leuco form, (2) a photooxidant taken from the group of hexaarylbiimidazole compounds, benzophenone, para-aminophenyl ketones, polynuclear quinones and thioxanthenones, and mixtures thereof and in the presence of the admixture is a 5-member-heterocyclic phenylhydrazide compound. The cyclic phenylhydrazide can be present in the admixture, or a dry coating of the admixture, after imagewise exposure, is treated with a solution of the heterocyclic compound. The system is useful in formation of colored images.

The formulations developed for this program, to give black, yellow, magenta and cyan films on simple exposure without processing were optimized by careful adjustment of photoinitiators, inhibitors, plasticizers, etc. These quickly produced four colorless coated film products that yielded attractive high resolution magenta, cyan, yellow and black films on exposures of ca. 60 sec. through lithographic separation negatives. It was important that the compositions gave full image density in the same time period irrespective of what color was formed. It was found desirable that the coatings have adequate background stability for 30 minutes when viewed in a "light box" containing daylight fluorescent lamps.

Formation of background color could be eliminated entirely by passing the films through a propanol–water solution of phenidone in a 10″ wide Hope X-ray film processor. Surprisingly, the selected leucodyes gave a remarkably good match for the traditional printing ink colors as were used in offset lithography.

Photo Products management, however, showed little interest in following up on this, and the program was abandoned in favor of a peel-apart system, which did give permanently stable images, but initially suffered some resolution problems until the required peel-forces were adequately controlled. Some years later, this work, though not commercialized, became important because of a possible patent infringement by a competitor.

8.16 J.C. PENNEY INVENTORY CONTROL SYSTEM (1977)

J.C. Penney approached DuPont with a novel idea—to include a photosensitive coating as part of a shipping inventory system. The concept was optically to record a mark on the photosensitive area after the bar code on the label had been successfully scanned. This would allow a more effective control of shipped merchandise, since it could be established at each contact point that it was received. The technical question was whether one could offset print a label onto DYLUX® 503B proof paper, or apply a coating on selected areas of the shipping label. Both approaches were readily demonstrated with the help of Mr. Russ Johnson, technical manager of the DuPont printing plant, who simply ran several sheets of DYLUX® through an off-set printing press. Johnson for many years had been a keen supporter of our attempts to introduce new technologies to the printing industry and could always be counted on coming up with meaningful advice.

> **U.S. 4,180,204. Automatic Inventorying System.** Koenig, Richard W. et al. The J.C. Penney Corporation, Inc. (New York, NY). December 25, 1979 (Cl. 235/385; 235/454; 235/472.01; 235/487; 382/3). Appl. filed: November 8, 1978. A method and means for automatically inventorying items having coded tags or labels using a character-recognition device, such as a wand scanner, in combination with a system for specially marking the labels when they have been successfully read and recorded by the scanner, which system comprises the use of a photosensitive dye-forming material on the label and an ultraviolet light-producing flash device on the scanner. The flash device is actuated upon the successful completion of a recognition reading and irradiates the label with ultraviolet light, which produces a visible and permanent mark on the label.

8.17 PHOTOMARKER GARMENT PATTERNS (1977)

Garment patterns were made by exposing large sheets of diazopaper for use in the clothing industries. The "markers", were placed over layers of fabrics and used to guide the cutter to produce unique parts.

Diazo paper requires moist developing, which may distort the pattern, and one of the industry leaders, Photomarker Co. asked DuPont to investigate making a low cost photosensitive paper embodying some, but not all the properties of DYLUX® proofpaper.

A relatively low cost paper product was produced using o-Cl-HABI, a mixture of leucodyes, quinones, and a red Rhodamine dye to enhance contrast. The product was successfully field tested, but was not commercialized because of internal problems at Photomarker Co.

8.18 INSTRUCTIONAL X-RAY PRINTS (1977)

The quality of images on DYLUX film or paper products was certainly not adequate to consider them as replacement for X-ray products. Nevertheless, DuPont's German marketing organization identified a market that was termed "instructional" X-ray products, in contrast to "diagnostic" products. It appeared as though physicians have a need to mark up X-rays to indicate locations of special interest, and use of the original was considered undesirable. Hence, a simple way of producing a copy on paper or film that could be used for this was believed to be marketable. The performance of proofpaper originally was considered adequate, but in time, it appeared that higher contrast and a black or near black image would be preferred. Combining an orange dye and LB-8 leucodye gave a visually more attractive image, but in time, the marketing group lost interest in pursuing product modification and equipment building for this opportunity.

8.19 DIGITAL DYLUX® PROOF PAPER (1995)

By the mid-1990s, it became evident that the anticipated digital revolution of the printing industrial was finally taking place. The concept of Computer-To-Plate (CTP) technology, which bypassed an intermediate lithographic film, meant that contact exposures onto a proofing medium were no longer feasible. Instead, it was found desirable to produce a proofing material that could be exposed in NIR-emitting printing engines, such as CREO's TRENDSETTER™ or SPECTRUM™.

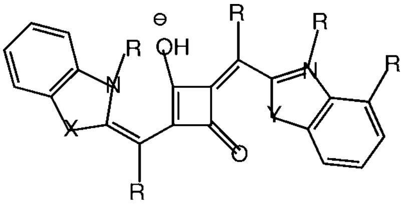
Could a formulation be developed that gave instant access images, when the imaging radiation was 837 nm? Scouting showed that this was indeed possible. However, to maximize image density, some significant changes were required in the formulation. The sum total of these changes were as follows:

1. Energy absorbed at 837 nm meant that a NIR-dye, strongly absorbing in that region had to be incorporated in the coating.
2. In order to maximize the effectiveness of the HABI component, o-ethoxy-HABI, which was somewhat less stable thermally than TCTM-HABI or TCDM-HABI, used in DYLUX® 503 proof papers was selected.
3. Instead of the cyan forming TLA-44 leucodye, Leuco Crystal Violet, was used as it yielded a more intense, purple image, which gave the imaged paper higher visual contrast.
4. As the presence of acid increased the autooxidation of Leuco Crystal Violet, tribromomethyl phenylsulfone was included in the formulation. This cleaved on photolysis or thermolysis, and the presence of bromine radicals enhances the image color formation.

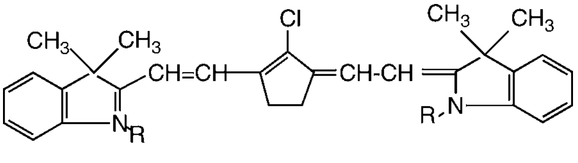
In early experiments, the coatings imaged quite well, but lacked room light stability. Because of the interaction of LCV with quinones, our traditional photofix concept could not be employed. Hence, to stabilize the coating against ambient light, UV-screening agents were added to the coating. The NIR-sensitizing dyes evaluated had strengths and weaknesses. Of all possible candidates, the most attractive were squaraine derivatives, which contributed minimal background color to the unexposed coating. Regrettably, the preferred squaraine derivative had a slight odor, which many people found offensive. It was then necessary to consider cyanine derivatives, all of which contained a relatively reactive halogen atom.

U.S. 5,858,583. Thermally Imageable Monochrome Digital Proofing Product with High Contrast and Fast Photospeed. Dessauer, Rolf (Greenville, DE); Caspar, Jonathan V. E. I. Du Pont de Nemours and Company. January 12, 1999 (Cl. 430/17; 346/135.1; 346/76.1; 430/332; 430/338; 430/342; 430/343; 430/344; 430/944; 430/964; 503/201; 503/217; 503/223; 503/224). Appl. July 3, 1997. Novel thermally imageable monochrome product compositions, elements, and processes are disclosed herein. These compositions and elements characteristically have high contrast and fast imaging speeds. The thermally imageable compositions of this invention comprise (a) at least one hexaarylbiimidazole (HABI) compound, (b) at least one leucodye, (c) at least one acid-generating compound, (d) a polymeric binder, (e) optionally at least one UV stabilizer and/or at least one inhibitor of color formation, and, in certain embodiments, (f) at least one near IR-absorbing dye. These compositions have the propensity for affording, upon thermal imaging, highly colored images having high optical density values. At the same time, background color is low in preferred compositions even after extensive exposure to ambient light. These compositions can be imagewise heated to effect color formation (i.e., generation of an image) or, in case of compositions containing at least one near IR-absorbing dye, can be imagewise exposed to near IR radiation from a laser or other device to effect color formation (i.e., generation of an image).

McKeever in U.S. 4,298,67 had shown that incorporation of diethyl hydroxylamine in LCV compositions stabilized the background. This did indeed also occur in the NIR-sensitive DYLUX® formulations as well, but regrettably, there was interaction between the hydroxylamine derivative and the NIR-absorbing dye. This was resolved by using more highly substituted derivatives, dibenzylhydroxylamine.



SQUARAINE



⊕ MEROCYANINE

U.S. 6,251,571. Non-Photosensitive, Thermally Imageable Element Having Improved Room Light Stability. Dessauer, Rolf and Caspar, Jonathan V. (E. I. Du Pont de Nemours and Company)

> June 26, 2001 (Cl. 430/343; 430/332; 430/338; 430/340; 430/964). Appl. March 10, 1998. Novel thermally imageable monochrome product compositions, elements, and processes are disclosed herein. These compositions and elements characteristically have high contrast and fast imaging speeds. The thermally imageable compositions of this invention contain at least one polymeric binder, a specified leuco dye and a specified hydroxylamine compound. These compositions have the propensity for affording, upon thermal imaging, highly colored images having high optical density values. At the same time, background color is low in preferred compositions even after extensive exposure to ambient light. These compositions can be imagewise heated to effect color formation (i.e., generation of an image) or, in case of compositions containing at least one near IR-absorbing dye, can be imagewise exposed to near IR radiation from a laser or other device to effect color formation (i.e., generation of an image).

In the trade literature, DuPont advertised DuPont Thermal DYLUX®

> "as the industry's only imposition proofing media designed to work with near-IR laser exposure CTP systems. This unique imposition solution enables an all-digital CTP environment. With DuPont Thermal DYLUX®, one can now check digital integrity and validate imposed digital plate files on the same device used for plate imaging. This means cost savings and greater utilization of the CTP investment. Coated on both sides of the paper-based media, DuPont Thermal DYLUX® yields instant front and back images upon exposure to 830 nm wavelength light. It is loaded in a manner similar to aluminum plates and imaged with the same optics, laser, and screening that is used to image the printing plate. Customers can produce a high-resolution imposition proof in less than six minutes. DuPont Thermal DYLUX® is for use with the following exposure devices: Heidelberg/CREO Trendsetter™ 3244 CREO Trendsetter™ Spectrum™ and Spectrum Proofer™".

However, for a variety of reasons, which probably had to do as much with marketing as with the technology and cost, DuPont Thermal DYLUX® failed to gain commercial acceptance.

8.20 MANUFACTURE

The manufacture of a totally new-coated product inevitably is a challenge. The ingredients must be available, their quality must be controlled and the equipment must be in good shape for the coating run. Once the product is coated, there is a need to store it and convert it into the desired sizes. Finally it must be distributed to warehouses and sales offices.

The DuPont manufacturing site at Towanda, PA has large coaters that produce products at speeds from 100 to 300 ft/minute, perhaps even more. The substrate can be anywhere up to 5 feet wide. Operations must be carried out in subdued light; because of the relatively low photosensitivity of DYLUX® products, operations can be carried out in a yellow-light environment is sufficient. For products, which are higher speed or visibly sensitized red light, illumination may be necessary. Additionally, clean-room environments are required to minimize the adverse effects of dust.

Quality control of the ingredients is essential, and has to be made by skilled technicians who compare materials with standards that had been previously found acceptable. The mixing process is critical; ingredients must be added in the proper order, and adequate stirring maintained to avoid heat buildup. There is a significant difference between small lab scale preparations and operating in 55 gallon or larger drums or kettles holding hundreds of gallons. The mixing areas are in one site on a plant; the coating area is elsewhere.

Through the history of DYLUX® products, many things have changed. In the 1960s, solvents were of little concern to the environment, and chlorinated solvents were popularly used. As a mater of fact, they were preferred because of their non-flammability. Coating equipment could be designed to recover solvents, so that the hazard of these solvents was minimized. More recently, however, flammable organic solvents, such as ketones and alcohols were preferred, as these did not need to be recovered, and could be burned to eliminate the need for storage of used materials.

Industrial coaters are huge machines that must be utilized nearly full time for reasons of economy. Thus, there are rigid schedules as to what is coated, and when. Regrettably, there are occasional accidents: the web may tear, a part malfunctions, something is spilled, etc. These and other events can delay the coating run of a particular material.

Coating solutions are tested prior to producing product on a large coater. With DYLUX® 503B proofpaper, one could readily see if the recipe "worked", i.e., that it had the correct performance characteristics when newly coated. Of course, prediction of the long-term performance is guesswork.

By the time a material is coated on a large production coater, it gas usually been coated many times on smaller, or pilot coaters. Here the speed of coating is anywhere from 5 to 50 feet/minute. As the drying conditions are likely to be different from those of the production coater, some uncertainty results.

These coaters contain a tank in which the coating solution is retained, from where it is pumped to the coating head from which it may be extruded, or it may be coated with wire-wound or smooth coatings rods, which deposit a thin uniform layer of coating lacquer on the substrate. Concentration of solids of the coating solution may be anywhere from 10 to 30%, and the solvent is removed in drying chambers before the coated product is rolled up. The coating temperatures must be carefully controlled, so as to avoid blistering. Manufacture of double-sided coatings imposes further restrictions on the process.

An important issue in coating of photosensitive materials is the uniformity of the coating over the width of the substrate. This is less of a concern on film bases, such as polyester film, than paper, which is composed of natural products, such as phenols, that are inherent to the paper manufacturing process. Soon after the coating run is started, it is stopped, and samples are taken, and tested for coating uniformity. This is done by cutting out with dies equal sized pieces, and weighing them. The coating is then stripped or dissolved off the base, and the latter reweighed. Additionally, with DYLUX®, it is possible to run exposures under controlled conditions, and quantify the image density attained. Where there is significant variation in coating weight across the web, it is necessary to realign the coating equipment, until a satisfactory level of uniformity is observed. Sometimes, extended coating runs require several rolls of paper or film substrates, and these are spliced so that the coating can continue without interruption.

Coated rolls of paper or film are wrapped and stored in black polyethylene bags. It should be realized that the uncoated and coated substrates must be handled by lifting equipment; they are too heavy to be carried by coating crews.

As many as 6 or 8 members of a coating crew are stationed in various locations of the coater to observe any obvious flaws, tears in the substrate, etc. When there is a need to stop the coating it is essential to do so quickly, to avoid generation of waste.

The rolls of coated product are finished in an area remote from the coating area. The latter must be kept especially clean to avoid dirt from getting into he coating lacquer or the moist coatings, to avoid streaks, pinholes, etc.

Slitting involves running the rolls through a cutting tool that converts a 5-foot web to several smaller sized rolls. These are then sheeted, so as to create popular sizes. DYLUX® was offered in many different dimensions, from 8 1/2″ × 11″ to many multiples thereof.

Finally the finished paper product is packaged. For DYLUX® proofpaper, it was found that paper bags, with a foil laminate on Kraft paper were acceptable. These were sealed after finishing. Ultimately, labels had to be available that could identify the product; these also contained a code which related to manufacturing date.

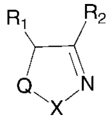
8.21 COMPETITION

8.21.1 Mead Corporation Cycolor™

During the 1980s, the Mead Corporation supported an extensive program to develop CYCOLOR™, a color printout system, which depended on microencapsulation of leucodyes. This program involved imaginative chemistry but at the present time (2006) seems to have seen little commercial activity. Over 100 Mead patents describing microencapsulated imaging systems, going back to U.S. 4,110,511, filed May 25, 1977 for a process for the production of a pressure-sensitive carbonless copy sheet using microcapsules formed in situ in a radiation curable binder (August 29, 1978). Only two Mead patents involved HABI chemistry. Many years earlier, ca. 1960, National Cash Register Co. pursued an ambitious program of microencapsulating photochromic spiropyrans for information storage applications. U.S. patent class 430/138, dealing with radiation sensitive materials involving microencapsulation lists 879 issued patents in this area from Jan. 25, 1976 to July 18, 2006.

U.S. 4,935,329. Negative Working Imaging Process Employing Photosensitive Microcapsules. Hipps, Sr., Jesse; Kiser, T. Kay; Feldman, Lyudmila. The Mead Corporation, June 19, 1990 (Cl. 430/138; 428/402.2; 428/402.24; 430/253; 430/394; 430/914; 430/945; 503/214; 503/215). Appl. June 1, 1988. A method for producing images utilizing photohardenable microcapsules and a reversal phenomenon is disclosed. The microcapsules contain a color former, a photopolymerizable or cross-linkable monomer and a photoinitiator. A substrate containing the microcapsules is imagewise exposed to a high intensity, short-term exposure of actinic radiation to cause reversal in the exposed microcapsules. The substrate is then given an overall exposure to polymerize the microcapsules which had not completely reversed. The microcapsules are then ruptured in the presence of a developer material to produce a negative image. In addition the inventive method may be used to produce copies by a "direct-write" copying process.

U.S. 5,079,126. Photohardenable Composition Containing Five Member Aromatic Group with Imine Moiety. Hipps, Sr., Jesse; Plageman, Claire M. The Mead Corporation, January 7, 1992 (Cl. 430/138; 430/281.1; 430/914; 522/14; 522/15; 522/8). Appl. August 27, 1990. A photohardenable composition comprising an addition polymerizable or crosslinkable material, a photoinitiator composition capable of initiating polymerization or crosslinking of said polymerizable or crosslinkable material, and a compound of the formula



wherein Q represents $-C{=}O$ or $-C{-}OH$; X represents S or N which is unsubstituted or substituted with alkyl or aryl groups; R_1 represents H, alkyl, aryl, alkoxy, benzoyl, arloxy, acyl or monosubstituted amino groups; and R_2 represents H, alkyl or aryl groups is disclosed. The composition is preferably contained in microcapsules and is used in photosensitive imaging systems. The five member aromatic group containing the imine moiety functions to reduce the likelihood of short time scale reciprocity failure of the composition and enable imaging using high intensity radiation sources. An imaging method using the inventive composition is also disclosed.

8.21.2 Fuji Photo Film Co. Ltd.: Copiart-3™

The Mead program confirmed that microencapsulation could be a very useful approach to developing novel imaging systems. Starting about 1989, Fuji Photo Film Co., Ltd. began to obtain patents that employed microencapsulation, leucodyes and hexaarylbiimidazoles. Between May 1990 and May 2002, 12 U.S. patents were issued to Fuji for microencapsulated color-forming systems containing leucodyes and hexaarylbiimidazoles, i.e., similar to the DYLUX® printout system. Altogether, over 50 U.S. patents refer to microencapsulation systems containing HABIs.

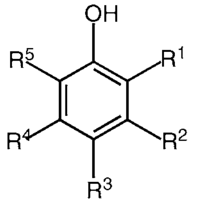
This approach obviously had the advantage that it made it possible to isolate competing reactions. It allowed Fuji to utilize less costly ingredients: o-Cl-HABI vs. CDM-HABI or TCTM-HABI as photooxidant and Leuco Crystal Violet vs. tris(*p*-diethylamino-*o*-tolyl)methane for color-forming systems. Additionally, LCV gave a much more intense image than the cyan-forming leucodye, which looked black when viewed in the yellow lighted environment that is common to the printing community.

The chemistry in certain examples employed a combination of o-Cl-HABI, Leuco Crystal Violet and tribromomethylphenyl sulfone, an extremely effective combination of color forming chemistry! This reaction was carried out inside microcapsules in the presence of plasticizers. The fixing reaction depended in certain cases on the interaction of the HABI with phenidone, retained outside the microcapsules until a thermal after-treatment post imaging caused the capsule to rupture, permitting the fixing reaction to take place. This rupture could be accomplished in a thermal processing unit.

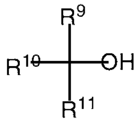
In DuPont's eyes, this appeared to conflict with the Dessauer patent U.S. 4,247,618 (Photoimaging Systems With Cyclic Hydrazides), which issued in 1/27/1981, since that clearly described the remarkable deactivation effect of this class of compounds, of which phenidone is the best known. In time this possible interference was settled, and Fuji's Copiart-3™ proof paper came onto the market. It had many attractive attributes; speed, appearance, more versatility due to the lack of restricted imaging/fixing wavelengths, but it did not greatly impact the market for DYLUX® proof paper.

Judging by the number of Fuji scientists (19) whose name appeared on these patents, the work represented a considerable research effort. In view of Fuji's subsequent expanded efforts with HABIs (as of Nov. 29, 2005, Fuji has had over 220 U.S. patents issued in which HABIs are mentioned), this may have been the beginning of a learning experience, leading to many other products, just as DYLUX® was a learning experience in this field for DuPont! Below is a listing of the pertinent Fuji patents containing HABIs and microcapsules and relating to optical printout.

U.S. 4,929,530. Light Image Forming Material and Image-Recording Method Using Such. Saeki, Keiso (Shizuoka, JP); Endo, Tosiaki (Shizuoka, JP). May 29, 1990. Appl. March 16, 1989. An optical image forming material comprising a support (A) at least one member selected from the group consisting of oxidative-developable leuco dyes, (B) at least one member selected from the group consisting of photo-oxidizing agents, (C) at least one reducing agent and (D) at least one organic sulfonamide compound and/or at least one member selected from the group consisting of hydroxy compounds represented by the following formula (I) or (II)



(I)



(II)

wherein R^1 to R^{11} are as described herein, the leuco dye (A) and the photo-oxidizing agent (B) being present in microcapsules, and the reducing agent (C) and the organic sulfonamide compound and/or the hydroxy compound (D) being present outside of the microcapsules.

Sample (1):

Leuco dye: Leuco Crystal Violet	3.0 parts
2,2′-Bis-(o-chlorophenyl)-4,4′,5,5′-tetra-phenylbiimidazole	3.0 parts
Tribromomethylphenylsulfone	0.6 parts
2,5-Di-tertiary-octylhydroquinone	0.4 parts
Methylene chloride	22 parts
Tricresyl phosphate	24 parts
Takenate D-110N	24 parts

Next, the following components were mixed.

Aqueous solution of 4% by weight polyvinyl alcohol	150 parts
Reducing agent: 1-phenylpyrazolidine-3-one (phenidone A)	30 parts
p-Toluene sulfonamide	30 parts

The mixture was dispersed using a Dyno mill (trade name, manufactured by Willy A. Bachofen A.G.) to obtain a reducing agent-containing dispersion having an average particle diameter of 3 μm. 9 parts of the capsule dispersion was mixed with 6 parts of the aforesaid reducing agent containing dispersion. Super-calendared wood free paper (with a basis weight of 64 g/m^2) was coated with the resulting dispersion mixture in an amount so as to give a coating weight of 10 g/m^2 on a solid basis. The coated paper was dried by heating at 50°C for one minute to obtain Sample (1).

U.S. 4,942,107. Image-Forming Material and Image Recording Method Using the Same. Saeki, Keiso (Shizuoka, JP); Endo, Tosiaki (Shizuoka, JP); Satomura; Masato (Shizuoka, JP); Shinozaki, Fumiaki (Shizuoka, JP). July 17, 1990 (Cl. 430/138; 430/203; 430/211; 430/224; 503/214; 503/216; 503/218). Appl. March 8, 1989. An image-forming material and an image recording method for using the same are disclosed. The image-forming material comprises microcapsule and a reducing agent which is present outside of the microcapsules, wherein the microcapsules contain (a) a leuco dye capable of oxidatively developing a color, (b) a photo-oxidizing agent, and (c) a phenolic compound. The image-forming material exhibits excellent image reproducibility, preservability before use, and image preservability.

U.S. 4,962,009. Microcapsule Containing Photo-Oxidizing Agent and Leucodye. Washizu, Shintaro; Yamaguchi, Jun; Shinozaki, Fumiaki; Shimomura, Akihiro; Usami, Toshimasa; Endo, Toshiaki; Saeki, Keiso. Fuji Photo Film Co., Ltd. October 9, 1990 (Cl. 430/138; 430/336; 430/337; 430/338; 503/205; 503/214). Appl. October 14, 1988. An image-forming material comprising: (a) microcapsules, in which at least one leucodye capable of developing a color by oxidation and at least one photooxidizing agent (preferably a combination of a lophine dimer and an organic halogeno-compound) are enclosed together, and (b) at least one reducing agent not enclosed in the microcapsules (preferably present in the form of an emulsified dispersion), thereby achieving image formation in a completely dried condition, and ensuring excellent freshness keeping property, image reproducibility and fixability.

U.S. 4,963,458. Image Forming Method and Material Using Photopolymerizable Composition. Ishikawa, Shunichi (Kanagawa, JP); Shinozaki, Fumiaki (Kanagawa, JP). October 16, 1990. Appl. September 6, 1988. A light-sensitive image forming method using a recording element which comprises a recording layer on a support is disclosed. The recording layer contains at least two active components of a photopolymerizable composition such as a polymerizable compound and a polymerization initiator, both of which are essential for a photopolymerization reaction. The components are separated from each other by the shell of microcapsules in such manner that at least one component is contained in the microcapsules which are dispersed in the recording layer and the other component is arranged outside of the microcapsule. The image forming method comprises the steps of: heating the recording element to form the photopolymerizable composition in the recording layer; and imagewise exposing to light the recording element to imagewise polymerize the photopolymerizable composition. When the recording element is heated, the component outside of the microcapsules are brought into contact with the component in the microcapsules by permeation of at least one of the components through the shell of the microcapsules. Heat-sensitive image forming methods are also disclosed.

U.S. 4,981,769. Light Image Forming Material. Saeki, Keiso; Endo, Tosiaki. Fuji Photo Film Co., Ltd. January 1, 1991 (Cl. 430/138; 428/402.22; 428/402.24; 430/338; 430/340; 430/906; 430/909; 503/214). Appl. August 18, 1989. A light image forming material comprising a support having provided thereon a layer comprising microcapsules containing a leucodye capable of developing a color through oxidation and a photooxidizing agent, a reducing agent provided outside the microcapsules, and the layer further comprising carboxy-modified polyvinyl alcohol and epoxidated polyamide resin for imparting high water resistivity.

U.S. 4,985,331. Multi-Color Recording Materials. Saeki, Keiso; Shinozaki, Fumiaki; Fujita, Yutaka. Fuji Photo Film Co., Ltd. January 15, 1991 (Cl. 430/138; 430/333; 430/337; 430/338). Appl. November 27, 1989. Multi-color recording materials where the color forming layers are established on the same side of the support are disclosed. The multi-color recording system may be either of: (1) a two-color recording material comprising a support having provided thereon: (a) a light-sensitive heat-sensitive color forming layer comprising (i) microcapsules containing a leucodye which is capable of forming a color by oxidation and a photooxidizing agent and (ii) a reducing agent; and (b) a heat-sensitive color forming layer having a colorforming temperature differing from the glass transition temperature of the microcapsule walls, and which comprises an electron donating leucodye capable of forming a color of a hue differing from that of the light-sensitive heat-sensitive layer and an electron accepting compound capable of reacting with the electron donating leucodye to form a color; (2) a multi-color recording material comprising a support having provided thereon: (a) a light-sensitive heat-sensitive color forming layer comprising (i) at least two types of microcapsules each containing a leucodye capable of forming a color by oxidization and a photo-oxidizing agent and (ii) a reducing agent, wherein the polymer walls of the at least two microcapsules have different glass transition temperatures from each other, and the leucodyes contained in the microcapsules have different hues from each other; and (b) a heat-sensitive color forming layer as described above; or (3) a multi-color recording material comprising a support having provided thereon: (a) a light-sensitive heat-sensitive color forming layer comprising (i) at least two types of microcapsules each containing a leucodye capable of forming colors by oxidation and a photo-oxidizing agent and (ii) a reducing agent, wherein the leucodyes contained in the microcapsules have different hues from each other, and the photo-oxidizing agents contained in themicrocapsules are activated by actinic light of different wavelengths; and (b) a heat-sensitive color forming layer as described above.

U.S. 5,030,548. Photopolymerizable Composition. Fujikura, Sadao; Iwasaki, Masayuki; Maeda, Minoru; Wada, Minoru. Fuji Photo Film Co., Ltd. July 9, 1991 (Cl. 430/281.1; 430/288.1; 430/907; 430/910; 430/916; 430/920; 430/92). Appl. August 10, 1989. A photo-polymerizable composition is disclosed, which comprises a thermoplastic polymeric binder; a non-gaseous ethylenically unsaturated compound; a photo-polymerization initiator system composed of 4,4 -bis(dialkylamino)-benzophenone, aromatic ketone and lophine dimer; an organic halogen compound; and a leucodye.

U.S. 5,035,974. Light-Image Forming Material. Saeki, Keiso; Endo, Toshiaki. Fuji Photo Film Co., Ltd. July 30, 1991 (Cl. 430/138; 430/523; 430/531; 430/539). Appl. June 15, 1989. A light-image forming material comprising a support having provided thereon a light-image forming layer comprising microcapsules containing an oxidative-developable leucodye and a photooxidizing agent, and a reducing agent as essential ingredients, wherein the material also includes a covering layer or intermediate layer containing a film-forming high-molecular binder and/or an inorganic or organic pigment.

U.S. 5,051,333. Optical Image-Recording Material. Yanagihara, Naoto; Iwakura, Ken; Endo, Tosiaki; Saeki, Keiso. Fuji Photo Film Co., Ltd. September 24, 1991 (Cl. 430/138; 430/203; 430/211; 430/224; 430/332; 430/343; 430/344; 503/214; 503/217; 503/218). Appl. June 21, 1990. An optical image-recording material comprising: (a) microcapsules, in which at least one leucodye capable of forming a color by oxidation and at least one photo-oxidizing agent are enclosed together, and (b) at least one reducing agent not enclosed in the microcapsules, or (c) microcapsules, in which at least one reducing agent is enclosed, and (d) both at least one leucodye capable of forming a color by oxidation and at least one photo-oxidizing agent not enclosed in the microcapsules, wherein the microcapsules have capsule walls made from a material which lowers its permeability barrier to at least one component selected from the photo-oxidizing agent and the reducing agent when the capsule wall material is heated above its glass transition temperature, and the leucodye is a xanthenecompound having an N-substituted anilino group substituted by an electron attracting group.

U.S. 5,055,373. Multicolor Recording Material. Saeki, Keiso; Shinozaki, Fumiaki; Endo, Toshiaki. Fuji Photo Film Co., Ltd., October 8, 1991 (Cl. 430/138; 428/402.2; 428/402.21; 430/203; 430/541; 430/913; 430/916; 503/204; 503/21). Appl. September 29, 1989. A multicolor recording material is disclosed, which comprises a support having provided thereon a coating layer comprising two or more kinds of microcapsules each containing at least a leucodye capable of being colored by oxidation and a photo oxidizing agent outside said microcapsules, and a reducing agent as necessary components, with two or more leucodyes capable of forming different colors from each other being retained in different kinds of said microcapsules respectively composed of walls of high polymers having different glass transition points.

U.S. 5,091,280. Light- and Heat-Sensitive Recording Material. Yamaguchi, Jun; Washizu, Shintaro; Matsumoto, Hirotaka; Iwakura, Ken; Fukushige, Yuuichi. Fuji Photo Film Co., Ltd., February 25, 1992 (Cl. 430/138; 430/203; 503/200; 503/216; 503/219; 503/225; 503/226). Appl. August 13, 1990. A light- and heat-sensitive recording material comprising a support having thereon at least one light- and heat-sensitive layer comprising, (1) microcapsules containing an electron donative colorless dye, and (2) a light-hardenable composition containing (a) a polymerizable vinyl monomer, (b) a photopolymerization initiator, and (c) an electron acceptive developer and a light- and heat-sensitive recording material comprising a support having thereon at least one light- and heat-sensitive layer comprising, (1) microcapsules containing an electron donative colorless dye, and (2) a light-hardenable composition containing (d) an electron acceptive polymerizable vinyl monomer and (b) a photopolymerization initiator.

U.S. 5,168,029. Multicolor Recording Material. Igarashi, Akira; Fujita, Yutaka. Fuji Photo Film Co., Ltd., December 1, 1992 (Cl. 430/138; 430/214; 430/215; 430/224; 430/332; 430/338; 430/340). Appl. February 2, 1990. A multicolor recording material is disclosed, which comprises a support having provided thereon at least two layers each containing a leucodye which is capable of forming a color by oxidation and a photo-oxidizing agent, wherein the leucodyes contained in each layer are capable of forming different color from each other and the photooxidizing agents contained in each layer respond to light having different wavelength from each other. Another multicolor recording material is also disclosed, which comprises a support having provided thereon a layer containing at least two kinds of heat-responsive microcapsules which have different response temperature from each other, each containing a leucodye which is capable of forming a color by oxidation and a

> photo-oxidizing agent, wherein the leucodyes contained in each kind of microcapsule are capable of forming different color from each other and the photo-oxidizing agents contained in each kind of microcapsule respond to light having different wavelength from each other.

8.22 CONCLUSIONS ABOUT MARKETING EFFORTS

The author had an ample opportunity to expand the applications of photooxidation of leucodyes into many business areas. Where that fit DuPont's perceived business objectives, such as products for the printing industry, it was only necessary to overcome the conventional wisdom of what was good and what was not, and to match performance of the system to real applications. That meant understanding markets, and learning about industry changes. Thus, the wise old men who had grown up in the silver photographic field did not predict the success of DYLUX® proofpaper in the market, and far more energy had to be expended to overcome internal resistance than should have been the case.

In some areas, there was no desire to expand the market in areas that were unfamiliar. The attraction of the imaging technology in the 'aca' clinical analyzer would argue that other similar opportunities might have existed, but no one was encouraged to find new customers.

Surely a toy developed and marketed by Mattel could have consumed a significant quantity of a photosensitive paper product. This would have involved a commitment to get involved in an industry that was unfamiliar to nearly all the scientists and engineers at DuPont. It was easier to reject the opportunity.

Other areas where the marketing efforts were unsuccessful suffered from the unwillingness to branch out into machine design and to build devices that would use the consumables. The UPC opportunity is a good example of this. Hobart had skill in building mechanical devices, but had little electro-optical expertise. DuPont had qualified engineers to help, but they were not used. Sponsoring work at a third party would have made sense, but that would have been admission of inability to solve the problems in house. The result: no devices and no product sales.

In summary: a lot of effort goes into getting new products to the markets. Contacts with people who can help, perseverance and timing are very important factors in success.

ACKNOWLEDGEMENT

Over 200 DuPont scientists, managers, marketers, technicians contributed to the success of the DYLUX® program. It should be pointed out that invention sometimes is the easy process, and the efforts behind commercialization and manufacturing are difficult and overlooked. With that in mind, the chemists and engineers at the Towanda plant, who contributed so much to keep the coaters rolling successfully, they were Thomas D. Sheets, David R. Logrando, William F. Mooney III and Jeffrey J. Patricia should be acknowledged.

Additionally, of course, the research group that initiated this work under the leadership of George Coraor, namely, Lawrence Cescon, Robert Cohen, Catharine Looney, Alexander Maclachlan, Peter Strilko, Charles Yembrick, and later Ed Abramson, John Caspar, John Neumer and Garrett Forsythe contributed significantly. The contributions to the development of markets by John DeCampi, Philip Botsolas, Lawrence Friar and William Wartell were outstanding.

9

HABIS AS PHOTOPOLYMERIZATION INITIATORS

9.1 HISTORICAL PERSPECTIVE

During the period up to 1963, hexaarylbiimidazoles were primarily studied for their physical, principally, photochromic properties. Work at the Organic Chemicals Department of the DuPont Company was primarily concerned with the color-forming interaction between HABIs and triarylmethane leucodyes. The group working in this area had little familiarity with photopolymerization, but did periodically try to interest another company division, the Photo Products Department in examining various novel HABIs as photoinitiators.

In 1964, two unrelated events occurred. The work by Cescon, R.L. Cohen and Dessauer was directed at an improvement in the imaging speed of the dye-based imaging system, then identified as UVI (Chapter 2). When it was realized that a higher-speed in the color-formation was difficult to attain by the development of a chain-reaction involving the color-formation step (initiated by the photooxidation of leucodyes), it occurred that a possible route might be a chain reaction involving the "deactivation" step, in which areas could be made to inhibit color formation. The color-forming system required the availability of plasticizers, and it was reasoned that if such plasticizers could be converted to oligomers that no longer act as such, then color-formation could be inhibited. Cescon and Cohen demonstrated that this was possible. In their initial experiments they included then standard photopolymerization initiators, e.g., anthraquinone derivatives and observed that the system did indeed "work" as proposed. Cescon found that the system also functioned when the anthraquinone was omitted. He and Cohen concluded that HABIs acted as initiators. A rather extensive list of experiments was performed, and became the basis of a patent that issued in 1974.

> **U.S. 3,615, 454. Process for Imaging and Fixing Radiation-Sensitive Compositions by Sequential Irradiation.** Cescon, Lawrence A.; Cohen, Robert L.; Dessauer, Rolf (E. I. du Pont de Nemours & Co). Issued 26 Oct 1971, Appl. 26 Jun 1968 (Cl. 96/35.1; G 03c). A multiple irradiation method which comprises providing a radiation-sensitive material comprising (1) a radiation-sensitive, multicomponent, intermolecularly reactive imageable composition whose imaging reaction is subject to diffusion control, mixed with (2) a radiation-sensitive polymerizable composition, imaging by irradiating with imaging radiation under imaging conditions, and deactivating the imageable composition in the unexposed areas by irradiating with the polymerizing radiation under nonimaging conditions, said polymerization being effective to rigidify the material so as to render the imaging reaction diffusion-controlled and thereby prevent the imaging components from diffusing together and reacting. In the imaging step it is only necessary that the imaging reaction occur before the polymerization reaction can deactivate the system. In the deactivation (or fixing) step it is only necessary that the deactivating radiation be applied under conditions ineffective for imaging. Imagewise exposing the composition first to the imaging radiation then to the deactivating radiation produces a negative image. On the other hand, imagewise exposing the composition first to the deactivating radiation creates a latent image, which is developed by exposing the unirradiated areas.

At Parlin, NJ, V.C. Chambers and his group were involved in a photopolymer based office copy system. He requested information about how we could make black images using our leucodye chemistry. The Photo Products office copy system was based on an unpolymerized coating, containing a triphenylmethane dye, which was "reflex exposed" and was then thermally transferred onto a piece of plain paper. We supplied Chambers with some neutral shade forming leucodyes and HABIs, and his technician observed that the polymerization reaction, which was an imagewise reflex-exposure, had higher speed as a result of the presence of hexaarylbiimidazoles and triphenylmethane leucodyes. This is described in French patent 1,481,819.

> **Fr. 1,481,819. Photopolymerizable Compositions and Elements.** E. I. DuPont de Nemours & Co. (by Glen A. Thommes, Peter Walker, and Vaughan C. Chambers, Jr.). (Cl. C08f, G 03c), May 19, 1967; U.S. Appl. June 3, 1965, and March 4, 1966; 14 pp. Photopolymerizable compns. for use in the production of color images contain $\geqslant 1$ nongaseous ethylenically unsatd. monomer capable of undergoing free-radical addn. polymn. with chain propagation; $\geqslant 1$ free radical-producing electron donor, e.g. a leuco dye, a tertiary amine a mixt. of a leuco dye and a photoreducible substance, or a mixt. of a leuco dye and triethanolamine; a 2,4,5-triphenylimidazole dimer; and optionally an energy-transfer substance to improve the sensitivity and (or) an additive to eliminate or reduce the induction period. The compn. is dispersed in a thermoplastic binder and contains various dyes, pigments, thermographic compns., and chromogens, and is coated on any appropriate support. Thus, a standard soln. was prepd. from a 10% cellulose acetate butyrate (20.5% Ac, 26% butyryl, 2.5% OH, and viscosity 9.0–13.5 poises) soln. in Me_2CO 110.0, a 10% cellulose acetate (39.4% Ac 55% HOAc, viscosity 130–82 poises) soln. in Me_2CO 32.5, pentaerythritol triacrylate 30.0, poly(ethylene oxide) (mol. wt. 400) (in 14 ml. MeOH) 2.0 g., and Me_2CO to make 200.0 g. The standard soln. 5.0, the dimer 2-(o-chlorophenyl)-4,5-diphenylimidazole 80, and CBr_4, 100-mg. were mixed, coated as a 0.15-mm. layer on a 0.03-mm. poly(ethylene terephthalate) support precoated with a layer of vinylidene chloride–Me acrylate–itaconic acid terpolymer, and dried for 30 min. at ambient temp. to give a 0.03-mm. film. The laminated product was contacted with an original, exposed to a photoflood lamp at a distance of 40.6 cm. for 30 sec., delaminated, developed, and passed with a receptor paper through 2 rollers heated at 125° to transfer the under exposed zones from the photopolymer layer to the receptor sheet thereby forming a well-contrasted and defined image on the paper.

Even though the project was terminated because office copy arena became exclusively an opportunity for electrophotography, DuPont applied for a patent, which was the first of many that identified HABIs as photopolymerization initiators. Cescon, R.L. Cohen and Dessauer's patent, issued much later, as further work was required to understand the extent of the chemistry involved therein.

Subsequently, the Photo Products research division enthusiastically extended the applications for HABI-based photoinitiator systems in a number of successful products including CROMALIN® and CROMACHECK® proofing systems, LYDEL® printing plates, OMNICRON® holographic film and RISTON® photoresists. In RISTON® photoresists, the simultaneous formation of a printout image, obtained by incorporation of a leucodye, which was oxidized by HABIs was found to be attractive by the users.

Much of the success of the RISTON® and CROMALIN® was derived from the availability of an exclusive, novel photoinitiator system based on hexaarylbiimidazole photoinitiators. The exclusivity was derived from a determined effort earlier in the Organic Chemicals Department of DuPont to obtain composition of matter patents, which eliminated competitors from applying this technology to their products. These photoinitiators were patented in 1974 and provided DuPont with a unique photooxidants and photopolymerization initiators.

U.S. 3,78,4557. Phototropic 2,4,5-Triphenylimidazolyl Radicals and Dimers Thereof. Lawrence A. Cescon (E. I. du Pont de Nemours and Company) 1/8/1974 (Cl. 548/313.4; 65/30.11; 65/60.3; 252/600; 548/343.5). Filed 3/21/1968 orig. 3/29/1962. 2,4,5-Triphenylimidazolyl radicals and their dimers (2,2′,4,4′,5,5′-hexaphenyl biimidazoles) having on the phenyl groups from 1 to 10 substituents free from a hydrogen atom capable of reacting with methyl magnesium iodide, one such substituent being in the ortho position on the 2-phenyl group and having a sigma value below 0.7. The 2-phenyl group can contain up to four substituents, while the 4 and 5 phenyl groups can contain up to three substituents each. The radicals and the dimers are stable and form a photochromic system, finding utility as components in sun shields or shades. They are prepared by oxidizing the corresponding substituted 2,4,5-triphenylimidazole to form the biimidazole, which is dark stable. The radical forms upon exposure of the biimidazole to a light source and is stable in the presence of the light radiation.

The novelty was derived from the fact that these unique materials possessed considerably better dark stability than then commercially available photoinitiators. This made it possible to produce photosensitive films that had excellent pre-image shelf life. This property is of course critical in commercial products, as the amount of time between manufacture and usage can stretch over a period of anywhere from three to 24 months or more.

The two patent publications cited above were the beginnings of HABI-initiated photopolymerization. Since then, more than a thousand subsequent U.S. patents identify HABIs as photopolymerization initiators.

Concurrent with the product developments, carried out primarily in Parlin, NJ, there were developments at the DuPont Experimental Station, particularly by Pazos and Nacci in extending the chemistry of these systems. Much of this work is buried in the patent literature and is herewith presented to illustrate the approaches considered.

Ger. Offen. 2,402,179. Photopolymerizable Materials Containing Nitroso Compounds. Nacci, George R.; Pazos, Jose F. (du Pont de Nemours, E. I., and Co.) (Cl. C 08f), 25 Jul 1974, US Appl. 324,877, 18 Jan 1973. Photopolymerizable compns. contg. a non-gas-forming ethylenically unsatd. compd. such as 3-(3-acryloyloxyphenyl)propionic acid (**I**), triethylene glycol diacrylate, or N-vinylsuccinimide, an org. light-sensitive, free radical-forming material, such as 2-o-chlorophenyl-4,5-bis(m-methoxyphenyl)imidazole dimer (**II**) and (or) 2-o-chlorophenyl 4,5-diphenylimidazole dimer (**III**), along with suitable photosensitizers and electron donors, and a thermal polymn. inhibitor, such as a nitroso compd. dimer are described. These compns. are esp. useful as photoresists. Thus, a soln. contg. 1,2-diphenoxyethane 1.7025, 1 0.1815, **II** 0.0491, **III** 0.0489, Michler's ketone 0.0208, 2-mercapto-5-tert-butylbenzoxazole 0.0201 g, and MeCOEt 20 ml was mixed with an equal vol. of a soln. of nitrosocyclohexane dimer (**IV**) 20 mg in Me_2CO 10 ml and 15 drops of this soln. was then evapd. and crystd. on a 2.5 × 7.5 cm grained Al support under yellow light at 85°. This plate was then exposed at 25° through a Kodak lA step wedge using a medium-pressure Hg; lamp for 17 sec and developed in a $CHCl_3$-C_6H_4 (9 : 91) mixt. to give 8 steps and no indication of thermal polymn. vs. significant thermal polymn. for a **IV**-free control.

U.S. 3,885,964. Photoimaging Process Using Nitroso Dimer. Nacci, George R. (du Pont de Nemours, E. I., and Co.) (Cl. 96-35.1), 27 May 1975, Appl. 476,134, 31 May 1974. Pos.-working photopolymn. systems are comprised of a free radical polymerizable monomer, an org. polymeric binder, a free-radical initiator, and a thermally dissociable nitroso dimer, which in its monomeric dissocd. form prevents free-radical polymn. Thus, a compn. comprised of trimethylolpropane triacrylate contg. ppm hydroquinone inhibitor 2.90, conventional plasticizers 0.8, triethylene glycol diacetate 0.44, poly(methyl methacrylate) 5.24, 2-o-chloro-phenyl-4,5-diphenylimidazole dimer 0.40, tris(4-di-ethylamino-2-methylphenyl)methane 0.03, adhesion promoter 0.02, Michler's ketone 0.01, nitrosocyclohexane dimer 0.015 g, and methylene chloride 40 ml was coated on a Cu-clad circuit board, dried, imagewise exposed at 50° (above the nitroso-compd. dissocn. point) for 0.5 min. cooled to 25° (below the dissocn. temp.) blanket exposed for 5 min. and developed to give a pos. image.

Ger. Offen. 2,511,486. Photopolymerizable Compositions for Relief Images. Nacci, George R. (du Pont de Nemours, E. I., and Co.) (Cl. G03F, H05K), 25 Sep 1975, US Appl. 452,338, 18 Mar 1974. Neg.-working, photopolymerizable, image-forming compns. contg. a nongas-forming ethylenically unsatd. compd. capable of undergoing free radical-induced polym., an org., light-sensitive free radical-forming system, and a thermally dissociable nitroso dimer to inhibit thermal polymn can be made pos.-working by the following steps: (1) exposing the mass at a temp. at which the nitroso dimer is dissocd. so that the free radicals react with the nitroso dimer and no polymn. takes place in the exposed area, (2) deactivating the nitroso dimer by cooling the material to $< 0°$ or heating at 90–125° to destroy the dimer, (3) exposing the unexposed areas to actinic radiation to cause polymn. in those regions; and (4) developing to give the image. Thus, to a soln. contg. trimethylolpropane triacrylate (contg. 245 ppm of hydroquinone as a polymn. inhibitor) 2.90, a com. plasticizer 0.88, triethyleneglycol diacetate 0.44, poly(Me methacrylate) 5.24, tris(4-diethylamino-2-methylphenyl)methane 0.03, an adhesion-improving agent 0.02 g, and CH_2Cl_2 40 ml was added 2-o-chlorophenyl-4,5-diphenylimidazolyl dimer 0.04, and nitrosocyclohexane dimer 0.060 g. This soln. was coated on a Cu-coated plate, and the solvent evapd. at 25° leaving a 0.51 mm layer. The plate was then exposed under vacuum to a line neg. for 10 min at 25° cooled at 0 for 5 mm, the neg. removed, and the plate reexposed under nitrogen at 0° for 10 min. to give a relief image with a depth of 90 μ.

U.S. 4,050,941. High Resolution Photohardenable Coating Compositions Containing Tetracyanoethane Compounds. Pazos; Jose Francisco (E. I. Du Pont de Nemours and Company). September 27, 1977 (Cl. 430/270.1; 430/905; 430/913; 430/920; 522/14; 522/65; 522/121). Appl. December 20, 1976. Photohardenable coating compositions containing A. a substantially solid, organic composition comprising a nongaseous, ethylenically unsaturated compound, B. a tetracyanoethane compound, and C. an organic, radiation-sensitive free radical generating system provide high resolution films and coatings such as photoresist coatings on substrates.

U.S. 4,050,942. Nitroso-Dimer-Containing Compositions and Photoimaging Process. Nacci; George Raymond (E. I. Du Pont de Nemours and Company). September 27, 1977. (Class: 430/288.1; 430/269; 430/328; 430/338; 430/917; 522/14; 522/18; 522/26; 522/63; 522/65; 522/121). Appl. May 21, 1976. Described are photopolymerizable compositions containing A. an ethylenically unsaturated compound, B. about 3–95% by weight of an organic polymeric binder, C. about 0.1–5% by weight of a nitroso dimer which is a noninhibitor of free-radical polymerization but thermally dissociates to nitroso monomer which is an inhibitor of free-radical polymerization, and D. about 0.1–2% by weight of an organic, radiation-sensitive, free-radical generating system. Positive-working, contour images are formed by applying a layer of this composition to a substrate, imagewise exposing the photopolymerizable layer to actinic radiation through an image-bearing transparency at about 20°–65°C, whereby free-radicals are consumed by nitroso monomer, deactivating the nitroso dimer inhibitor system, re-exposing at least the unexposed portion of the photopolymerizable layer to actinic radiation while continuing to maintain the nitroso dimer inhibitor system in the deactivated state, and developing the resulting image. The nitroso dimer inhibitor system may be deactivated by cooling the photopolymerizable layer to below about 10°C, and reexposing the layer to radiation that does not appreciably dissociate the nitroso dimer at a temperature below about 10°C, or by heating the photopolymerizable layer at about 80°–150°C thereby destroying the nitroso dimer inhibitor system, and reexposing the layer to actinic radiation at about 20°–60°C.

U.S. 4,168,982. Photopolymerizable Compositions Containing Nitroso Dimers to Selectively Inhibit Thermal Polymerization. Pazos, Jose F. (E. I. Du Pont de Nemours and Company). September 25, 1979. Cl. 430/281.1; 430/917; 522/16; 522/18; 522/28; 522/63; 522/65; 522/76; 522/121; 522/167; Appl. December 7, 1977. Thermally stable photo-polymerizable compositions comprise (i) at least one nongaseous ethylenically unsaturated compound, (ii) a nitroso dimer which is a noninhibitor of free-radical polymerization but thermally dissociates to nitroso monomer which is an inhibitor of free-radical polymerization, and (iii) an organic, radiation-sensitive free-radical generating system.

U.S. 4,180,403. Photohardenable Films Having High Resolution Containing Nitroso Dimers. Nacci, George R. Pazos; Jose F. (E. I. Du Pont de Nemours and Company). December 25, 1979 (Cl 430/281.1; 430/917; 522/14; 522/16; 522/18; 522/26; 522/63; 522/65; 522/121). Appl. December 7, 1977. Photohardenable films containing a photoactivated free-radical initiator and an inhibitor system composed of a noninhibiting nitroso dimer which dissociates to inhibiting nitroso monomer characterized by a dissociation constant of about 10^2–10^{10} in solution at 25°C and a dissociation half-life of at least about 0.5 minute in solution at 25°C, and having an optical density to initiating radiation of about 0.02–1.25 have high resolution after exposure at the proper energy density and time.

U.S. 4,198,242. Photopolymerizable Composition Containing an o-Nitroaromatic Compound as Photoinhibitor. Pazos, Jose F. (E. I. Du Pont de Nemours and Company). April 15, 1980. (Class: 430/286.1; 430/301; 430/910; 430/917; 522/26; 522/28; 522/63; 522/65; 522/79; 522/109; 522/121). Appl. June 8, 1978. A photopolymerizable coating composition comprising (1) a nongaseous, ethylenically unsaturated, polymerizable compound, (2) a specified nitroaromatic compound, and (3) an organic, radiation-sensitive, free-radical generating system is useful for making a positive or negative polymeric image on a substrate.

U.S. 4,269,933. Methods of Developing Photopolymerizable Compositions Containing an o-Nitroaromatic Compound as Photoinhibitor. Pazos, Jose F. (E. I. Du Pont de Nemours and Company). May 26, 1981 (Cl. 430/291; 430/281.1; 430/302; 430/306; 430/311; 430/312; 430/325; 430/328; 430/916; 430/917; 522/4; 522/14; 522/17; 522/18; 522/65; 522/121). Appl. September 28, 1979. A photopolymerizable coating composition comprising (1) a nongaseous, ethylenically unsaturated, polymerizable compound, (2) a specified nitroaromatic compound, and (3) an organic, radiation-sensitive, free-radical generating system is useful for making a positive or negative polymeric image on a substrate.

9.2 THE MECHANISM OF FREE RADICAL PHOTOPOLYMERIZATION

The mechanism of free radical photopolymerization is described by Cohen and Walker in *Imaging Processes and Materials* [1], Free radical initiated addition photopolymerization has been the technology of choice for commercial polymer imaging systems because of its excellent photosensitivity, stability, and overall process versatility. The initiation step involves activating a spectral sensitizer, using electromagnetic radiation in the wavelength region 300–700 nm. This region corresponds to the output of the most convenient exposure sources and transmission of conventional photomasks.

In some systems, sensitizing dyes are employed to increase the overall efficiency of the system. HABIs have high absorption at 360–380 nm, and in many cases work well without sensitizers. The greater the efficiency of radiation absorption by the sensitizers, the greater the photospeed of the photopolymer system:

$$\mathrm{S} + h\nu \rightarrow \mathrm{S}^* \qquad \text{(light absorption)}$$

Energy from the excited sensitizer molecule may be transferred to a HABI initiator molecule L–L (L· = lophyl radical) if certain photochemical criteria are satisfied:

$$\mathrm{S}^* + \mathrm{L{-}L} \rightarrow \mathrm{S} + \mathrm{L{-}L}^* \qquad \text{(energy transfer)}$$

The initiator may also be directly excited if it efficiently absorbs the incident radiation:

$$\mathrm{L{-}L} + h\nu \rightarrow \mathrm{L{-}L}^* \qquad \text{(direct activation)}$$

The excited initiator molecule may then directly cleave to form two free radicals:

$$\text{L–L}^* \rightarrow \text{L}'\cdot + \text{L}''\cdot \qquad \text{(radical formation)}$$

or it may undergo a bimolecular collision with an electron or hydrogen donor RH:

$$\text{L–L} \rightarrow \text{L}'\cdot + \text{L}''\cdot$$

The imidazolyl radicals may recombine to form the starting dimer. Considering the rather large molecular weight of o-Cl-HABI (MWt. 660) or TCTM-HABI (MWt. 848) the bulky radicals may not move much in a viscous medium and show a tendency to recombine. This ability to recombine is responsible for the stability of HABI based imaging systems.

$$\text{L}'\cdot + \text{L}''\cdot \rightarrow \text{L–L}$$

$$\text{L–L}^* + \text{RH} \rightarrow \text{LH}\cdot + \text{R}\cdot$$

In an efficient photopolymerization system, the excited photoinitiator L–L* must be sufficiently energetic and long-lived to decompose spontaneously or to interact with a second component to produce the active free radicals. Once formed, the free radical R· (here the imidazolyl radical L· reacts with the chain transfer agent, e.g., 2-mercaptobenzoxazole, the monomer M as in thermal polymerization, undergoing propagation, chain transfer, and termination steps:

$$\text{R}\cdot + n\text{M} \rightarrow \text{RM}\cdot + \text{M}_{n-1} \rightarrow \text{RM}_n\cdot \qquad \text{(propagation)}$$

$$\text{RM}_n\cdot + \text{RH} \rightarrow \text{RM}_n\text{H} + \text{R}\cdot \qquad \text{(chain transfer)}$$

$$2\text{RM}_n\cdot \rightarrow \text{polymer} \qquad \text{(termination)}$$

Termination of the growing polymer chain $\text{RM}_n\cdot$ may also occur by reaction with oxygen or other inhibitors:

$$\text{RM}_n\cdot + \text{O}_2 \rightarrow \text{RM}_n\text{OO}\cdot \qquad \text{(inactive radical)}$$

$$\text{RM}_n\cdot + \text{inhibitor} \rightarrow \text{inactive products}$$

Each of these reactions takes place will a certain rate of efficiency. The rate constants in the equations above refer to radical termination, initiation, propagation, and termination. Assuming steady-stale radical concentration, the rate equal is $R_\text{p} = k_\text{p}[\text{M}](R_\text{i}/2k_\text{t})^{1/2}$, where R_i is the rate of initiation and k_t is the rate constant for termination, independent of mechanism.

For photoinitiations the rate of initiation is $R_\text{i} = 2\text{Ø}I_\text{a}$, where Ø is the quantum efficiency for initiation and I_a is the intensity of absorbed light. At low levels of absorbance:

$$R_\text{p} = k_\text{p}[\text{M}]\{2.3\text{Ø}\varepsilon I_0 d/k_\text{t}\}^{1/2},$$

where ε is the molar extinction coefficient at, I_0 the incident intensity and d the thickness of the sample. The extent of polymerization depends on the balance of the desired propagation reaction and termination of the initiation reactions.

In practical photopolymer systems, depending on absorbance, the rate of polymerization can very greatly across the thickness of the sample. It has been shown mathematically, and confirmed experimentally that uniform polymerization rate through the sample occurs up to a molar extinction coefficient of 0.43, where maximum response occurs. At higher values of ε surface polymerization occurs (Thommes and Webers, J. Imag. Sci. 29, 112–116 (1983)).

In practical polymer systems the readout efficiency of the overall reaction depends on three other factors: (1) the extent to which physical properties of the photopolymer composition are changed during conversion of monomer to polymer, (2) the ability of the image development system to discriminate these changes in properties; and (3) the sensitivity of the process of use to detect these changes.

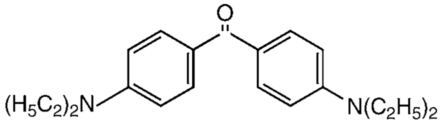
An examination of the reasons for the wide acceptance of HABIs as a photoinitiator of choice in free radical polymerization, one can list the following attributes:

(1) Excellent pre-image life in the coating formulations, i.e., no or little premature polymerization initiation. This may well be because the very large dimer molecule is not very mobile in the coating matrix, and if some cleavage occurs, the formed radicals may recombine. Naturally, the choice of proper substituent in the 2-*o*-phenyl position influences this.

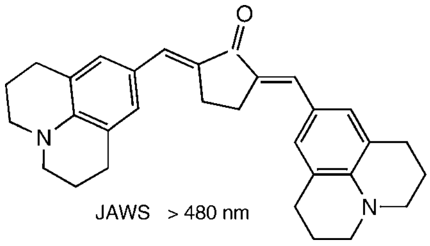
(2) The absorption spectrum of HABIs can be shifted by modification in the structure. It is remarkable that some 40 years after the discovery of o-Cl-HABI, this compound is still the preferred photoinitiator. Whether this is due to the economics of manufacture, or due to the lack of enthusiasm of synthetic chemists to develop new compounds because of the environmental issues associated with introduction of new compounds is unclear. The desirability of having a less yellow background in certain imaging applications, as well as the desirability of not having halogens in coatings that need to be combusted has resulted in incorporation of certain o-alkoxy-HABIs, rather than o-Cl-HABIs in coating recipes. HABIs can be sensitized by a large number of sensitizing dyes, as can be seen from the many patents that describe this phenomenon.

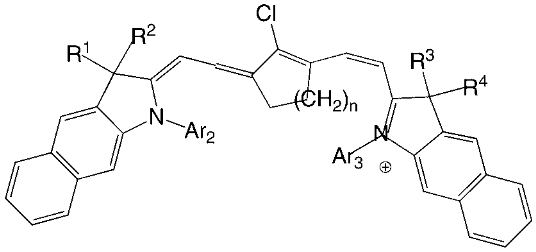
(3) Hexaarylbiimidazole-based initiator systems, which are sensitive to visible light, have been developed for laser imaging and other radiation sources with high visible emission. The sensitization reaches out into the near infrared. In the development of an infrared initiated imaging system, it was found that more effective oxidation of a leucodye resulted when a somewhat less thermally stable HABI was used instead of conventional HABIs. This raised the question as to whether the HABI was cleaved by energy transfer from the sensitizing dye, or whether the localized heating, resulting from absorption of the NIR energy was the cause for the radical formation.

Typical HABI sensitizing dyes:



MICHLER'S KETONE 360 nm



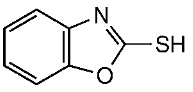


NEAR IR DYE (U.S. 5,995, 224)

(4) The formed HABI radical has remarkable half-life, depending on the structural modifications. This is illustrated in detail in U.S. 4,252,887, describing the utility of dimers derived from unsymmetrical 2,4,5-triphenylimidazole compounds as photoinitiators. It is likely that this extended radical life allows the radical to be more selective in finding the preferred coinitiator, which ultimately initiates the polymerization reaction.

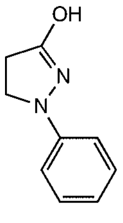
(5) HABIs are not oxygen sensitive.

(6) HABIs themselves do not initiate polymerization. An aromatic *t*-amine, or preferably a mercaptobenzoxazole or benzthiazole is a preferred coinitiator.



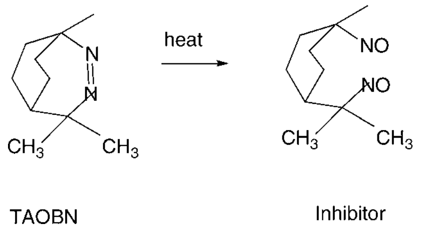
MERCAPTOBENZOXAZOLE

(7) Inhibition of HABIs is performed efficiently with a wide variety of compounds. Commonly used are phenols, but the most efficient inhibitor found was 3-phenylpyrazolidinone (phenidone). This inhibition in certain coating formulations minimizes halation effects.

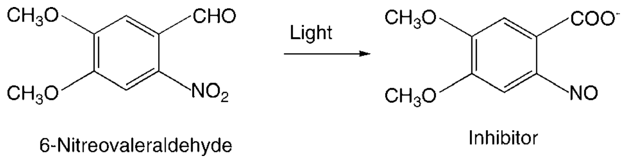


PHENIDONE

(8) Thermal inhibitors that work well with HABIs were discovered in the 1970s (U.S. 4,168,982); preferred is a nitroso dimer.



(9) Photoinhibition of HABIs, to prevent photooxidation was illustrated early by Maclachlan et al. More recently, Pazos and Nacci et al. identified additional chemistry, which permitted selective reduction of HABIs by a visible light exposure, so as to allow subsequent UV exposure to initiate to produce a subsequent polymerizing exposure by a blanketing ultraviolet light source.



(10) Ability to combine a printout process (photooxidation of a leucodye) with a polymerization process has been a considerable advantage in letting the user of certain products observe that the samples have been properly exposed. Additionally operations where sequential exposures are required benefit from such printout images.

(11) The reduction product resulting from the interaction of HABIs with mercaptans is essentially colorless. Hence, unlike some other photoinitiators, HABI systems do not give rise to slight colored coatings.

(12) K. Maeda in *Processes in Photoreactive Polymers* [3] pointed out that in the majority of photocurable and photoimaging polymers, the initiator consumption during imaging is less than 10%. The remaining initiator can diffuse out of the imaged polymer or form a crystalline inclusion separating from the cured polymer. Because of the large size of the substituted HABI molecules and steric restrictions, HABI retains its isotropic distribution in the films after the imaging and does not cause undesired fogging (crystallite formation) of the polymer films.

So what is wrong with HABIs?

HABIs are readily manufactured from accessible starting materials. The biimidazoles in general possess some level of thermochromism, i.e., radicals are formed at elevated temperatures. This has restricted the use of these photoinitiators in certain applications, e.g., where extrusion technology, rather than solvent coating is the manufacturing process.

9.3 INDUSTRIAL PHOTOPOLYMER TECHNOLOGY

Applications of industrial photopolymer technology can be divided into two general classifications based on the exposure mode of the applied radiation.

The two exposure modes are imaging, where the photopolymer material is exposed in a "pattern-wise" process, and non-imaging, where the photopolymer is given an "overall" or non-pattern exposure. Many of the high "value-in-use" applications are in an imaging category (e.g. film and liquid resists, printing plates) while the largest worldwide applications for photopolymer-based products are in a non-imaging classification (e.g. photosensitive protective and decorative coatings, adhesives, sealants). In the former, hexaarylbiimidazoles have played an important role, due to their unique properties and versatility. In the non-imaging applications, the relatively high cost of HABIs vs. simpler systems has restricted their usage.

Photopolymerization involves the reactions of a photoinitiator with a monomer to produce a polymeric material. In free radical initiated systems of acrylate monomers, the presence of oxygen in the system results in some sort of inhibition or termination, as the peroxide formed prevents propagation of the polymerization reaction. The inflow of oxygen is reduced or eliminated by superimposition of a cover sheet over the photosensitive layer. In some instances, conditioning to exchange the oxygen present in the coating with an inert gas, e.g., nitrogen. In other instances, additives that act as oxygen scavengers are incorporated in the coating layer. However, the oxygen inhibition effect also has a positive aspect in that it prevents premature polymerization during storage. The polymerization causes a change in the coating composition that may result in a significant property alteration, such as change in

- Solubility—printing plates, resists, filters, displays.
- Adhesion—proofing products.
- Phase change—wave guides.
- Change in refractive index—holographic films.
- Change in electrical conductivity—xeroprinting films.

9.4 APPLICATIONS

In their extensive chapter on *Polymer Imaging in Neblettes Photoimaging Materials* [2], Cohen and Walker described many aspects of this technology as applied to image forming systems. This chapter did not devote a great deal of space to the actual chemistry involved, but rather dealt with all the technical development that occurred in the field in the period up to 1989. The authors reviewed many of the implications of research carried out over a 20-year period by DuPont colleagues. During this period, hexaarylbiimidazoles became a valuable component of the products manufactured by DuPont, as shown by the extensive patent estate that was developed.

Two photopolymer developments, RISTON® photoresists and CROMALIN® proofing products proved to be immediate consumers for the novel photoinitiators. Historically, there was a fortunate coincidence. The DuPont Organic Chemicals Department, which funded research, which lead to the DYLUX® Instant Access Imaging system, developed hexaarylbiimidazole chemistry and was seeking to expand the market for these as photoinitiators. Photo Products Department was looking for novel opportunities in the field of photopolymerization, and quickly realized that incorporating these new photoinitiators gave rise to stable precoated products [4].

How did these developments come about? A research manager, D.E. Woodward asserted that DuPont's solid photopolymer compositions might be used to make printed circuits for incorporation in all kinds of electrical devices. At that time, a Kodak system employing a liquid photoresist had been used for several years. Before this technology became available, coarse printed circuits had been prepared by printing chemically resistant patterns on copper and etching away the unprotected metal. In the Kodak process, which was basically similar to the one that DuPont developed, a liquid photoresists was applied over a copper and plastics laminate; after the liquid dried, a template or negative of the circuit was laid over the composite and exposed to ultraviolet light, which initiated chemical reactions that made the photopolymer in the circuit areas insoluble. Next, a solvent was used to wash out the unexposed polymer, leaving a circuit pattern defined by the resist. Finally, the unprotected area was etched away and the photoresist removed, leaving a copper printed circuit. As had been the case with DYCRIL® printing plates. Woodward believed that a solid film would be easier to use than the existing liquid system. Initially, the market for printed circuits also did not appear to be large or rapidly growing. But subsequent developments would prove these assumptions false.

The research division had been working for some time on a proofing system for high quality color reproductions. Color graphics in magazines and other printed material are made by printing four separate images, each a different color. The photographic films used to make these images are black and white but have been sensitized for a particular color—red, yellow, blue, or white. The only method to determine what the final photograph would look like was to prepare printing plates from the photographic films and run a test picture. High-quality reproductions, which most advertisers and many magazines demanded, usually required several iterations of the process in order to balance the colors properly so that, for instance, a model's skin color had the wrong shade. Each time the original photographs were touched up, a new set of plates had to be made and tested. Overall, the proofing process was time-consuming and expensive. In the early 1960s, 3M introduced its Color Key system employing four separate single color films, which required wet processing in order to remove the unexposed coating.

DuPont developed a precolored foil product, CROMACHECK®, that could be exposed and peeled apart to yield separate colored imaged films that could be overlaid, without any processing. Additionally, a surprint material, which allowed colored layers to be formed on top of each other and more accurately, simulated the ultimate print.

The novelty was derived from the fact that these unique materials possessed considerably better dark stability than those made with earlier commercially available photoinitiators. This made it possible to produce photosensitive films that had excellent pre-image shelf life. This property is of course critical in commercial products, as the amount of time between manufacture and usage can stretch over a period of anywhere from three to 24 months or more.

REFERENCES

[1] Imaging Processes and Materials, Nebeltte's eighth edition, Van Nostrand Reinhold, 1989, p. 231.

[2] Imaging Processes and Materials, Nebeltte's eighth edition, Van Nostrand Reinhold, 1989, p. 226.

[3] Processes in Photoreactive Polymers, Krongauz and Trifunac (Eds.). Chapman Hall, a Division of International Thompson Publishing Co., 1995, p. 231.

[4] Science and Corporate Strategy, DuPont R&D, 1902–1980, by Hounshell and Smith, 1988. Cambridge University Press, 1989, p. 549.

10

HABIS IN COLOR PROOFING SYSTEMS

A number of different products are used to establish the ultimate quality of printed documents prior to a printing run. As printing presses run at high speeds and produce many impressions in a short time, it is desirable to establish the quality of the printing plates prior to the run. At one time, this had to be done with proof presses, which required mounting the plates, inking them, and generating a few paper copies. Modern technology has been developed to allow careful analysis of the lithographic negative from which the plates are generated.

This may be done with color overlay systems, which offer a quick assessment. These were the first color proofing systems—precolored films, which could be exposed to corresponding color separation films and developed in a solvent to give appropriately colored proofs. By superimposing four colored transparencies in register the printer could check color balance and other quality control parameters.

Where quality color work is replicated on the printing press, it is essential to establish that the different plates used in offset lithography are of adequate quality, free of defects that may have been caused by pin holes in the negative, overexposure of the separation negatives, etc. This verification process begins with a careful examination of the photographic negative. DuPont offered several systems to "proof" the lithographic negative.

10.1 COLOR OVERLAY SYSTEMS

The process of transforming a multicolor original into an accurate and pleasing color reproduction involves a series of complex manipulations: conversion of continuous tones into halftones: separation of multicolor images into individual films for the three primary colors and black; and adjustment of color balance and composition. Prepress color proofing systems make it possible to check accuracy of these transformations without the high cost and time delay of on-press proofing.

The first color proofing systems were precolored films, which could be exposed to corresponding color separation films and developed in a solvent to give appropriately colored proofs. By superimposing four colored transparencies in register the printer is able to check color balance and other quality control parameters.

CROMACHECK®, a totally dry overlay negative proofing system, introduced by DuPont in the 1980s, produces color overlay proofs instantly alter exposure by simply peeling off the cover film. CROMALIN®, a product that is used to make surprints ("overprints" that are deposited on a paper substrate) was introduced in the 1970s.

Color overlays can be made quickly, but are only suitable for internal quality control because of grayed whites and highlight tints caused by internal reflection between films.

Table 10.1. Coating recipes

Ingredients amount (%)	Yellow	Magenta	Cyan	Black
Pigment	9.00	8.93	4.37	11.18
Polymethylmethacrylate	39.38	37.17	44.80	38.99
Polymethylmethacrylate/ 2-ethylhexylacrylate (63/37)	2.25	4.53	1.46	9.59
Methacrylated epoxy adduct of bisphenol A (epichlorohydrin, methacrylic acid)	39.85	39.85	39.85	37.17
(2-*o*-Chlorophenyl-4,5-diphenylimidazolyl) dimer	3.00	3.00	3.00	2.65
2-Mercaptobenzoxazole	1.72	1.72	1.72	1.72
4,4′-Diethylaminobenzophenone	2.00	2.00	2.00	2.00
Brightener	2.00	2.00	2.00	2.00
Poly(ethylene oxide)	0.70	0.70	0.70	0.70
Fluorad® FC430, liquid nonionic surfactant	0.10	0.10	0.10	0.10

CROMACHECK® consists essentially of the above system. This, and related materials are disclosed in U.S. Pat. Nos. 4,489,153 and earlier patents. Each color sheet is imagewise exposed through the appropriate color separation and peeled to give cyan, magenta, yellow and black images on separate supports, which are then overlaid in register to give a non-critical proof. The peel apart elements generally comprise (in order) a strippable cover sheet, a photoadherent layer, a non-photosensitive tacky contiguous layer and a substrate.

> **U.S. 4,489,153. Process for Preparing a Positive Overlay.** Ashcraft, Robert W.; Moehlmann, Jon G. (E. I. Du Pont de Nemours and Company). December 18, 1984. Appl. December 22, 1983. Process for preparing a positive overlay using an imagewise exposed peel apart photosensitive element comprising a strippable cover sheet, photoadherent layer containing a colorant, a tacky, nonphotosensitive contiguous layer, and a support wherein after peeling apart the element bearing the contiguous layer and complementary colored unexposed areas is adhered to a transparent receptor, and the transparent and colored unexposed image adhered thereto are removed. By repeating the procedure with peel apart elements of different color and overlaying the images in register colored proofs are prepared.

Coating compositions for several different colored films are described in Table 10.1.

CROMACHECK® was made available in the standard process colors, as well as several other popular colors, metallics and whites. A colored layer is coated and laminated to tacky elastomer coating composition.

10.2 COLOR SURPRINT SYSTEMS

The concept of how the CROMALIN® system works is basically simple. A clear photopolymer is laminated to a sheet of receptor stock (a plain white piece of paper), and is exposed with a negative or positive image (depending upon the laminate type used). After exposure the top cover sheet of the laminate is pulled off to uncover the tonable surface. The areas that are to be toned are sticky and will accept whatever color powder toner is applied. If multiple colors are desired then the process is repeated:

Lamination
Exposure
Removal of cover sheet
Application of next toner.

Positive CROMALIN® is exposed from a positive film image. Wherever light strikes the laminate material it is hardened and will not accept toner.

Originally, positive CROMALIN® was used by both negative working and positive working shops. Since it was the only surprint proofing system on the market, people working with the negative format would contact the final negative image onto contact film to reverse the image to positive format so that it could be proofed. With the introduction of, and continued improvement of, negative CROMALIN® and other negative surprint proofing systems the market has been gradually changing over to negative surprint proofing. A large part of the publication industry still uses positive acting printing plates; therefore, there is still a great need for positive surprint proofing. Equipment used in the CROMALIN® system described below are the five main pieces of equipment used in the CROMALIN® system. Laminator: the photopolymer layer is applied to the receptor stock through heat and pressure. The basic requirements for the laminator have not changed since CROMALIN®'s introduction, but a new laminator was introduced in 1988, with improved heating and tension systems. Toning console: from 1972 to 1981 all toners were applied to CROMALIN® proofs by hand. Today some specialty color work is still done on the toning console, but most process color toning is done through an automatic toning machine. In the 1990s, a colored frangible foil was offered as part of the EUROSPRINT system. These foils were available in the process colors and speeded up the proof preparation greatly. The system is described in U.S. 4,806,451.

> **U.S. 4,806,451. Process for the Production of Multicolor Proofs Using Precolored Toning Films.** Frohlich, Helmut H. (E. I. Du Pont de Nemours and Company). February 21, 1989. The invention relates to a process for producing an image on a light-sensitive tonable layer comprising the steps of: (A) exposing the light-sensitive layer imagewise to produce imagewise tacky and complementary non-tacky areas; (B) bringing the imagewise-exposed layer into surface-to-surface contact with a supported non-photosensitive transfer layer containing at least one finely divided powder and/or a dissolved dye in a binder; and (C) separating the transfer layer from the light-sensitive layer, whereby the transfer layer adheres selectively to the imagewise tacky areas, the improvement wherein, the binder of the transfer layer consists essentially of (a) about 55–97 wt. % of at least one polymer in the form of a powder having a minimum film-forming temperature of above 50°C., and (b) about 3–45 wt. % of at least one thermoplastic and/or one thermoplastic-elastomeric polymer, having a minimum film-forming temperature when used as a latex, or, a glass transition temperature when used as a dissolved polymer, which is at least 10°C. lower than the minimum film-forming temperature of polymer (a), whereby polymer phases (a) and (b) are incompatible.

Positive CROMALIN® is described in the following patents.

> **U.S. 4,356,253. Photoimaging Process for Forming Multicolor Images.** Buzzell, John G. (E. I. Du Pont de Nemours and Company). October 26, 1982. Appl. December 12, 1980. Improved process for forming multicolor proofs by laminating to a receptor a positive-working photopolymer element having an electrical discharge treated polyethylene terephthalate support bearing a photopolymerizable layer containing a monomeric component of or mixture of monomeric components as defined; a compatible polymeric acrylate binder and optionally a polyvinyl acetate binder, the weight ratio of polyvinyl acetate to acrylate binder being less than 4 to 3, and an initiator or initiator system; exposing the layer imagewise; removing the support, applying and distributing colorant, removing the colorant in the exposed areas and repeating the steps at least once with another photopolymer element, the lamination being to the previously laminated element.

> **U.S. 4,734,356. Positive-Working Color Proofing Film and Process.** Bauer, Richard D.; Buzzell, John G.; Koenigkramer, Rusty E. (E. I. Du Pont de Nemours and Company). March 29, 1988. Appl. April 30, 1986. Photopolymer positive surprint color proofing film based on epoxy acrylate monomer exhibits low dot gain, low time dependence of toning and good tonal range. Binder can be methylmethacrylate/ethyl acrylate/acrylic acid copolymer, preferably crosslinked with zinc ions and plasticized with a second acrylate monomer and a mixture of triacetin and trimethylol propane.

Table 10.2. Comparison of positive and negative CROMALIN® recipes

Patent number CROMALIN® type Ingredient	4,734,356 Positive % solids	4,247,619 Negative % solids
Poly(methyl methacrylate/methacrylic acid) (90/10)		50.79%
Polymethylmethacrylate	32.18%	
Polyoxyethylated trimethylolpropane triacrylate	7.72%	
Polyvinyl acetate	12.87%	
Trimethylolpropane trimethacrylate	36.04%	
Dipentaerythritol acrylate (50% tetra, 50% penta)		44.02%
Polyoxyethylene (4) lauryl ether	7.72%	
Hydroquinone	0.05%	
2-*o*-Chlorophenyl-4,5-bis(phenyl)imidazolyl dimer	1.54%	2.71%
2-Mercaptobenzoxazole	0.77%	
2-Mercaptobenzothiazole	0.01%	
7-(4′-Cl-6′-Et$_2$N-1′,3′,5′-triazine-4′-yl)amino-3-phenylcoumarin	1.03%	
2,2′-Dihydroxy-4-methoxybenzophenone	0.06%	0.01%
Optical brighteners		2.45%

Negative CROMALIN® was later introduced in 1977. Negative CROMALIN® is exposed through a negative film image. Wherever light strikes the laminate material it hardens a piece of the photopolymer. This hardened area is removed with the cover sheet to uncover a tonable area on the proof. DuPont color proofing—CROMALIN® consumable materials used in the CROMALIN® system laminate material. There are two types of light sensitive photopolymer laminate materials available, one to be exposed with positive images and the other with negative images. Topcoat is a second type of laminate available for the final layer on negative CROMALIN®. It is not light sensitive and will not tone. It acts as a protective layer for tone layers below, removes UV light and allows a matte or glossy surface finish. Toners: toners are colored powders that are available in different colors and intensities. They are chemically treated to work in the negative or positive system. There is also a distinction for hand or machine toners. Toners are the heart of the CROMALIN® system's versatility. They allow the users to select virtually any printing color and match it on the proof.

> **U.S. 4,489,154. Process for Preparing a Surprint Proof.** Taylor, Jr., Harvey, W. (E. I. Du Pont de Nemours and Company). December 18, 1984. Appl. December 22, 1983. Process for preparing a surprint proof using an imagewise exposed peel apart photosensitive element comprising a strippable cover sheet, a photoadherent layer containing a colorant, a tacky nonphotosensitive contiguous layer, and a support wherein after peeling apart, if exposed through a separation negative, a positive colored photoadherent image on the cover sheet is adhered to a substrate, or, if exposed through a separation positive, a positive colored photoadherent image on the supported contiguous layer is adhered to a substrate. By repeating the process different colored layers can be built upon the substrate to form the surprint proof.

Negative CROMALIN® is described in the following patent.

> **U.S. 4,247,619. Negative-WorkingMultilayer Photosensitive Tonable Element.** Cohen, Abraham B.; Fan, Roxy N. (E. I. Du Pont de Nemours and Company). January 27, 1981. Appl. December 20, 1979. An improved peel apart photosensitive element comprises a strippable cover sheet, a photoadherent layer, and a tacky, non-photosensitive contiguous layer receptive to colorant or particulate

> material, and a support. The element is useful in applications such as color proofing. Such elements are capable of producing reverse toned or colored images as well as duplicate colored images with greatly improved tonal range and image fidelity. An overlay type negative-working proof was made in the following manner: I. Nontonable photoadherent layer: photopolymerizable coating composition. For the photoadherent layer a coating solution of a photopolymerizable composition was prepared by mixing together the following ingredients: the photosensitive layer was laminated to a coating of styrene–butadiene block copolymer (30/70) and highly stabilized glycerol ester resin of abietic acid.

Coating recipes of positive and negative CROMALIN® compositions are compared in Table 10.2.

11

ELECTROPHOTOGRAPHIC MASTER PROOFING (EMP)

11.1 HISTORICAL BACKGROUND

Electrophotographic master proofing is the story of a grandly conceived concept, which involved many scientists, a great deal of money and good research, but ultimately ended in failure. The reasons for this were not only technical, but had to do with the structure of partnerships between large companies, personnel shifts, changes in the market and other factors that had little to do with science. Here is an attempt to review the technical aspects of this development.

Proofing products of the early 1980s were unable to generate multiple copies. Technology that would generate multiple copies of proofs was therefore sought for next generation products. Proofing systems of the future were perceived to be imaged digitally, probably by visible-light emitting lasers (note: NIR-lasers were not considered during this period). In the early 1980s, these were primarily lasers that operated in the 400 to 550 nm range. The presence of sensitizing dyes in CROMALIN® and CROMACHECK® would result in products, which had a yellow component, which was unacceptable for a color-proofing system.

An extensive search for alternate technologies was undertaken, and ways of employing electrophotography were considered. Could DuPont, with a very limited background in electrophotography combine this with areas of expertise, such as silver photographic systems or photopolymeric systems? James Riesenfeld had shown in the 1970s, that a LYDEL® printing plate could be used as a master for electrophotography. His work, however, was ignored, but fortunately remembered by Dr. W. Bindloss some ten years later!

Dr. T.D. Smith, then Assistant Director of Research asked Dr. John Bierlein to initiate studies aimed at assessing different technologies. Contacts were made with companies that could possibly license applicable technology to DuPont. There were interactions between DuPont and Savin Industries, then in the electrophotographic copier field, who had manufactured printers, or had these manufactured for them by Ricoh Corp. In time, Savin lost their strong position in the field. Savin, however, had made contacts with Indigo, an Israeli company, which was working intensively on liquid electrostatic toners.

Bierlein asked me to examine routes to applying electrophotography for making multiple proofs, using proprietary DuPont technology. Bindloss called my attention to Riesenfeld's work. I instructed my technician, Bill Ferguson to coat a mixture similar to the one used to make LYDEL® plates onto aluminized MYLAR®. The imagewise exposed coatings were charged and toned with toners obtained from Indigo in Israel. The toner was transferred to a paper substrate. This indicated that a polymerizable system on a flexible support could be used for xeroprinting.

11.2 EMP MASTERS

A literature search disclosed that Gil Ingersoll of DuPont had made some electrostatically active coatings (U.S. 3,286,025 (issued 11/15/66)) involving polymerization. At the time I demonstrated success with the aluminized polyester films, these patents had expired, and the question was whether we could get around this "prior art". Fortunately, Ingersoll had not had available our preferred initiator systems, involving HABI/co-initiators, which we found to be more effective in giving us the desired difference between conductive and dielectric properties.

In short order, we were able to demonstrate that we could sensitize the photoinitiator in these coatings, which would then allow us to capture images with longer wavelength light and tone the exposed areas after charging. The toner was transferred without imparting a yellow color to the resulting imaged paper.

The initial concept of how the system worked was that the polymerization of the coating changed the dielectric properties in that the charge would be retained on the exposed areas, and the charge dissipated rapidly in the unexposed areas. We thought that this might be due to impurities, which were trapped in the polymerized areas, but not in the unpolymerized areas. Using this concept as a model, we did in time seek more purified monomers, but could never really verify this.

After the initial success with the photopolymer system that I had formulated, Dr. Joy Hunter was assigned to make measurements of various compositions, which I had developed. These were primarily based on compositions of binders, acrylates or methacrylates, HABI photoinitiators and co-initiators. For purposes of broadening a potential patent application other additives were included.

A parallel effort (1984–1986) at Central Research Department, under sponsorship of Photo Products Department investigated the use of silver photographic materials, and it was shown the areas from which silver had been removed were more charge-retaining. This work was done by Drs. Allan Cairncross and Catharine T. Chang (U.S. 4,913,998 and U.S. 4,868,081). Although the CRD work offered potentially higher imaging speed, it required wet processing. This was considered undesirable conceptually, as a dry system was desired. Chang was then assigned to the polymer approach.

The initial successes with the silver and polymer systems stimulated considerable management activity toward establishing a relationship with INDIGO NV, which had licensed technology to Savin. In time, Savin offered licenses to Xerox Corp. for copier applications, Harris Intertype for printing applications, and DuPont for graphic arts applications, i.e., proofing. Later we considered that short-run printing would be a possible DuPont application.

In 1984 Dr. Alan S. Dubin was assigned to head the group, which then consisted of myself, Joy Hunter and Dr. Sandy Marcus, a physicist who was to assist us in making measurements. Parallel to that, the group then doing toner research, based on the Indigo work, was enlarged. This consisted of Drs. David Mitchell, Steve Schmidt, James Larson, Tom Felder, Lyla El-Sayed. After Joy Hunter was reassigned to a new position at CRD, Dr. Catherine Looney was hired as a consultant and was involved with measurement problems.

In 1984 the entire group working on this area was invited to Rochester, NY, to visit Savin Industries and meet Benzion Landa, the force/brains behind Indigo. It was Landa's belief that liquid electrostatic toners would yield improved image quality (density, resolution), and would make it easier to design machinery where multicolor imaging was required. He maintained that printing inks had always been liquid, and that dry powder printing, as in dry electrophotography, is essentially an aberration.

At that time, what was considered to be the Electronic Imaging arm of photoproducts was quartered at the Eagle Run site. In July 1984, Dr. John Bane returned from being R&D director at Neu Isenburg, Germany to manage the technical end of Electronic Imaging, under T.D. Smith. The Eagle Run group was expanded to include several engineers under Steve Toton and Dr. Harry R. Zwicker: Tom Kelmartin, Kerry Yura, Ben DuPont and physicists, Drs. Graciela Blanchet and Lawrence Cheung. The objective of their work was to quantify the work of the toner/master groups, and initiate some ideas on device design.

Initial work on masters was aimed at demonstrating that the concept that we were to call electrostatic master proofing (EMP) technology was viable. It was shown that coatings exposed through a silver lithographic negative with an ultraviolet light source could be used as xeroprinting masters without significant image degradation during repeated charging and toning cycles. Also we demonstrated that the system would work with sensitized coatings, which could be digitally imaged with a laser.

It was decided to show the results of our work at DuPont's exhibit at DRUPA 1986. Several 4-color proofs made by our "new" technologies were exhibited. At that show, Eastman Kodak introduced their SIGNATURE™ proofing system, which also aimed at making multiple proof copies. Sometime during this period, Phil Sweeter, formerly with GE headed the Electronic Imaging Organization. In November 1986, T.D. Smith announced his retirement. In November 1986 a meeting was held in Hilton Head Island, where a group from Xerox and one from DuPont interacted with the goal of forming a joint venture and to explore synergisms. Soon thereafter a contract was signed to have Xerox in Webster, NY design and build a proofing machine, which employed the photopolymer masters. This machine was to be demonstrated to selected would-be customers at Graph Expo 1987 (November) in Chicago.

In 1985 it became obvious that we would not progress with the program unless we could provide large size masters for imaging. The goal proofs were to be ca. 18″ × 24″, and it was decided to involve the Towanda R&D Laboratory at an early time so that we could manufacture coatings on a production coating line, capable of $>50''$ width. During the period between 1984 and 1985 we regularly employed the Towanda Pilot Coater to prepare 10″ wide coatings for the experimental test devices, which were being built at Eagle Run. We had made contact with Dunmore Corp., who provided us with quality aluminized MYLAR®. We obtained good co-operation from Sartomer Co. of West Chester who supplied monomers. Polysciences, Inc. provided us with a variety of binders. Towanda assigned Jim Williams to assist in scale up work and Barbara Booker to undertake ingredient analysis. An engineer, David Logrando was assigned to supervise the plant coatings, which were initiated some time in 1986.

At the outset of this work, the quality of the imaging materials was ahead of the devices employed. Gradually, as the latter improved, the flaws in the coated films became more evident, and required modifications. Our formulations underwent many changes as time went on. The preferred solvents for the liquid toners were various Isopar® liquids available from Exxon, and it was necessary that the compositions were Isopar-insoluble. I decided to include a leucodye so that we could visually observe the imaging process as it occurred. In time, Lawrence Cheung showed that the backtransfer, which occurred during the toning process, was reduced by the presence of the leucodye/dye system. Graciela Blanchet developed more sophisticated measuring devices and took over formulation work. She concluded that addition of triphenylamine improved imaging properties. Cathy Chang undertook component studies to develop systems less sensitive to temperature/humidity changes. Later on, Blanchet showed that addition of phenidone would improve image resolution. The various patents issued cited inventors Bindloss, Blanchet, Chang, Cheung, Dessauer, Dubin, Looney, Fincher and Riesenfeld).

The use of a silver-negative, to expose a master, in which the exposed, polymerized areas would accept toner, would lead to a negative-mode proof. This is what the U.S. market demanded. Europe and Asia required positive-mode proofs. Four ways were conceived for this to occur:

1. Employ the masters available from the system described and manipulate the electrical properties of the master (U.S. 4,911,999) to effect reversal of the toning process (Caruthers, Looney).
2. Produce a master in which the exposed areas would become conductive relative to the unexposed area.
3. Employ a two-exposure system, in which the initial, image-wise exposure would effect inhibition of a later polymerization, and subsequent blanket expose the master to UV: U.S. 4,859,551 (Kempf).
4. Form a cationic dye path by omitting the monomer of the system, and increase the concentration of leucodye, U.S. 5,043,237 (Kempf, Dessauer and Freilich).

All these systems were demonstrated satisfactorily and scaled up.

Additionally, in 1989 we prepared sensitized coatings, employing the improved formulations as these were developed plus sensitizing dyes, such as our proprietary JAWS and imaged these without an intervening master on a machine developed by Crosfield Electronics in England. The exposed images were then used to form 4-color images on our machines in Lionville. This work, however, was not patented.

Stability of masters was not found to be an issue, as the coversheet protected the system effectively, and the recipe(s) were sufficiently close to those of the stable CROMALIN® proofing film. Nevertheless effort to obtain enhanced performance were made and patents issued for a photohardenable electrostatic master containing a conductive sealant layer: U.S. 4,911,911 (Legere) and a polyolefin backside coating for photosensitive reproduction element, U.S. 5,139,905 (Legere).

U.S. 4.911,999. Electrostatic Master Containing Thiourea or Thioamide Electrostatic Decay Additive for High Speed Xeroprinting. Legere, Carolyn C. E. I. Du Pont de Nemours and Company. March 27, 1990. Filed: December 13, 1988. An improved electrostatic master is disclosed that contains a thiourea or thioamide electrostatic decay additive in a photopolymerizable composition of an ethylenically unsaturated monomer, an organic polymeric binder, and a photoinitiator system.

U.S. 5,139,905. Photohardenable Electrostatic Master Containing a Conductive Sealant Layer. Leger-Krongauz, Carolyn C. E. I. Du Pont Nemours and Company. August 18, 1992. Filed: October 9, 1990. A photohardenable electrostatic master comprising an electrically conductive substrate; a photohardenable layer, and a conductant sealant layer, the conductant being a thiourea or a thioamide present in an amount sufficient to control the discharge characteristics of the sealant layer. The master is particularly useful in the graphic arts field, especially in the area of color proofing wherein proof are prepared to simulate the images produced by printing.

11.3 DX IMAGING

The DuPont–Xerox partnership was inaugurated sometime late in 1987, and was terminated in 1991. It was located in Lionville, PA, and occupied a large part of a building which required significant modification before it could be used as a laboratory or manufacturing site.

The construction was completed some time in 1988. At its peak, DXI employed around 300 people. About 60 of these had come from DuPont, 30 from Xerox, and the remainder was hired for the new company. Its mission was to develop technology for graphic arts applications for DuPont and for office applications for Xerox. In all cases, the new technologies would employ electrostatic liquid toners, which were to be manufactured at DXI, and in time, a manufacturing line for toners was designed and built. DXI also was to undertake contract work for affiliated companies, e.g., Fuji Xerox.

DXI's technical efforts were primarily centered on the EMP proofing machines, and eight were built. One of these was demonstrated life at DRUPA in 1990 and evoked considerable interest. Another was installed in 1990 at a Beta-Site, Pioneer Printing in New York City.

The technical work on the proofing program was divided into three groups;

1. A chemical division, headed by Dubin was primarily involved with developing a line of liquid toners and in coordinating preparation and evaluation of the film masters,
2. A process group under Harry Long undertook optimization of the imaging process,
3. A machine design group under Steve Toton, which had responsibility of producing the imaging machines.

There was good cooperation between the groups. The development of the masters for the process was under the leadership of Dr. Chris Hipp at DuPont and consisted of Blanchet, Chang and Kempf. R. Dessauer was liaison between Towanda and DXI, participated in patent work on the master and in an interference action by Olin. Additionally, Dessauer and Legere worked on a next generation visible light sensitive imaging masters, and initiated work on evaluating paper properties.

A lesser effort was directed at a copier working with liquid toners under the direction of J. Osterhut.

The major chemical effort at DX-Imaging was aimed at the invention and production of liquid electrostatic toners. It had been assumed that the Indigo technology, which DuPont acquired, was further advanced than it was, and thus a considerable effort had to be expended here.

One of the goals of the proofing machine was that it would work with any paper base, which the printer chose. This was a requirement that was difficult to meet; it should have been recognized that ordinary black/white electrostatic copiers, which have far less stringent requirements than to produce a high quality print, require special paper stock to maximize performance. As a result, image quality differed significantly on various paper stocks, and the system had to be optimized around several of the common proofing paper stocks.

11.4 MACHINE DESIGN

One basic problem inherent to the design of the first proofing machine by Xerox in 1987 was that it incorporated much of what Xerox had learned about building copiers—design a drum on which the masters would be mounted, and produce images therefrom. With selenium drums, as were components of the first Xerox copiers, this gave a right-reading image, as the light reflected from the originals would discharge the charged areas of the drum. Unfortunately, when the exposed masters were toned and transfer made, the resulting image was inverted. In offset lithography, this problem is resolved by the inclusion of a "blanket", i.e., another drum, which serve to "reverse" the image. In time, DXI designed an imaging station, in which the negative was imaged through the base to solve this problem. This, however, required that the master on imaging had to possess improved resolution.

As the imaging machinery improved, the flaws in the master's base material became more obvious. Slight variations in base thickness resulted in undesired print quality. Initially it was hoped to resolve this by employing "better" polyester base; the center cut of master rolls gave more uniform base. Still later, CRONAR® was selected as an improved base material.

11.5 TECHNICAL WORK

The following is a summary of the technical work relating to the xeroprinting masters.

It was found that the conductivity of unpolymerized areas of coatings on a metalized film bas was conductive relative to the exposed areas. The exact reason for this conductivity was not clear. Nevertheless, exposed coatings could be charged and after the charge leaked through the unexposed areas, charged toner could be applied; the toner adhered to the dielectric areas. Transfer of the toner to paper from the toned master gave high-resolution images.

> **U.S. 4,732,831. Xeroprinting with Photopolymer Master.** Riesenfeld, James; Bindloss, William; Blanchet, Graciella; Dessauer, Rolf; Dubin, Alan S. (E. I. Du Pont de Nemours and Company). March 22, 1988 (Cl. 430/49; 430/126). Xeroprinting process involving imagewise exposing a photopolymer master, charging on a conductive support, toning with dry or liquid electrostatic toner, and transferring to another surface. Photopolymer systems comprising preferred combinations of polymeric binders, ethylenically unsaturated monomers, HABI initiators and chain transfer agents. Appl. June 1, 1987.

When a triphenylmethane leucodye was incorporated in the coating, the exposed area became colored, giving some indication of the exposure. Additionally, the photohardenable electrostatic master had improved charge decay and back transfer.

> **U.S. 4,818,660. Photohardenable Electrostatic Master Having Improved Back Transfer and Charge Decay.** Blanchet-Fincher, Graciela B.; Fincher, Jr., Curtis R.; Cheung, Lawrence K.-F.; Dessauer, Rolf; Looney, Catharine E. November 4, 1987. Cl. 430/281.1; 430/283.1; 430/287.1; 430/915. Photohardenable electrostatic master comprising an electrically conductive substrate, e.g., aluminized polyethylene terephthalate, bearing a layer of a photopolymer comprising an organic polymeric binder, compound having at least one ethylenically unsaturated group, photoinitiator, an aromatic amino compound, as defined, and an acid, e.g., p-toluene sulfonic acid, or an oxidized substituted aromatic amino compound. The photohardenable electrostatic master having improved charge decay and back transfer is used for electrostatic proofing, etc. Appl. November 4, 1987.

It was then found that certain additives, e.g., triphenylamine, improved charge decay characteristics.

> **U.S. 4,849,314. Photohardenable Electrostatic Master Containing Electron Acceptor or Donor.** Blanchet-Fincher, Graciela B.; Fincher, Jr., Curtis R. (E. I. Du Pont de Nemours and Company). July 18, 1989 (Cl. 430/49; 430/916). Appl. November 4, 1987. Photohardenable electrostatic master comprising an electrically conductive substrate, e.g., aluminized polyethylene terephthalate, bearing a layer of a photopolymer comprising an organic polymeric binder, compound having at least one ethylenically unsaturated group, photoinitiator and at least one organic electron acceptor or donor compound, e.g., the acceptor and donor having an oxidation potential of less than $+2.5$ eV and reduction potential larger than -3.0 eV, respectively. The photohardenable electrostatic master is used for electrostatic proofing, etc.

The coatings thus made showed too much variation in performance as a result of temperature and humidity changes. This was corrected by employing a mixture of polymeric binders.

U.S. 5,006,434. Photohardenable Electrostatic Element with Improved Environmental Latitude. Blanchet-Fincher, Graciela B.; Chang, Catherine T.; Fincher, Jr., Curtis R. (E. I. Du Pont de Nemours and Company). April 9, 1991. Cl. 430/49; 430/281.1 Appl. May 12, 1989. Photohardenable electrostatic master with improved environmental latitude comprising (1) an electrically conductive substrate, and (2) a layer of photohardenable composition consisting essentially of (a) at least two organic polymeric binder, at least one having a Tg greater than 80°C. and at least one having a Tg less than 70°C., (b) at least one monomeric compound having at least one ethylenically unsaturated group, and (c) a photoinitiator or photoinitiator system, the shift in transit time of the photohardenable layer in the range of 30% to relative humidity of 60% and 15.6°C. A xeroprinting process is described using the master. The master is used in graphic arts, color proofing which duplicates images produced by printing, preparation of printed circuit boards, resists, soldermasks, etc.

U.S. 5,064,740. Photohardenable Electrostatic Element with Improved Environmental Latitude. Blanchet-Fincher, Graciela B.; Chang, Catherine T.; Fincher, Jr., Curtis R. (E. I. Du Pont de Nemours and Company). November 12, 1991. Cl. 430/126; 430/49. Appl. December 3, 1990. Xeroprinting process comprising (A) exposing imagewise to actinic radiation a photohardenable electrostatic master comprising (1) an electrically conductive substrate, and (2) a layer of photohardenable composition consisting essentially of (a) at least two organic polymeric binders, at least one having a Tg greater than 80°C. and at least one having a Tg less than 70°C., (b) at least one monomeric compound having at least one ethylenically unsaturated group, and (c) a photoinitiator or photoinitiator system, the shift in transit time ($a._T$) of the photohardenable layer in the range of 30–60% relative humidity and 15.6–27°C. temperature (B) charging the photohardenable master electrostatically, (C) applying an oppositely charged electrostatic toner, and (D) transferring the toned image to a receptor surface. The xeroprinting process uses the master in graphic arts, color proofing which duplicates images produced by printing, preparation of printed circuit boards, resists, soldermasks, etc.

Improvement in resolution was observed when limited amounts of certain inhibitors, for example phenidone were incorporated in the coating recipe.

U.S. 5,043,237. Inhibitor-Containing Photohardenable Electrostatic Master Compositions Having Improved Resolution. Blanchet-Fincher, Graciela B.; Chang, Catherine Teh-Lin (E. I. du Pont de Nemours and Company). August 27, 1991. Cl. 430/49; 430/43; 430/281.1. Appl. January 12, 1990. Photohardenable electrostatic master with improved environmental latitude and dot shape comprising (1) an electrically conductive substrate, and coated thereon (2) a layer of photohardenable composition having a speed that requires an exposure energy in the range of 3 to 90 mjoules/sq. cm. consisting essentially of (a) at least two incompatible organic polymeric binders, (b) at least one monomeric compound having at least ethylenically unsaturated group, and (c) a photoinitiator or photoinitiator system that activates polymerization of the ethylenically unsaturated monomer upon exposure to actinic radiation, (d) a chain transfer agent, and (e) at least one polymerization inhibitor in an amount of at least 0.1% by weight based on the total weight of photohardenable composition. A xeroprinting process is described using the master. The master is used in graphic arts, color proofing which duplicates images produced by printing, preparation of printed circuit boards, resists, soldermasks, etc.

The system involving photopolymerization as the image-forming step gave rise to positive working imagery. For the domestic American market a negative working system was desired. One approach was to make use of chemistry that had been developed during other programs; using a distinct absorption band imagewise to form an inhibitor, followed by an overall blanketing exposure to form polymer in the unexposed areas. This thus yielded negative mode images.

U.S. 4,859,551. Process for Preparing Positive and Negative Images Using Photohardenable Electrostatic Master. Kempf, Richard J. (E. I. Du Pont de Nemours and Company). August 22, 1989. Cl. 430/49; 430/291; 430/306; 430/309. Appl. November 4, 1987. Process for producing negative or positive images from a photohardenable electrostatic master comprising an electrically conductive

> substrate bearing a photohardenable layer containing a photoinhibitor and a visible light sensitizer wherein the negative image (1) is prepared by (a) imagewise exposing to visible radiation, (b) charging electrostatically the master, (c) developing the charged image with an electrostatic toner, e.g., liquid electrostatic developer, and (d) transferring the toner image to a surface, e.g., paper. The positive image (2) is prepared by (a) imagewise exposing to ultraviolet radiation. (b) exposing overall to visible radiation followed by steps (b), (c) and (d) above. Multiple images can be prepared from the same master as well as color proofs using different color toners or developers and transferring in register over the original image.

Another route to a negative working master made use of a difference in conductivity resulting from the formation of a cationic dye by exposure of a HABI-leucodye system. By proper selection of binder and the HABI/leucodye system, conductive paths could be photolytically formed.

> **U.S. 4,945,020. Photosensitive Leuco Dye Containing Electrostatic Master with Printout Image.** Kempf, Richard J.; Dessauer, Rolf; Freilich, Steven C. (E. I. Du Pont de Nemours and Company). July 31, 1990 (Cl. 430/49; 430/56; 430/73; 430/76). Appl. June 30, 1989. High resolution, photosensitive electrostatic master which is positive-working with a single imagewise exposure comprising a conductive support bearing a layer of a photosensitive composition consisting essentially of (A) at least one polymeric binder, (B) a hexaarylbiimidazole photooxidant, (C) leuco dye, preferably stabilized, oxidized by (B), (D) a nonionic halogenated compound, preferably a hydrocarbon, and (E) compatible plasticizer. A process of making positive images by a single imagewise exposure is described. The master is useful in making proofs that duplicate the image achieved by printing, etc.

The humidity/temperature sensitivity of the master could be controlled by careful selection of mixtures of binders with specified T_g's.

> **U.S. 5,145,760. Positive-Working Photosensitive Electrostatic Master with Improved Environmental Latitude.** Blanchet-Fincher, Graciela B.; Chang, Catherine T.; Kempf, Richard J. (E. I. Du Pont de Nemours and Company). September 8, 1990 (Cl. 430/73; 430/49; 430/56; 430/76; 430/96; 430/343). Appl. October 26, 1990. High resolution, photosensitive electrostatic master which is positive-working with a single imagewise exposure comprising a conductive support bearing a layer of a photosensitive composition consisting essentially of (a) at least two polymeric binders, at least one binder having a Tg greater than 80°C. and at least one binder having a Tg of 70°C. or less such that the shift in transit time ($a._T$) of the photosensitive layer in the range of 30% relative humidity 60% and 65°F (18.3°C.) to 80°F (26.7°C.) is 10 or less, (b) a hexaarylbiimidazole photooxidant, (c) leuco dye, preferably stabilized, oxidized by (b), (d) a nonionic halogenated compound, preferably a hydrocarbon, and (e) at least one compatible plasticizer. A process of making positive images by a single imagewise exposure is described. The master is useful in making proofs that duplicate the image achieved by printing, and manufacture of printed circuit boards, etc.

11.6 THE END OF DX-IMAGING

DXI announced its closing on January 15, 2001, and the facilities were officially closed on March 15, 2001.

Several reasons were offered for the demise of DX Imaging.

Possibly, the desire to build so complex a machine in so short a time was overly ambitious. Most of the people working at DXI believed that another year would have been sufficient economically to resolve the remaining problems. However, as the machines were continually improved, parts could only be ordered from outside vendors in limited quantities thus driving up their price significantly.

Cost: the machines were initially assumed to cost $200K, but in late 1990 it looked as though $300,000 would be more realistic. In the author's opinion, the machine cost was irrelevant, as the money would be earned from the consumables, which could be produced at a reasonable price. The master's had low mill cost, and required no modification in the Towanda plant's facilities, except acquisition of novel test devices. The liquid electrostatic toners could have been made on-site, or outsourced.

Several of the earlier supporters of the joint partnership, such as T.D. Smith, John Bane, etc. were no longer involved. Similarly, Xerox reassigned people. Additionally, a dispute as to when the proofing machines were "commercial" caused considerable animosity between the partners, who felt that they should jointly pay research costs, but not to improve commercially viable products.

Also, strategically, the proofing machines were aimed at satisfying the most difficult portion, the upper 10% of the market. Had the entry goal been set lower, it might have been attainable.

Rather, it was a number of business decisions, which were responsible for the closing. Initial funding of DXI was generous, but as annual funding by the partners was required, there was a factor, which had little to do with DXI performance, but rather that of DuPont and Xerox. The imaging business was no longer as profitable as before, and additionally, over-expansion of the department, with acquisitions of Crosfield Electronics, plate-making manufacturer Howson, Champion Paper coating facilities in Texas, etc., all became financial liabilities.

12

HABIS IN DUPONT PHOTOPOLYMER FILMS FOR THE ELECTRONICS INDUSTRY

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Until a few years ago, I had an old tube radio. The tubes were mounted in sockets that were affixed to a metal chassis which served as a way of holding everything in place and also as the common ground. Discrete wires, commonly called point to point wiring, electrically connected all components to one another. In addition to the tubes there were various condensers and resistors and a tuner and other components required to make the radio function. All the wires and components were electrically connected to one another by hand soldering. The first computers, for example the ENIAC developed at the University of Pennsylvania, which became operative in 1946, used 17,468 electronic vacuum tubes and was wired in the same way. In terms of processing speeds, the ENIAC was capable of performing 5000 additions per second or 300 multiplications per second… rates unheard of at that time. Obviously it was a monumental task to fabricate and maintain such a system. The invention of the transistor changed all that. Now a small solid-state device could perform the function of a tube. And that was only the beginning since even bigger changes came with the invention of the chip and the integrated circuit, commonly called the IC. While the transistor could perform the function of a single tube, ICs could perform the function of many tubes. Tubes had large physical size, which limited their proximity to one another. Transistors and ICs could be mounted much closer to one another. Some alternate way of making interconnections was required to take advantage of their large capacity to perform electronic function at 100 million additions per second and ever increasing. While it is beyond the scope of the section to chronicle the development of the printed wiring board (commonly called a printed circuit board or PCB), it became the way of the future for making the requisite interconnects among the various components in electronic devices.

The entire idea in developing a photoresist was to make a coating that could be applied to a copper surface, then to harden or change the solubility of selective areas of the coating by exposure to light imagewise using a photographic negative of the circuit traces. In the case of a hardening or polymerization, the exposed areas remained attached to the copper while a developing solvent or solution washed the unexposed areas away. The surface was now protected in selective areas against the action of some other chemical agent, a copper etchant. This was used to etch away the unwanted copper forming discrete copper circuit traces. Alternatively, the unprotected areas could be selectively electroplated to fabricate other types of PWBs using a different series of process steps. The thin copper layer bonded to a thicker non-conductive substrate, usually rigid, acted as the support.

Non-silver photosensitive materials had long been known using synthetics or colloids such as fish glue with a sensitizer. Kodak had much of the early PWB market with their KPR and KMER liquid resists based on polyvinyl cinnamate chemistry. These were the photoresists of choice in the early days, but under production conditions they were slow photographically and uniform coatings free of pinholes were difficult to achieve.

As the electronics industry was going through these periods of serious growth, it was clear there was a need for a technology for making high density and reliable PWBs. While the concept for a RISTON® photopolymer film resist type product may be obscure, during the 1960s the Development Department of DuPont held conferences with other large companies where DuPont would discuss various technologies and developments it had in progress. These companies would discuss their needs. So it may well have spawned from one of these interchanges.

DuPont had been investigating photopolymerization for some period of time, but the major break through came when Jack Celeste applied a test coating to a sheet of MYLAR® polyester film, dried it and laminated the combination to a copper substrate. It worked and the process became the basis of DuPont's proprietary patent position for using dry film resists to fabricate PWBs. Not only did the MYLAR® offer a perfect substrate on which uniform high quality, pin free coatings could be manufactured, it also provided a barrier layer against oxygen diffusion. Oxygen diffusion into the coating acts as an inhibitor to the polymerization process. Use of MYLAR® permitted higher tack coatings to enhance initial adhesion to copper and eliminated any unwanted sticking to other surfaces during exposure steps. Additionally it protected the thin coating against damage from physical abuse during these process steps.

One factor set RISTON® apart from the various HABI containing products that DuPont developed for the printing industry. In printing applications, a single printing plate could be used to make a very large number of finished printed copies. Thus one square foot of printing plate surface and one square foot of DYLUX® yielded many thousands of square feet of printed pages. In fabricating one square foot of copper PWB surface, one square foot of photoresist is consumed. If the circuit board has copper on two sides, then 2 square feet are consumed. So there is the one to one relationship of photoresist to PWB surface area plus the explosive growth in the electronics industry, which made the products in the RISTON® family so successful for DuPont.

The science of photopolymerization has been reviewed elsewhere and it is not the intent of this section to present any detailed discussion of that. Inventions aside, there are many practicalities that enter into the picture when developing a successful commercial product. While the above only skimmed the basic concept of a photoresist, the entire process and the various subtleties as well as market factors all had their effects on the various products that were developed for the market over time. And always there are many trade offs to be made. In formulating the various products that were marketed, often the performance for one important parameter comes at the expense of sacrificing performance in another important one. Commercial reality is that processes needed to be highly reliable and reproducible, free of problems, quick, inexpensive and have minimal health and environmental effects.

Compositionally the RISTON® films are composed of polymeric binders, which are the film formers, multifunctional acrylate monomers for their ability to rapidly polymerize and their low volatility, photoinitiators such as HABI (in combination with the leucodye tris(*p*-diethylamino-*o*-tolylmethane) and benzophenone—Michler's ketone that initiated the polymerization under the action of light, adhesion promoters to enhance adhesion to copper, thermal stabilizers, inhibitors to prevent polymerization from occurring prematurely or during product manufacture, plasticizers to impart flexibility, dyes to aid in identification and components including HABI to provide a DYLUX® type of print out image. Most films were coated to be 1–2 mils in thickness.

The basic RISTON® process requires a series of steps. For DuPont, it involves preparing a formulation and making a coating on wide stock rolls of MYLAR® film at a high rate of speed, carefully controlling thickness and drying. The film is laminated to a thin polyolefin film, typically polyethylene, prior to rolling up. Rolls are subsequently slit to a variety of widths for customer usage. Due to the softness of the coating, the cores are supported by end pieces so none was allowed to rest on its side. The customer starts with a purchased copper clad laminate material, typically fabricated from woven fiber glass mats embedded in an epoxy matrix to which thin copper sheets are thermally laminated in a press.

In the simplest process, called print and etch, the photoresist layer and MYLAR® are laminated to the cleaned copper surfaces and exposed in a contact printing mode in a vacuum frame using a photo tool. This is a name given to the silver halide or diazo negative of the circuit trace pattern. For print and etch, the circuit traces are transparent to UV light. Following exposure, the polyester cover sheet is removed and the panels run through a developing machine that sprays solvent or solution thus washing away the unpolymerized photoresist from the areas surrounding the circuit traces. The panel is then processed through an etching machine that sprays a copper etchant, most commonly cupric chloride solution, to etch away the unwanted copper. Then the resist is stripped—the polymerized resist is removed from the panel leaving a pattern of the desired circuitry in copper on the non-conductive epoxy surface.

Another common method of fabrication uses double sided plated through hole (DSPTH) technology. This requires first drilling holes in the laminate material followed by an electroless copper process in which a very thin copper coating is deposited on all surfaces including in the holes in order to achieve electrical conductivity between the circuitry on both sides of the board. Electroless copper is a chemical process for depositing metallic copper principally on non-metallic surfaces that have been catalyzed. These holes also function as mounting holes for most components. Following electroless, the panel is laminated with photoresist, typically 1.5–2.0 mils thick. It is then exposed imagewise as in the previous process, but now using the opposite mode of phototool in which the circuit traces are opaque. Development opens the channels in which the electroplated metal will be subsequently deposited. A several step cleaning process removes residual traces of photoresist and assures a firm bonding with subsequent electroplated metal. Copper is electroplated principally to increase the thickness of copper in the drilled holes so the plated barrel of copper can withstand subsequent molten solder temperatures without cracking. Then typically tin/lead solder was electroplated though lead free solders are now in use. Following stripping of the resist, the panel is run through a spray etching machine using initially chrome/sulfuric acid which was replaced by ammoniated etchants for environmental reasons. The solder plating itself acts a resist against this etchant thus protecting the copper in the holes and on the circuit traces. The unwanted copper is etched away leaving the discrete circuit traces and holes covered with a solderable coating.

These methods of fabrication are called subtractive since copper sheets, typically 1.4 mils thick, cover the entire panel at the start of the process. Most of that copper has to be etched away to get to the desired discrete circuitry. Several manufacturers employed fully additive plating in which the photoresist was applied to an epoxy surface, exposed and developed. The surface was then activated, catalyzed and plated with copper. This was an aggressive process and only the solvent processable photoresists could survive it.

Dry film photoresists have largely been used in high performance and high reliability applications. The largest markets for PWBs fabricated using RISTON® have traditionally been computers, telecommunications, aerospace and military.

While double sided circuit boards usually have the circuit traces running horizontally on one side and vertically on the other, even they quickly became limiting. With the ever-increasing need for higher densities, multilayer circuit boards came into prominence. Typically print and etch inner layers are prepared, placed in a sandwich with interposed epoxy sheets and placed in a press to make a single structure. The outer layers are then processed in a DSPTH process. The number of layers refers to the layers of circuitry. Very complex boards may have as many as 40–60 layers.

DuPont designed and manufactured various pieces of equipment necessary to operate or facilitate performing the basic photoresist processes. Some were specifically designed while others were modifications of existing equipment. Laminators capable of handling 24″ width used heat and pressure to laminate the RISTON® and MYLAR® to one sided or two sided substrates while winding the poly onto a core. Exposure units were fabricated in 24″ and 30″ widths having double vacuum drawers with top and bottom side mercury lamps capable of exposing both sides of the panels at the same time. These process steps as well as the developing process were performed in yellow rooms... referring to the type of lighting. To prevent unwanted polymerization from the UV or blue component of room light, gold fluorescent lamps were commonly used.

The first series of products developed and commercialized were the solvent processable resists called RISTON® I. A 24″ wide conveyorized spray developer was fabricated that used 1,1,1-trichloroethane (methyl chloroform) as the developing solvent. After development, the PWB panel was then ready for etching or electroplating. Following that, it was necessary to strip away the polymerized resist. Methylene chloride or azeotropes with methanol were the initial stripper chemistries and DuPont fabricated 24″ conveyorized equipment to perform that operation. The developer and stripper equipment both fabricated from stainless steel, required in-line solvent stills that would continuously feed a fresh supply of clean distillate solvent through a series of spray chambers and in a counter flow direction to that in which the boards were traveling. Smaller fabricators often stripped using a series of dip tanks.

This stainless steel equipment was costly and while it was widely adopted by the large captive houses and job shops, smaller fabricators needed a less expensive path. With that came developments in polymeric binder chemistry mainly by the Dynachem Corp., which led to semi-aqueous resists. These used much less costly plastic developing and stripping equipment and the processing chemistries were totally water-soluble. The developing solutions were based on Butyl Cellosolve® and borax while the stripper chemistry was either amines or caustic with other glycol ethers. These were called semi-aqueous resists and lead to the introduction of the Laminar® and RISTON® II series films. Further development in the area of polymeric binders, also by Dynachem, lead to fully aqueous films. These could be developed in much less costly sodium carbonate developer and stripped in caustic. These are the predominant films in commerce today.

The earliest formulations of RISTON® films did not use HABI as an ingredient, primarily because films based solely on HABI could not be easily stripped. HABI by itself was too efficient as a photoinitiator. So they were based on benzophenone–Michler's ketone (BP/MK). But as the subsequent processes became more chemically demanding on the resists, it was essential to incorporate HABI as a co-initiator together with the BP/MK. These led to more chemically resistant films that could still be readily stripped and remain to this day. As pointed out in a previous section, HABI by itself does not initiate polymerization upon irradiation but requires the presence of one or more coinitiators. These may be *t*-amines or heterocyclic mercaptans. The combination with TLA-454 as used in the color forming of DYLUX® was adopted. Later HABI was used by DuPont in combination with Leuco Crystal Violet to produce a visible printout image on exposure. This eliminated confusion in the fabrication process since yellow room operators sometimes mixed up racks of exposed and unexposed panels. The printout image became even more important when very expensive multilayer panels were being fabricated and inspectors could verify the image and registration to drilled holes before the panel was etched. If there was a problem, the film could be washed off, and the panel cleaned and laminated afresh thus reducing scrap. Incorporation of HABI also imparted brittleness to the exposed photopolymer. In some applications it is necessary to cover drilled holes with the polymerized photoresist to protect the plated barrels inside the hole against a given chemistry. Exposed resist is capable of reliably tenting over most drilled holes when the composition is carefully formulated to achieve this end result. However, if the HABI levels are too high, the polymerized film can shatter under the spray action required for developing or etching.

HABI differs from other photoinitiators because it imparts a faster photospeed to the resist film and also rapidly converts monomer to high polymer. The resultant higher degree of crosslinking in the polymer imparts greater chemical resistance in the subsequent chemical processing steps. But it is a bit of a balancing act. If HABI is the sole initiator, it gives rise to resist films that can not easily be stripped. So blends of HABI and BP/MK became most commonly used and the ratio of the two has to be carefully controlled. The processing speeds for developing and stripping also have to be roughly comparable using available equipment and chemistry. This became important with the dedicated develop-etch-strip lines used to manufacture innerlayers for multilayer panels. It was one of the various approaches to automating and simplifying many of the process steps. Automation was always being pursued and that involved a combination of equipment and special films formulated for such things as a peel apart system which could eliminate the need for a developing step and various in line systems. None proved commercially viable.

A smaller market segment exists for photoresists in the area of photo chemical machining (PCM) commonly called chemical milling. PCM technology is used to fabricate parts from a variety of metals as well as in decorative etching. Photoresists are laminated to carefully cleaned sheets of mostly thin metals, then exposed, developed and etched to give the pattern of a finished metal part. This technology competes against metal stamping where smoother edges are required or for parts too small and too thin to stamp. It also reduces the time and cost of fabricating a stamping dye. Some common parts made by this PCM include electric razor heads, small springs and parts and finely detailed jewelry. For example, in inexpensive filigree jewelry, a drawing is prepared of the finished part at 30–100× size. It is then photographed to near the actual finished size. Using step and repeat equipment typical of that used in the printing industry, multiple images are prepared on a single phototool. In that way, it is possible to fabricate many parts, dozens and up to hundreds from a single sheet of metal. Brass is most commonly used for decorative jewelry. Following etching and stripping, the parts can be electroplated with a thin layer of gold to make the jewelry most attractive. In PCM, a variety of substrates can be used including ferrous and non-ferrous metals, copper and brass alloys, and more exotic substrates such gold, silver, titanium, glass and others. Thick etching was shown on metal surfaces up to 62 mils thick, but much of that is done by laser cutting today. One side etching can be used to make such items as nameplates and large decorative panels where a change in surface texture from the etching process creates a visual image.

Obviously a successful product involves the efforts of many people not only in R&D, but manufacturing, sales, marketing, technical service and customer service. Additional people contributed in support areas such as legal, environmental and chemical safety. There are too many to name. Over the years from invention until the early 1990s when this writer retired, more than 600 people were directly assigned full time to the division in various capacities.

13

HABI PHOTOINITIATORS IN PHOTOPOLYMER FILMS DEVELOPED FOR HOLOGRAPHIC APPLICATIONS

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The advent of commercially available lasers in the late 1960's sparked research efforts at DuPont into many new areas. In one of the early successes of this effort, E.F. Haugh in 1972 patented a unique application for photopolymers, as holographic media [1].

Researchers at DuPont reasoned that differences in refractive index could be created on a submicron scale in dry photopolymer films, that such refractive index differences could function as diffraction gratings, and that lasers could be used to produce these structures. In initial experiments, photopolymers were exposed using lasers beams diffracted by commercial gratings, and polymerized structures in exposed photopolymers confirmed that very high spatial resolution was possible [2]. This work led to the development and commercialization of holographic photopolymer film from DuPont.

To create a hologram, a laser beam is expanded and split with a partially reflecting mirror. An object is irradiated with one of the beams, and the other beam, the "reference", is directed onto the recording medium, in this case photopolymer film. The "object" beam reflected onto the film intersects with the "reference" beam, creating a complex pattern of constructive and destructive interference in the photopolymer composition. In regions of constructive interference, monomers congregate onto a growing polymer, leaving the local region depleted of monomer. In regions of destructive interference, of course, monomer concentration remains unchanged. The result is a complex pattern of refractive index variations in the film. When this film is irradiated by the original laser wavelength at the reference beam angle, the beam is diffracted in a complex pattern that reforms an image of the original object in space, appearing to an observer as a three-dimensional monochromatic recreation of the original object. This is the phenomenon of holography. The technical foundation of holography has been covered in great detail in numerous publications [3–5].

Bis-imidazole photoinitiators are well-suited to photopolymer holographic films because these photoinitiators are sensitive, can be stored indefinitely, can be sensitized to all visible wavelengths, and are readily compatible with binder systems. It was the coincident development of bis-imidazole photoinitiators which catalyzed the rapid growth of photopolymer films in DuPont, holographic films in particular. The ready sensitization of bis-imidazoles has been exploited in a wide variety of holographic photopolymer films sensitized to all major visible commercial lasers, including panchromatic sensitization for the production of full-color

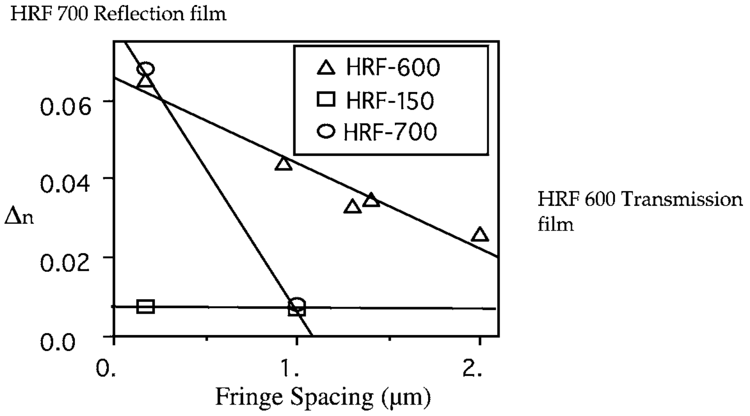

Figure 13.1. Plot of refractive index modulation as a function of pattern spacing for several holographic film families.

holograms. DuPont's holographic photopolymers have been described extensively [6–10]. A survey of several manufacturers' holographic photopolymers is given by Natarajan et al. (1996) [11].

DuPont has developed materials with excellent photospeed across the visible spectrum, extending from the UV at about 350 nm out to far red at about 700 nm. Typical sensitivities range in the few to tens of mJ/cm^2, which is competitive with most other photopolymer systems and even approaches the photospeed of the ultra-fine grained silver halide materials [12] that are employed to record similar structures.

The choice of monomers, binders and other polymers or oligomers determines the bulk refractive index and refractive index change (i.e. index modulation in gratings). In addition, bulk physical properties such as diffusion lengths are determined by the choice and proportion of film components. This allows the design of films that record primarily small grating periods (reflection gratings and reflection holograms) or primarily larger periodic structures (transmission gratings and transmission holograms). It is also possible to record a wide range of pattern spacings and structures in films suitable for both transmission and reflection holography. A plot of grating spacing and index modulation for several different families of holographic films from DuPont is shown [7] in Fig. 13.1.

DuPont holographic recording films were initially commercialized under the tradename Omnidex®, where films with series designations Omnidex® 600 are suitable for transmission holography, Omnidex® 700 is suitable for monochromatic reflection holography, and Omnidex® 800 is for intended panchromatic color holography. The film is supplied in roll form on polyester base with a non-birefringent coversheet that can remain in place during imaging.

13.1 EXPERIMENTAL FIT TO COUPLED WAVE THEORY

A simple theoretical model of volume phase holograms based on coupled waves in an index-matched medium has been provided by Kogelnik [13]. Specific fitting of measured spectra to Kogelnik's model is shown in Fig. 13.2. A 10 μm thick reflection film is recorded at 514 nm at 0° incident angle, with a simple mirror laminated to the back side of the holographic film. This produces a grating with a spacing of 0.2 μm. In the graph shown in Fig. 13.3, measured

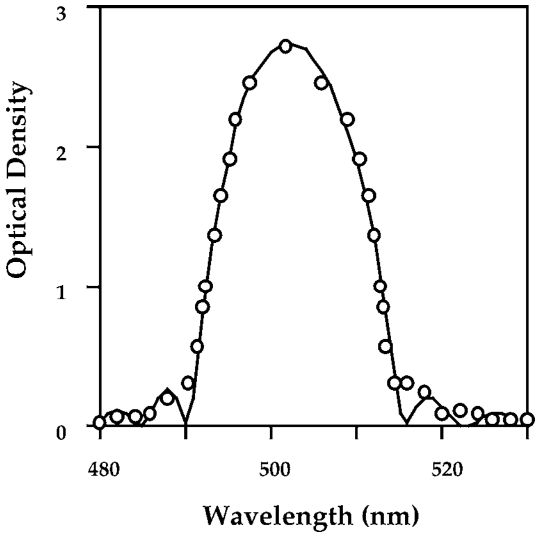

Figure 13.2. Experimental fit of 10 micron-thick reflection hologram to Kogelnik [23] expression.

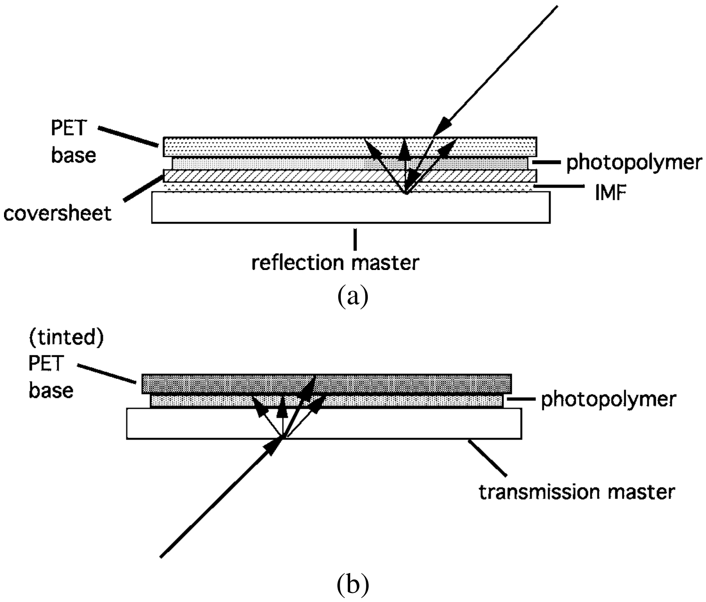

Figure 13.3. (a) Stack for producing a replicate of a reflection hologram. (b) Stack for producing a replicate of a transmission hologram.

optical density is shown as open circles; the calculated spectra is fit to a sinusoidal grating with a Δn of 0.059 and thickness of 10.4 μm and is shown as a solid line.

13.2 REPLICATION OF HOLOGRAMS

Holograms can be replicated by simply bringing unexposed holographic film into contact with another hologram, then illuminating with a coherent laser beam at the reference beam angle.

Table 13.1. Performance enhancement by baking for two photopolymer films

	Omnidex® 706		HRF-700X001-20	
	After exposure	After baking	After exposure	After baking
Bragg λ (nm)	508 ± 1.3	509 ± 1.0	511	503.9 ± 2.0
Peak OD	0.55 ± 0.1	3.1 ± 0.5	0.7	4.2 ± 0.4
FWHM (nm)	6.5 ± 0.2	17 ± 0.5	7.5	21.6 ± 0.5
Δn	0.012 ± 0.002	0.041 ± 0.004	0.014	0.060 ± 0.002

Unwanted internal reflections can be eliminated by using an index-matching fluid, such as a high-boiling hydrocarbon, between the layers. As illustrated below, the illumination beam intersects holographically-diffracted beams in the unexposed film, and a replica hologram is produced.

13.3 PRODUCTION OF HOLOGRAMS

Holograms form during laser exposure in photopolymer films, and can be viewed in white or laser light immediately upon turning off the recording beam. In practice, the film is then fixed using incoherent long-wave UV exposure. The hologram can then be baked in a forced-air oven to complete the diffusion and polymerization of locally unpolymerized monomer, a step which raises diffraction efficiency. Examples of performance enhancement by baking are given in Table 13.1.

Reflection holograms were recorded at 514 nm at 0° incidence with a mirror laminated to the back of the film, UV cured, and heated. These results show that baking a UV-cured hologram raises the hologram's peak optical density substantially, along with the spectral full-width half maximum (FWHM), and Δn.

Mass-replication of holograms into photopolymer recording materials may be accomplished using any of several established methods including step-and-repeat or continuous scanning. In most applications incorporating photopolymer holograms, the hologram is applied as a decal or is assembled into an optical element. Transfer adhesives or pressure-sensitive adhesives can be laminated to both sides of the processed photopolymer film, after first removing the base and coversheet films.

13.4 APPLICATIONS

In recent years there has been an increasing demand for optical materials and devices that manipulate light efficiently. Photopolymer holograms have found uses in a number of new areas, ranging from security and printing to data display and information storage. Using holographic film, diffractive elements can be designed which perform the roles of lenses, dichroic mirrors, dichroic filters, and broadband or wavelength-selective diffuse reflectors. Photopolymer holograms offer a solution to a wide variety of optical engineering requirements, and provide copy-protection advantages in security labeling and document protection.

13.4.1 Security and product authentication

Holograms have found considerable utility in the security area. The need for security and authentication labels is expected to intensify from both governments and commercial product manufacturers. Product diversion and counterfeiting are major problems today; the United States International Trade Association has estimated that 5% of the value of world trade is accounted for by counterfeit goods [14].

Most graphic arts holograms used for these purposes today are of the embossed type, which imprints the hologram as a relief pattern on the surface of the film. Typically, a reflective coating is used to reflect the image back to the viewer. Embossed holograms are found on many credit cards and are used for security, product/brand authentication, packaging, promotions and publishing. They can be produced at extremely low cost. Their color rendition, depth, and contrast are limited, however, and their holographic efficiency is constrained by the physics of surface gratings [5]. In contrast, photopolymers record true volume phase holograms [3], allowing the recording of images with high efficiency, high perceived depth and tight color control. Their unique look and increased sophistication offers an improved level of security.

13.4.2 Laser eye protection filters

For laser eye protection for military personnel, the eyewear must block the laser lines that are potential threats and allow good transmission of other visible wavelengths for acceptable vision. Reflection holograms can be designed to act as narrow band filters, tuned to a particular range of incident angles and wavelengths. In this application very high efficiency holograms reflect and reject narrow laser lines and pass other visible wavelengths. These laser notch filters have been applied to Raman spectrometers [15] using gelatin materials, and to laser eye protection spectacles [16] and visors [17] using photopolymers. The intended environment can range from brightly lit daylight scenes to night vision. The high transmissivity of photopolymer holograms is especially critical in night vision applications.

13.4.3 Liquid crystal display systems

Rapidly expanding applications for holographic elements are now being seen in the area of liquid crystal display (LCD) devices. The applications of holograms to LCD’s have been discussed in detail previously [18–28]. Due to the low overall light throughput in LCDs, there is a strong need for components and system designs which efficiently utilize available ambient or backlight. More effective utilization of light would produce a brighter, higher-contrast display, and reduce demand on the power supply of backlit displays.

In conventional backlit LCDs, losses in the backlight, polarizers and color filter lead to low light throughput. For a reflective LCD, the availability and efficient use of ambient light is a critical consideration in brightness. Color reflective LCD’s have especially low light throughput. Recently, holographic approaches for more effective light management have been introduced for backlit LCDs [26] and for reflective LCDs [27,28]. In these approaches, the photopolymer hologram’s wavelength selectivity, controlled spectral bandwidth, high diffraction efficiency, and controllable diffraction angle enables efficient use of the available light. Displays can be viewed with a bright holographic reflection spatially separated from specular glare, noticeably improving perceived contrast.

In a conventional LCD projector system, light throughput is limited by losses inherent in color separation using dichroic mirrors and multiple LCD panels. Color LCD projector systems suffer from the added complexity of using three LCD panels, one each for red, green, and blue images. For a three-panel full-color LCD projector system, it is estimated that only

2% of the light from the lamp reaches the display screen. Single-panel LCD projectors have measured efficiency of, typically, only 0.8% [22]. Approaches using a combination of dichroic mirrors and micro-optics have been successfully applied to this problem, but issues of the high cost of dichroics and sensitive alignment of the components remain [33]. Approaches using pixilated holograms have been demonstrated, using diffractive or holographic components to replace the color filters and significantly improve the light throughput of the overall system, by a factor of 2–4× [22,24,25].

13.4.4 Full-color holography

Brilliant full-color holograms can be produced with panchromatically-sensitized Omnidex 800 film [29]. Exposure conditions for color balancing have been discussed [30]. An interesting application has been commercialized by Zebra Imaging of Austin, Texas. To produce on-demand 3D renderings, film is exposed under computer control in pixilated format using three laser wavelengths. Since imaging is performed in small areas in rapid succession, the size of the final hologram is not limited by the conventional constraints of laser uniformity and intensity reduction in expanded beams. As a result, very large full-color holograms can be produced. This capability has been exploited to produce complex "overlay" design drawings, where different levels can be visualized at various view angles.

13.4.5 Holographic data storage

There is an ongoing world demand for faster and denser data storage systems. Holographic storage provides the potential of holding more than a terabyte of information in a conveniently-sized medium with transfer rates exceeding 1 gb/sec and data access times less than 100 microseconds [31]. This is possible because individual pages of data are stored throughout the volume of the recording media and are accessed a page at a time.

In holographic storage, information is recorded when a reference laser beam interferes with an object beam carrying data imparted on the beam by a spatial light modulator. The resulting interference pattern is recorded in the holographic storage medium as a complex three-dimensional pattern. Multiple pages of data can be stored by angle or wavelength multiplexing. Data can be retrieved by illuminating the recording media containing the stored hologram with the reference beam used to record it, and passing the resulting beam through charge coupled devices which convert the optical display to an electronic signal.

Inorganic photorefractive crystals have typically been the choice for data storage recording media [32]. Their typically high thicknesses allow for storage of large amounts of information, and because their operation depends on generation of electric fields within the substrate, these materials can be erased and rewritten. Their cost and complexity of use, however, have limited their practical application.

Information recorded in photopolymers is permanent and can be used only for write-once memories (WORM's). Their thicknesses are generally limited to a maximum of 150 μm. On the other hand, photopolymer films are less expensive than lithium niobate crystals, relatively simple to use, and have inherently greater refractive index change leading to high diffraction efficiencies. In recent years significant progress has been made in demonstrating the practicality of holographic data storage [33,34].

13.5 CONCLUSION

The introduction of commercial lasers coupled with newly-developed bis-imidazole photoinitiators in the 1960's provided the key tools necessary for the successful development of holographic films. As discussed in this article, the applications which ensued have been diverse and continue to expand as needs multiply for efficient management of light.

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14

HABI ENHANCED ATTRIBUTES PROVIDE UNIQUE PHOTOPOLYMER WAVEGUIDE TECHNOLOGY FOR OPTICAL INTERCONNECTIONS AND FUNCTIONAL PHOTONIC COMPONENTS

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What electronics meant for the 20th century is anticipated to be multiplied many fold by photonics in the 21st century. Since the mid 1980's there has been a pervasive and explosive growth in optical communications as the solution to the ever-increasing need for bandwidth and high data rates. The capabilities enabled by optical communications already have and promises to continue having extensive impact on our lives in this new age of photonics. Worldwide optical fiber based infrastructure is now in place for telecommunications spanning all the oceans into the central offices and out to the users. Fiber to the home is now being rapidly implemented to provide high-speed DSL lines for computer data, telecom/cable, and ordinary telephone communications. Wireless phones are fed and made possible by optically connected towers. High speed computing technology is being driven to adopt photonic interconnects to handle data and clock rates in excess of 10 GHz that is expected to begin to be implemented late this decade down to the board and chip to chip level interconnectivity. Aerospace and defense vehicles are adopting optics both for weight and EMI immunity in mission and flight control systems. Biochips combining micro fluidics with internal optical access represent a promising developmental area. In short photonics is coming of age.

Photonic communication implementation involves primarily glass fiber interconnections between high-data rate modulatable optical diode laser sources and semiconductor high-speed detectors. Optical fibers have been primarily coupled directly to the light sources and detectors. Increasingly, there is a growing recognition that it would be advantageous to couple arrays of light sources and detectors first to planar waveguides links at the chip, board, and component level, and then through array interconnections to waveguide interconnects on board or to optical fiber arrays (ribbons) to go off board. To meet this need, polymer waveguide based interconnections and devices are increasingly considered as a promising technology due to low cost, minimal weight, high density potential, ease of configurability, versatility for implementation and scale up to high volume production. As a result of the promise and potential for planar polymer waveguides, and the growing interest for board level array interconnectivity, a number of polymer waveguide technologies have been and are being explored and developed for these optical interconnection applications.

This paper focuses on a polymer waveguide technology whose attributes are enhanced and made possible by the HABI initiator system combined with a unique waveguide formation process amenable to high volume manufacture with significant application and process attributes. This waveguide technology originated from initial work where modifications were made on a HABI based light induced self-developing holographic photopolymer, which grew out early developments by Rolf Dessauer, to facilitate waveguide creation. This chapter's author while a DuPont employee in 1985 recognized the potential that the self-development process based on light exposure induced internal monomer diffusion could create a unique and superior technology for constructing optical waveguides. As a result of this vision, waveguides can now be created in large pre-coated film sheets using precision photomask imaging that initiates the self-development phenomena resulting in well-defined precisely controlled high index of refraction regions that guide light. Since that time material properties have been modified in combination with extensive process and configuration developments critically necessary for a practical optical interconnection system. This polymer waveguide technology, know as Polyguide™ at DuPont, and GuideLink™ at Optical CrossLinks, Inc., (OXL) founded by the author and his former DuPont team in 1998, is now being used to produce prototype optical interconnection links and functional devices commercially for a growing customer base.

This chapter reviews (1) the requirements for a practical system, briefly the (2) alternative waveguide technologies as compared to the self-development approach, and (3) the GuideLink™ technology and application embodiments that are facilitated by the diffusion based HABI initiated process.

14.1 WAVEGUIDE TECHNOLOGY APPLICATION REQUIREMENTS

Optical waveguides are increasingly needed to provide the coupling links between sources and detectors with or without intervening optical fibers. They can be substrate or circuit board attached, and/or serve as both substrate bound and self-supporting for polymer flex circuits. Of increasing importance is the need to have extremely high-density waveguides forming closely spaced arrays, or stacked in layers for 3D circuits for interfaces to semiconductor sources and detectors. Polymer waveguides have clear density advantages over glass fiber for dense connectorization. For example, using a standard connector footprint format, glass fibers may reach 50 per connector interface while over 500 polymer waveguide interfaces can be achieved in the same connector space. With properly designed photomasks polymer guides can also satisfy the growing need for added functionality including splitting, combining, multiport to multiport coupling called star-couplers, crossovers, and numerous others.

Whatever the technology used to create an optical interconnection system it must be capable of forming an effective fully interconnected stable system. An effective practical system requires a balance of material properties for a broad thermal operating range, ease of optical coupling to sources, detectors, optical fibers with industry compatible connectivity and acceptable total optical loss. Practical applications also require capability for versatile configurations and be process forgiving. For example, compatibility with common industrial assembly processes like solder reflow for electronic or E/O component attachment and interfaces.

Stability and reliability for long-term operations and with adequate shelf life under various storage conditions are essential. And all of these attributes must be cost effective to justify implementation.

Attributes essential for waveguide technology application involve creation of precisely defined stable waveguide structures, excellent precision machinability for connectivity, good adhesion, versatile stable packaging, compatible thermal expansion for stable coupling to typical components and substrates, thermal cycling stability and amenability to solder reflow processes for attaching electronic E/O components.

14.2 WAVEGUIDE PROCESS ALTERNATIVES

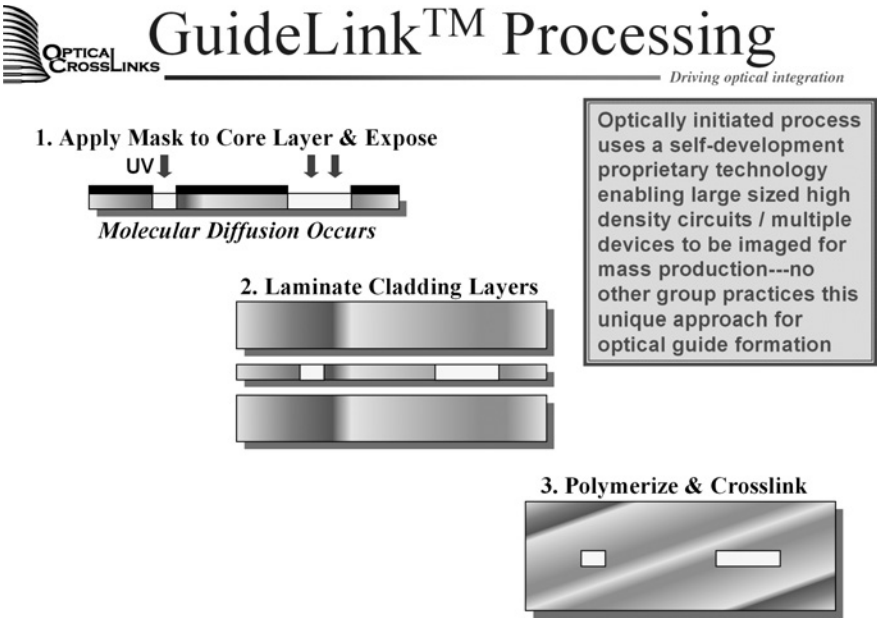
Several very different processes have been explored to create polymer waveguides. For other than the GuideLink™ process, the alternative processes to create the photo defined high refractive index region are embossing, molding, and etching based on removal by wet chemical or reactive ion processes. These routes all have the potential for process induced optical loss due to embossing tools, molds or etching processes. These can create imperfections on the waveguide walls larger than 0.1 microns that can scatter light and thus create higher optical loss for the waveguide than that of the fundamental polymer materials. Typically, the waveguide patterns are imaged by using a photo mask. In addition they require a back fill step of another polymer to provide a protected and cladded uniformly lower index surround than the waveguide. There are a range of procedure options and steps that are not discussed here for the various alternatives. Typically for etching techniques the unexposed polymer materials are spin coated on the substrate of choice for final application, etched for waveguide definition and then backfilled to encapsulate or clad the defined guide region. Pre-coated materials are required for embossing. Alternatively expensive molds are used to create guide patterns. Subsequent processing is required from that point for all of these techniques. Of course molded or embossed guides although not formed on the substrate of choice must still be backfilled for the final waveguide structure to be formed. Polymer removal, embossing or mold processing is not amenable to really high-density waveguide array creation or incorporating embedded novel structures inside the waveguides. When constructed on the application substrate, processing for connectivity is not as readily achieved, and certainly performance-confirming QC cannot readily be made. Thus, if there is a defect the board or substrate upon which the guide is created may need to be discarded or must be recycled.

14.3 GUIDELINK™ WAVEGUIDE PROCESS AND APPLICATIONS

14.3.1 Exposure process

The GuideLink™ process as currently formulated depends on light induced polymerization of a very mobile combination of acrylate monomers in a cellulose acetate butyrate binder polymer.

The photomask defined localized polymerization as depicted in Fig. 14.1 allows for more mobile monomers to diffuse into the exposing polymerizing region thereby increasing the density and the relative quantity of polymer in that region by a diffusion based mass transfer. With subsequent lamination of similar layers on the top and bottom additional diffusion insures that the high index guide forming region is uniform and the surrounding clad layers



Optically initiated process uses a self-development proprietary technology enabling large sized high density circuits / multiple devices to be imaged for mass production---no other group practices this unique approach for optical guide formation

Figure 14.1. GuideLink™ processing.

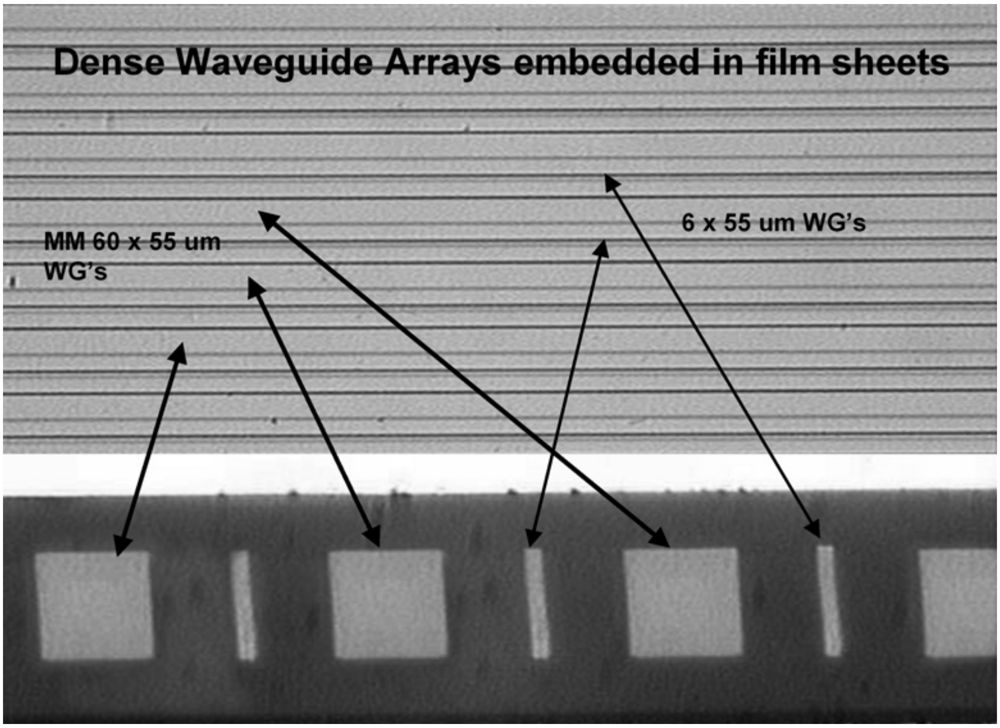


Figure 14.2. Waveguide cross sections and profiles.

are also uniform in refractive index that is lower than the waveguide. Process conditions for optimum guide index profiles and magnitude can be balanced by controlling exposure power, temperature and time, as well as the presence of oxygen, which inhibits further polymerization. The final steps involve optical flooding for complete polymerization followed by a heat cure at 125°C to crosslink any remaining monomer and stabilize the system.

The initial unexposed monomer and polymer coatings are made on a temporary MYLAR® base, which after multi-layer lamination and total polymerization are removed and discarded. Coatings have been typically made a foot wide and hundreds of feet long. With the balance of inhibitors and HABI initiator the shelf life before exposure can be for many years before exposure. Some coatings have been exposed after 6 years with good performance. Once exposed and cured lifetime is excellent. Waveguides exist today that were made over 15 years ago that still have excellent performance. During exposure photomask defined guide forming regions with very sharp walls are created with no "bleeding" or graded guide edges transitioning into the unexposed regions. This is facilitated by the HABI systems balance of initiators and inhibitors. Also during exposure a self-focusing occurs as the local guide index initially increases from top to bottom during the exposure such that the guide walls do not flare out in cross section and remain well defined as depicted in Fig. 14.2.

When the exposure is complete a uniform profile throughout the guide can be achieved. Shown at the bottom of the figure are the ends of the waveguides looking at the film edge. Here narrow 6 micron wide guides around 55 microns deep are well defined vertically. The larger guides are essentially square. At the top of the figure the waveguides are viewed from the above the film sheet containing the guides showing how well defined they are.

14.3.2 Multimode waveguide waveguides

The large approximately 55 by 60 micron square high index regions form what are called multimode guides. Multimode polymer waveguides are primarily used today for circuit board interconnections on the order of less than a centimeter to around 30 to 50 centimeters in length. They can couple off the circuit board to multimode fibers for relatively short low data rate applications. Multimode polymer waveguides must have the waveguide refractive index around 0.03 or more higher than the surround to provide good coupling to optical fibers and small bend radius of curvature around 5 mm for practical systems. Multimode optical links are alignment forgiving for optimum interconnectivity. As noted they are used for short length optical interconnections typically data communication applications up to 100 meters or so. Multiple paths of stably propagating light called modes can be propagated with each mode having a slightly different angle within the guide relative to the guide center and thus a different path length through the waveguide. Thus high data rate signals can be smeared out as the different path lengths taken for the various modes results in overlapping signals with lost resolution or degraded transmission particularly with greater distances. Wavelengths typically used for short length multimode data communication applications are typically around 850 nm, 980 nm with some growing interest at 1300 nm where most polymers have good low loss transmission.

14.3.3 Single mode waveguides

Imaged waveguides with the dimensions of the narrow 6 micron width in the figure with lower refractive index increase produces what are called single mode waveguides. Thin films approximately 6 microns thick are used to image and form the waveguide with subsequent clad layer on either side applied to form a film around 100 micron or so thick with packaging layers for stability. The waveguide is about 6 by 6 microns square. Single mode guides essentially propagate light with a very small angular distribution with a Gaussian intensity profile with nearly 30% of the light traveling evanescently outside of the guide. The refractive index increase in polymer single mode guides that couple well with low loss to/from optical fibers must be tightly controlled to around 0.006 ± 0.0005. These small polymer guides can provide similar interconnecting board level links and functional devices as discussed for multimode guides but they also have unique properties enabling additional functions like evanescent coupling and phase related switching and modulation, which are not the focus of this chapter. Single mode optical glass fiber links are used for long distance transmission and very high data rate signals since the one path length traveled enables the data to reach the end with transmission often over many 100's of kilometers with well defined data signals without path length variant signal blurring. Wavelengths typically used for long distance single mode telecommunications are around the 1300 nm and 1550 nm range due to the excellent low loss fiber transmission. Thus, typical polymer interconnections require very short board level lengths or need to have reasonable low loss at these wavelengths that often is achieved with some degree of fluorination to the usual carbon hydrogen polymer chemistry.

14.3.4 Single and multimode GuideLink™

The HABI based initiator system permits fine tuned exposure control of the index profiles and magnitude to be achieved for both multimode and single mode requirements. Formulations are different for single and multimode systems but within each there is some latitude for guide index control by varying power, energy, time, oxygen environment, and temperature parameters that provides great versatility in achieving desired performance. Conversely, fixed polymer systems used for embossing, molding, and etched based processes need to configure the index profiles by choosing the correct polymers for substrates, guide layers and backfill or surrounds. On the other hand, for GuideLink™ incredible performance and exposure reproducibility has been obtained between different material batches as well as within large coating runs with exposure control for fine-tuning performance adequate without altering polymer formulations.

14.3.5 Stable temperature operation

Another unique attribute using a diffusion-based system is that the waveguide and the surround are the same basic polymer. Thus both regions, inside and outside the guides have the same bulk index dependence with temperature. The difference in index we have referred to as the guide index determines the propagation characteristics. Over a large operating temperature range the difference in bulk index between the waveguide and the surround remains fixed for the GuideLink™ HABI based system. When different polymers are used as for the other guide forming processes great care must be taken to choose not only the correct indices of the different polymers to form the guide but assure that the bulk index temperature dependence to maintain constant guide properties is carefully controlled/chosen over the operating temperature range desired. Since most polymers decrease about 3×10^{-4} in refractive index with each centigrade degree increase, variations in operating temperature can have a large performance impact particularly with single mode systems. GuideLink™ technology obviously has a broad operating temperature range over which there is no change in waveguide propagation characteristics.

14.3.6 Guide wall definition

The HABI based diffusion process produces very smooth waveguide walls with sharp definition as depicted in Fig. 14.2 and thus faithfully reproduces with very high sub tenth micron resolution any photomask pattern or defect. GuideLink™ waveguide walls are therefore optically defined by the photomask and accurately image the photomask construction details. Using photomasks with resolution equal or better than 0.1 micron steps essentially no light scatter from the waveguide sidewalls even around curves is produced. This means that the GuideLink™ waveguide losses are identical to the bulk material optical losses and are not increased by the waveguide formation process for either small single mode or large multimode guides. Obviously this situation is potentially very different for the alternative embossing, molding, and etching processes where the guide edges are defined by a mechanical tooled part or by a disruptive etching process regardless of mask quality such that there is usually a waveguide process dependent loss in addition to bulk material losses.

14.3.7 Robust packaging

Once the GuideLink™ waveguide containing film sheet is constructed and stabilized, with all the Mylar temporary carrier upon which the unexposed material is coated discarded, layers of low CTE and high T_g polymer are bonded to both sides to create a robust stable self-supporting film of up to a square foot or so in size depending on the photomask. This effective low CTE and high T_g packaged system remains dimensionally stable and enables good stable optical coupling for all waveguides in an array over a broad operating temperature range for flex circuits or substrate bonded circuitry. Robust flexible guides have been shown to be stable from −45°C to 125°C the typical max range required. During solder reflow operations to bond electronic components on common substrates one minute IR thermal spikes up to 300°C have been successfully completed with no loss of optical alignment or degradation of optical performance for board mounted waveguides in the GuideLink™ films.

By subjecting waveguide-containing films to extended times at various temperature, Arrhenius plot extrapolations were developed. These indicated that for 850 nm operation there would be a loss increase of 0.1 dB/cm to about 0.18 dB/cm over the initial 0.08 dB/cm when held at 85°C for 5 years. For 1300 nm operation where the initial loss is 0.35 dB/cm the loss was projected to increase 0.01 dB/cm when held at 85°C for 5 years.

14.3.8 Precision machining

The ability to make well-defined high-density waveguides in self-supporting robust structures enables precision machining to occur before adhesion to substrates or packaging for connectorization. Thus connectorization and coupling mirrors if needed can be completed followed by quality performance testing before applying the part to a substrate or embedding in a package. A computer controlled excimer laser is used where ±0.2 micron position reproducibility is achieved. This is a critical step for enabling precisely aligned low loss connectivity for multiple waveguide arrays. Waveguide strips with guide arrays precisely centered within the strip for example within a fraction of a micron are regularly achieved. These strips are inserted into similarly accurately cut alignment plates and mounted on a supporting ferrule. Thus single and multilayer waveguide arrays are connectorized for coupling to other polymer waveguides, arrays of solid-state semiconductor components or to optical fiber arrays. Out of plane mirrors are also machined at the film edge to couple light vertically to and from arrays of vertical cavity surface emitting lasers (VCSEL's) and detectors.

For right angle 90° daughter board to backplane interconnectivity GuideLink™ capitalizes on inherent robust flexibility by bending a precisely machined array waveguide strip though 5 mm ROC (radius of curvature) held in a ferrule supporting the 90° bend. The guide strip leaves the backplane supported by the ferrule and thus provides coupling connectivity to a daughter board edge connector at 90° to the backplane. Flexibility is achieved within the 90° ferrule to be compatible with other electronic pin connectors at the daughter board to backplane interface.

Self-supporting functional splitters are singulated and connectorized using precision machining as described and packaged with extremely good balanced splits, low total loss, small size, and light weight—all attributes of great interest for aerospace fly by light applications where optics is being used to reduce adverse EMI impact. Splitters for 1 × 16 outputs are machined with two 8 over 8 outputs by slicing between the two halves to enable all 16 outputs to fit into a standard MT connector in an 8/8 format since 16 in a row cannot fit within the connector dimensions. Thus precision machining with GuideLink™ technology provides a broad range of stable low loss connectivity solutions that enables and has demonstrated a broad range of diverse practical applications.

14.3.9 Internal imaged guide structures

An additional capability very unique to the HABI controlled inhibitor/initiator process is the ability to image small unexposed regions inside larger multimode waveguides. By creating for example 4 micron wide unexposed regions, which remain imaged through the depth of the guide as depicted in Fig. 14.2, located around the junction of two crossing waveguides, extremely low loss crossovers for dense circuit board routing is achieved. Visualize for right angle crossing guides a low index square like a picture frame in the cross region of the two guides. The light propagating in each guide remains guided in the cross region even though the guide is only a small square. Without these precisely imaged low index regions the light entering the crossing region would radiate and produce crossing loss typical with all other guide forming technologies.

Using waveguides that are crossing at low angles instead of right angles and cutting them at the apex of the cross region, unique sensors have been created. Here light inputs in one guide, reflects or scatters for example (1) off a pattern for a position encoder, or (2) off a mirror covered with sensitive nanotubes, or (3) off particulates in a capillary all going back into the other collecting guide for a very efficient sensor system. Thus a family of diverse sensor applications is made possible by the ability to precisely control the exposure pattern and define side walls with no exposure bleeding that is facilitated by the unique and extremely useful capability inherent with the GuideLink™ HABI based diffusion system.

14.4 SUMMARY

Application details and more in depth discussions can be found in the attached references and on the Optical CrossLinks (OXL) WEB site (http://opticalcrosslinks.com). OXL believes that capitalizing on the unique chemistry and process with potential material evolutionary and enhancing modifications offers significant application potential. Therefore, an extremely broad range of valuable optical communication, biochip, and related applications are all facilitated by the HABI based initiator chemistry and light induced self-development diffusion process.

As a final note, the process is most amenable to a continuous or step and repeat mask imaging replication process for high production volumes in excess of 100's of square feet per day. The cost drivers are the subsequent processing steps after creation of the waveguide film structure. These processes include precision machining for singulation, connectorization, and novel application specific configurations, final assembly of guides, connectors and board mounting/packaging, and for final testing QC. OXL believes that dedicated workstations can enable the throughput in the more labor-intensive steps to be scaled up to meet anticipated commercial needs with appropriate application specific investment.

SELECTED POLYGUIDE™/GUIDELINK™ RELATED PUBLICATIONS

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15

MORE APPLICATIONS FOR PHOTOPOLYMERS

More applications for photopolymer-based products appear as technology advances. Changes are influenced by, e.g., novel light sources (importance of near infrared radiation equipment for laser imaging), environmental considerations (avoidance of halogenated solvents), economics, and demands for improved performance.

In examining the patent literature, it is striking how many different technology areas involve photopolymer technology and more specifically HABIs. In general, because of the cost of HABIs, their use is limited to imaging type applications rather than to non-imaging areas, such as radiation curing. Whether this will always be so is open to question; conceivably there may be less expensive HABIs, or more effective materials or systems, which would eliminate the cost sensitivity. At one time, the use of HABIs was considered as photoinitiators in food packaging materials, where the bulky size of the HABIs or corresponding biimidazoles might have been less likely to be extractable from the coating.

Below are listed abstracts of issued U.S. patents that describe the utility of HABIs; the ingredients of the applicable recipes are also reported, to allow the reader to differentiate between materials employed for different applications. It is striking how much similarity there really is between all of them. Inevitably there is a photoinitiator (almost always o-Cl-HABI), a chain transfer agent, one or more acrylate or methacrylate monomers, one or more binders, additives such as sensitizing dyes, plasticizers, dispersants or coating assistants. Inhibitors, which prevent premature polymerization as a result of accidental heating or adverse storage conditions, are also part of the system. Coatings are inevitably made on polyester substrate and the coversheets are frequently polyolefin films. More recently, HABIs have been used in combination with other photoinitiators, e.g., metallocenes.

The choice of binders and monomers is governed by the application: depending on whether the material will be used in aqueous or solvent washout systems, etc.

Inevitably, economics play a major role in the development of formulations, and the least costly HABI and most effective chain transfer agent or coinitiator.

15.1 COLOR FILTERS

An emerging application is in the field of color filters and displays. To some extent this involves modification of resist technology by incorporation of finely divided colorants that then serve to reduce transmission of certain wavelengths of light.

> **U.S. 6,733,935. Colored Resist Material Set and Color Filter.** Dai Nippon Printing Co., Ltd. (May 11, 2004). Describes a set material of photoinitiators, which prevent a reduction in the light transmittance of each colored resist. The colored resist material set comprises at least colored resist materials having three colors and consisting of a red resist material, a green resist material and a blue resist

material, each resist material containing a reactive monomer, a photoinitiator and a dye and/or a pigment, wherein the photoinitiator contained in the red resist material has a photoabsorption region on the side of wavelengths shorter than 570 nm, the photoinitiator contained in the green resist material has a photoabsorption region on the side of wavelengths shorter than 460 nm, and the photoinitiator contained in the blue resist material has a photoabsorption region on the side of wavelengths shorter than 400 nm, each photoinitiator using at least two or more photoinitiators. Recipes include Binder Polymer 1, DPHA (dipentaerythritol hexaacrylate), 2,2′-Bis(o-chlorophenyl)-4,5,4′,5′-tetraphenyl-1,2′-biimidazole, Diethyl-aminobenzophenone, Pigments 1.2, Pigment dispersant: Solsperse 24000 and Propylene glycol monomethyl ether acetate solvent. Appl. August 17, 2001.

U.S. 6,627,364. Ink Jet Color Filter Resin Composition Color Filter and Color Filter Production Process. Seiko Epson Corporation and JSR Corporation (September 30, 2003) describes a resin composition for producing a color filter by an ink jet system containing (A) a colorant, (B) a binder resin and (c) a solvent having a boiling point of 245°C. or more at normal pressure, wherein the color filter is produced by discharging the above resin composition from an ink jet head into light transmitting regions on the surface of a transparent substrate having banks formed thereon to store the resin composition in the light transmitting regions defined by the banks; forming a pixel pattern by drying the resin composition stored in the light transmitting regions; and forming a protective layer to cover the pixel pattern. 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetrakis(4-ethoxycarbonyl-phenyl)-1,2′-biimidazole and 10 parts by weight of 4,4′-bis(diethyl-amino)benzophenone are employed as photopolymerization initiators. Appl. April 26, 2000.

U.S. 6,624,861. Color Filter Subject to Impurity Extraction Treatment and Liquid Crystal Display Device Having High Voltage Holding Ratio. Dai Nippon Printing Co., Ltd. (September 23, 2003). Discloses a color filter, which can prevent, on a higher level, a liquid crystal layer from being contaminated with ionic materials, and a liquid crystal display device having improved display quality. The color filter comprises at least a substrate and a colored layer of a plurality of colors provided in a predetermined pattern on the substrate, and, after impurity elution, permits a liquid crystal to have a voltage holding ratio of not less than 90%. The liquid crystal display device comprises: this color filter; and a counter electrode substrate provided so as to face the color filter while leaving a gap between the color filter and the counter electrode substrate through a seal member; and a liquid crystal layer sealed into the gap. Red, Blue and Green dispersion employ pigments, Irgacure 907 and 2,2′-bis(o-chlorophenyl)-4,5,4′,5′-tetraphenyl-1,2′-biimidazole photoinitiators and Monomer SR399 (Sartomer), Polymeric binder and Solsperse 24000 Dispersant. Appl. April 25, 2001.

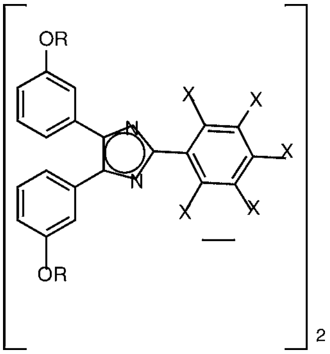
15.2 PHOTORESIST TECHNOLOGY

Photoresists are a large application area for HABI technology, going back to Nov. 23, 1971. New patents, describing HABI uses continue to issue with much frequency.

U.S. 3,622,334. Photopolymerizable Compositions and Elements containing Heterocyclic Nitrogen-Containing Compounds. E. I. Du Pont de Nemours and Company (November 23, 1971). A photopolymer resist compositions comprising (A) an ethylenically unsaturated compound containing at least one polymerizable ethylenic group ($CH_2{=}C{-}$) capable of firming a high polymer by photoinitiated addition polymerization: (B) a thermoplastic organic polymer binder and (C) a improved adhesion to a solid support in aqueous plating solutions whereas the composition includes a small amount of a compound having the formula where R is substituted or unsubstituted ortho arylene, X is CH_3, NH, S, O, or Se, Z is N or C–Y, where Y is H, NH_2, halogen, alkyl. Coating recipe contains mixtures of polymethacrylates, triethylene glycol diacrylate, o-Cl-HABI, benzimidazole, Victoria Blue Dye and polyacrylate monomers.

U.S. 6,524,770. Hexaaryl Biimidazole Compounds as Photoinitiators, Photosensitive Composition and Method of Manufacturing Patterns Using the Compounds. Hitachi Chemical Co., Ltd.

(February 25, 2003). A hexaaryl biimidazole compound useful as a photoinitiator, represented by



wherein each R group represents an alkyl group which may be the same or different, and each X group is independently a fluorine or hydrogen. The compound (I) is particularly useful as an initiator in a photosensitive composition containing a polyimide precursor, which is curable under pattern wise low radiation exposure to give a patterned layer having heat and chemical resistance. (1) Preparation of Photosensitive Polyimide Precursor Composition 10 g of the polyimide precursor obtained in the Synthesis Example was stirred with a mixture of 10 g of g-butyrolactone and 2 g of cyclopentanone. To the resulting mixture, 2.5 g of tetraethyleneglycol diacrylate monomer, and m-OMe-2, 6F-HABI and N-phenylglycine The product was filtered with 3 μm-type filter paper under pressure to give a solution of photosensitive polyimide precursor compositions. Appl. September 15, 2000.

U.S. 6,555,290. Photosensitive Resin Composition and Photosensitive Element Using the Same. Hitachi Chemical Co., Ltd. (April 29, 2003). A photosensitive resin composition comprising (A) a binder polymer having carboxyl groups, (B) a photopolymerizable compound having at least one polymerizable ethylenically unsaturated group in the molecule, and (C) a photoinitiator can provide a film excellent in mechanical strength, chemical resistance, flexibility, and suitable for producing a photosensitive element. solution of copolymer of methacrylic acid/methylmethacrylate/ethyl acrylate/ethyl methacrylate, 2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetraphenyl-biimidazole, N,N′-tetraethyl-4,4′-diaminobenzophenone Leuco Crystal Violet and Malachite green. Appl. November 14, 2000.

U.S. 6,861,201. Near IR Sensitive Photoimageable/Photopolymerizable Compositions, Media, and Associated Processes. E. I. Du Pont de Nemours and Company (March 1, 2005). Novel photopolymer compositions are disclosed which contain dyes that absorb strongly in the near infrared (near IR) region of the electromagnetic spectrum. These dyes are useful as photosensitizers for initiating a variety of photoimaging and photopolymerization reactions. Imaging Media are disclosed herein which are sensitive in the near infrared (near IR) region of the electromagnetic spectrum and which can initiate polymerization of ethylenically unsaturated monomer components in negative-acting photopolymer systems and/or which can initiate conversion of a leuco dye to its corresponding colored dye form. These imaging media comprise either a near IR dye photochemical sensitizer, a hexaarylbiimidazole (HABI) photoinitiator, a chain transfer agent, and a photopolymerizable material or a near IR dye photochemical sensitizer, a hexaarylbiimidazole (HABI) photoinitiator, and a leuco dye. These imaging media are useful in a variety of photopolymer products, including photoresists, proofing films, and holographic recording films. Appl. April 7, 2004.

U.S. 6,855,480. Photoresist Composition. Shipley Company, L.L.C. (February 15, 2005). Disclosed are photoimageable compositions having improved stripping properties as well as methods for manufacturing printed wiring boards using such photoimageable compositions. What is claimed is: 1. A photoresist composition comprising a branched polymeric binder, a monomer and a photoactive component, wherein the branched polymeric binder comprises as polymerized units one or more difunctional branch-point monomers having two polymerizable end groups and a backbone comprising 2 or more base cleavable functionalities, provided that if the difunctional branch-point monomer is free of urethane linkages and both polymerizable end groups are (meth)acrylate esters the difunctional branch-point monomer has a molecular weight of ~ 450. The composition of claim 1 wherein the photoresist is negative-acting dry film photoresist. The composition of claim 1 wherein the photoactive component is selected from the group consisting also of 2-(o-chlorophenyl)-4,5-diphenylimidazole dimer, 2-(o-chlorophenyl)-4,5-di(m-methoxyphenyl) imidazole dimer, 2-(o-fluorophenyl)-4,5-diphenylimidazole dimer, 2-(o-methoxyphenyl)-4,5-diphenylimidazole dimer, 2-(p-methoxyphenyl)-4,5-diphenylimidazole dimer, 2,4-di(p-methoxyphenyl)-5-phenylimidazole dimer, 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole dimer and 2-(p-methylmercaptophenyl)-4,5-diphenylimidazole dimer. Appl. April 6, 2002.

15.3 SOLDERMASK

U.S. 5,405,731. Aqueous Processable, Multilayer, Photoimagable Permanent Coatings for Printed Circuits. E. I. Du Pont de Nemours and Company (April 11, 1995). The use of a two layer photoimagable, aqueous processable, resist with a hydrophilic binder in the outermost layer provides a permanent coating highly resistant to printed circuit processing chemicals. This resistance results in levels of adsorbed or absorbed ionic contamination less than 14 micrograms per square inch. Preferred photoinitiator systems are 2,4,5-triphenylimidazolyl dimers in combination with chain transfer agents Soldermask processing conditions are as follows: Exposure of all examples is between 100 and 300 mj/cm^2. Development conditions are 105°F. and 20 to 50 seconds in aqueous 0.85% sodium carbonate at 20 to 30 psi spray pressure. The cure for all examples is exposure to uv radiation of 2 to 8 joules followed by a thermal cure of 150°C. for one hour, or in the reverse sequence. Appl. December 22, 1992.

U.S. 5,240,817. Lamination of a Photopolymerizable Solder Mask Layer to a Substrate Containing Holes Using an Intermediate Photopolymerizable Liquid Layer. E. I. du Pont de Nemours and Company (August 31, 1993). A process is disclosed for applying a preformed photopolymerizable solder mask film and a photosensitive liquid to a printed circuit substrate containing a plurality of holes wherein reduced failure is obtained in photopolymerized areas of the solder mask film above the holes as determined after a soldering operation. The photosensitive liquid contains at least one ethylenically unsaturated compound capable of forming a high polymer by addition polymerization and a first photoinitiator system, which has an absorption maximum in a first spectral region. The preformed photopolymerizable film contains at least one ethylenically unsaturated compound capable of forming a high polymer by addition polymerization and a second photoinitiator system, such that the preformed photopolymerizable film has an absorption maximum in a second spectral region and is activated by actinic radiation therein and has an absorption minimum in the first spectral region and transmits actinic radiation therein. Appl. December 20, 1991.

15.4 ELECTRICAL DEVICES

U.S. 4,369,247. Process of Producing Relief Structures Using Polyamide Ester Resins. E. I. Du Pont de Nemours and Company (January 18, 1983). An improved process for forming relief structures on electrical devices such as capacitors, integrated circuits, printed circuits and semiconductors; a solution of a composition a polymeric heat resistant photopolymerizable composition of a polyamide ester resin containing photopolymerizable groups is applied to substrate such as a coated silicon wafer, which forms the base an electrical device, and is dried to form a film, the film is exposed to radiation through a pattern and photopolymerized; the unexposed and unpolymerized part of the film is dissolved off and the resulting relief structure is converted to a polyimide structure having a sharp definition and good mechanical, chemical and electrical properties; to reduce radiation exposure time and increase the rate of photopolymerization the following constituents are used in the composition: a radiation sensitive polymerizable polyfunctional acrylate compound and a photopolymerization initiator of an aromatic biimidazole. Composition contains Polyamide ester resin 10.0, o-Cl-HABI 0.7, Michler's ketone 0.25, Tris(diethylamino-o-tolyl)methane 0.20, Trimethylol propane trimethacrylate 2.0, N-methyl pyrrolidone 30, Thinner (ethylene glycol monoethyl ether/n-methylpyrrolidone 1/1 ratio) 10. Appl. December 24, 1981.

15.5 PHOTOIMAGEABLE COVERLAY COATINGS

U.S. 6,218,074. Flexible, Flame-Retardant, Aqueous-Processable Photoimagable Composition for Coating Flexible Printed Circuits. E. I. du Pont de Nemours and Company (April 17, 2001). A flexible, flame-retardant, aqueous processable, photoimagable resin composition for forming a permanent, protective coating film for printed circuitry and a multilayer photoimagable element containing a layer of the photoimagable resin composition in combination with a low tack photoimagable resin sublayer and a temporary support film are disclosed. The photoimagable resin composition has excellent aqueous developability and provides a cured coating film having good flexibility, adhesion, solvent resistance, surface hardness, thermal resistance, electrical insulating properties and flame retardancy. Appl. July 21, 1999. Example 1 illustrates a flame-retardant composition containing a brominated blocked polyisocyanate to improve flame retardancy. It contains Brominated diacrylate monomer Ebecryl™ 6700,3-MT, o-Cl HABI, Benzophenone, PVP K-120, Blocked isocyanate #2, Brominated copolymer, DayGlo™ HM022A19, Amic acid copolymer.

15.6 PRINTING PLATES

Many patents describe HABI photoinitiators for the manufacture of printing plates. The earliest one involving HABIs goes back to October 26, 1971.

U.S. 3,615,567. Image Intensifiers for Preparing Lithographic Plates. E. I. du Pont de Nemours and Company (October 26, 1971). The photopolymeric coating consists of an addn. polymerizable compd., a free radical donor, polymn. initiator 2,4,5-triphenylimidazolyl dimer, a protective layer of film-forming org. polymer, and $\geqslant 1$ inorg. halide image intensifier. Upon exposure, an intense visible image is obtained. E.g., a mixt. contg. 2-ethoxyethanol 3.21., Me methacrylate methacrylic acid copolymer 1000, 2-(o-chlorophenyl)-4,5-dimethoxyphenyl imidazolyl dimer 37.4, tris-p-(diethylamino)-o-tolyl)methane 30.0, bis(dimethylamino)benzophenone 20.0, C. I. Solvent Red 109, and mixed ester of triethylene glycol dicaprate and dicaprylate 120.0 g is stirred for 3 hr, 25.6 g $CaCl_2 \cdot 2H_2O$ is added with stirring for 15 min, 380 g trimethylolpropane triacrylate is added, and after stirring 15 min the mixt. is filtered and the filtrate discarded. The compn. is then coated on a grained Al plate, dried, and overcoated with a compn. contg. H_2O 920, poly(vinyl pyrrolidone) 135, poly(vinyl alc.) 9 g, 2-ethoxyethanol 5, surfactant 1.5, and EtOH 5 ml. After exposure and development, the lithog. printing plate thus formed is ready for the printing press. Appl. August 20, 1969.

U.S. 3,718,473. Photopolymerizable Elements Containing Hydrophilic Colloids and Polymerizable Monomers for Making Gravure Printing Plate Resists. E. I. du Pont de Nemours and Company (February 27, 1973). A photopolymerizable element comprising a support strippable from a photopolymerizable layer comprising a hydrophilic, macromolecular organic polymer dispersion medium including a dispersed phase containing (1) at least one ethylenically unsaturated monomer having a boiling point above 100°C. at normal atmospheric pressure and being capable of forming a high polymer by free radical-initiated, chain propagating addition polymerization: and (2) in reactive association with said monomer, at least one free-radical photoinitiator activatable by actinic radiation in an amount constituting from 0.01 to 20.0 percent b weight of the total solids in said dispersion. The elements are useful for making continuous tone gravure printing plates and printed circuit etching resists, On exposure to actinic radiation, the dispersed monomer droplets polymerize or harden to various degrees and the layer becomes resistant to diffusion of aqueous etching solutions in proportion to the exposing radiation.. Exposure, first to a conventional gravure screen pattern then to a continuous tone positive or negative, leaves an image in the resist which may be pressed against and transferred to a moistened metal plate and the support stripped off. The resist bearing metal plate is then etched with an etching solution, e.g., aqueous ferric chloride, to produce a continuous tone gravure image suitable for printing. Appl. May 17, 1970.

U.S. 4,123,272. Double-Negative Positive-Working Photohardenable Elements. E. I. Du Pont de Nemours and Co., Inc. (October 31, 1978). A positive-working imaging element is described comprising a support coated first with a negative-working, solvent-developable, photohardenable stratum, then over-coated with a second negative-working, solvent-developable, photohardenable stratum; the second stratum serves as a mask for the first stratum since it contains ingredients which strongly absorb radiation actinic to the first stratum. The second stratum is imagewise exposed, solvent developed, and the resulting actinically opaque image used as a negative in exposing the first stratum, which is solvent developed to remove the composition in unexposed, but not in exposed areas. Optionally, a separating layer can be present between the photohardenable strata and a cover layer can be present over the second stratum. Positive-working low relief images suitable for lithographic printing plates, printed circuit resists, and contact-speed lithographic films are obtained from the elements of this invention. Appl. May 17, 1977.

U.S. 4,147,549. Lithographic Printing Plate Having Addition Polymerized Areas and Binder Areas. E. I. Du Pont de Nemours and Company (April 3, 1979). A lithographic printing plate is prepared from a layer of a photopolymerizable composition comprising an oleophilic macromolecular organic binder and a leachable hydrophilic ethylenically unsaturated compound by exposing the layer and then leaching the compound from the unexposed areas by treating with a suitable developing solvent, preferably water, producing an oleophilic surface. A similar plate may be prepared from a composition containing a hydrophilic binder and oleophilic leachable compound by imagewise exposure and solvent leaching producing an oleophilic surface in exposed areas and a hydrophilic surface in unexposed areas. Appl. June 22, 1977.

U.S. 4,198,236. Method for Preparation of Lithographic Printing Plate Having Addition Polymerized Areas and Binder Areas. E. I. Du Pont de Nemours and Company (April 15, 1980). A lithographic printing plate is prepared from a layer of a photopolymerizable composition comprising an oleophilic macromolecular organic binder and a leachable hydrophilic ethylenically unsaturated compound by exposing the layer and then leaching the compound from the unexposed areas by treating with a suitable developing solvent, preferably water, producing an oleophilic surface. A similar plate may be prepared from a composition containing a hydrophilic binder and oleophilic leachable compound by imagewise exposure and solvent leaching producing an oleophilic surface in exposed areas and a hydrophilic surface in unexposed areas. Appl. November 30, 1978.

U.S. 4,264,708. Radiation Sensitive Element Having a Thin Photopolymerizable Layer. E. I. Du Pont de Nemours and Company (April 28, 1981). A photopolymerizable element, preferably a lithographic plate, is provided. This element comprises a substrate bearing a photopolymerizable layer having a weight of about 1 to about 90 mg/dm^2, said layer comprising: (1) at least one ethylenically unsaturated diester polyhydroxy polyether of the formula $CH_2{=}CR{-}CO_2CH_2C(OH)HCH_2[{-}O{-}C_6H_3R^4{-}(CR^5R^6)_p{-}C_6H_3R^4{-}(OCH_2C(OH)HCH_2]_n$ $-O_2CR{=}CH_2$ wherein R is H or CH_3; R_4 is H or an alkyl of 1–4 carbon atoms; n is 1–15; p is 0 or 1; and, when p is 1, R^5 is H or CH_3, and R^6 is H, CH_3 or C_2H_5; (2) an organic, radiation-sensitive, free-radical generating system comprising 2,4,5-triarylimidazolyl dimer and p-aminophenyl ketone; and (3) a macromolecular, organic, polymeric binder. A polymeric image is formed by imagewise exposing the layer to actinic radiation and then developing the resulting image such as by removing unexposed portions of the layer with a solvent. Appl. March 26, 1980.

U.S. 3,782,951. Photopolymerizable Compositions Capable of Yielding Reverse Images. E. I. Du Pont de Nemours and Company (January 1, 1974). Photopolymerizable compositions are described containing an ethylenically unsaturated monomer, an organic polymeric binder and, as the initiator system, a hexaarylbiimidazole and a hydrogen-donor compound. These inventive compositions are capable of yielding reverse photopolymer images since relatively intense radiation prevents polymerization, while less intense radiation yields photopolymerization. The first (intense) exposure is imagewise and the second (less intense) exposure is non-imagewise. The compositions are useful in the graphic arts where a positive-working system is required, e.g., for relief or planographic printing plates, direct positive copying films, and the like. Appl. July 31, 1972.

U.S. 6,929,895. Lithographic Printing Plate Precursor. Fuji Photo Film Co., Ltd. (August 16, 2005). A lithographic printing plate precursor comprising an aluminum substrate, an image-recording layer and a hydrophilic film, the aluminum substrate being subjected to an electrochemical surface-roughening treatment in an aqueous solution comprising hydrochloric acid and provided with the hydrophilic film having a heat conductivity of 0.05 to 0.5 W/mK and/or at least one of a density of 1,000 to 3,200 kg/m^3 and a porosity of 20 to 70%; and a lithographic printing plate precursor comprising an aluminum substrate, an image-recording layer and a hydrophilic film, the aluminum substrate having a surface-roughened shape comprising a small pit wherein an average opening size of the small pit is 0.01 to 3 μm and a ratio of an average depth of the small pit to the average opening size is 0.1 to 0.5, and being provided with the hydrophilic film having a heat conductivity of 0.05 to 0.5 W/mK and/or at least one of a density of 1,000 to 3,200 kg/m^3 and a porosity of 20 to 70%. Appl. December 23, 1997.

U.S. 6,514,668. Photosensitive Lithographic Printing Plate. Mitsubishi Chemical Corporation (February 4, 2003). A photosensitive lithographic printing plate having a photosensitive resin layer formed on an aluminum substrate subjected to electrolytic surface roughening in nitric acid or in an electrolyte composed mainly of nitric acid and further to anodic oxidation treatment, wherein the photosensitive resin layer is made of a photopolymerizable composition comprising (A) Ethylenic monomers, (B) 2,2′-Bis(o-chlorophenyl)-4,4′,5,5′-tetra(p-carboethoxyphenyl)-biimidazole. 2-Mercapto-benzothiazole, Ethyl N,N-dimethylbenzoate photopolymerization initiator, and (C) a polymer binder, wherein the addition-polymerizable ethylenically unsaturated bond-containing monomer, Copper phthalocyanine pigment and additives, (A) contains a phosphate compound having at least one (meth)acryloyl group. Appl. December 23, 199.

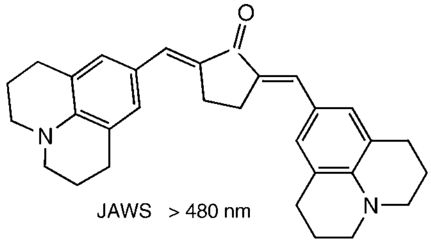
U.S. 6,514,657. Photosensitive Composition for Lithographic Printing Plate and Photosensitive Lithographic Printing Plate. Kodak Polychrome Graphics (February 4, 2003). The present invention provides a photosensitive lithographic printing plate with a long press life, high sensitivity, and excellent storage stability, and a photosensitive composition for a lithographic printing plate for producing such a photosensitive lithographic printing plate. The photosensitive composition for the lithographic printing plate includes (A) a binder resin, (B) a diazo resin, (C) a monomer or oligomer, a molecule of which has at least two polymerizable ethylenically unsaturated double bonds, (D) a photopolymerization initiator, (E) an o-tert-butylphenol derivative, and (F) a 2-mercaptoimidazole derivative such as 2-mercaptobenzimidazole. Claimed is (1) A photosensitive composition for a lithographic printing plate, comprising: (A) a binder resin; (B) a diazo resin; (C) a monomer or oligomer compound having at least two polymerizable ethylenically unsaturated double bonds; (D) a photopolymerization initiator; (E) an o-tert-butylphenol derivative; and (F) a 2-mercaptoimidazole derivative. A photosensitive composition for a lithographic printing plate according to claim (1), wherein said photopolymerization initiator is selected from the group consisting of: α-carbonyl compounds, acyloin ethers, α-hydrocarbon substituted aromatic acyloin compounds, polynuclear quinone compounds, combinations of a triaryl biimidazole and a p-aminophenyl, trihalomethyl-s-triazine based compounds, oxadiazole compounds, acridine compounds, phenazine compounds and benzothiazole based compounds. Appl. July 17, 2001.

U.S. 6,875,557. Plate-Making Method of Printing Plate. Fuji Photo Film Co., Ltd. (April 5, 2005). A plate-making method of a printing plate comprising exposing a printing plate precursor having a photosensitive layer comprising a photopolymerizable composition containing (i) a crosslinking agent having two ethylenic polymerizable groups and (ii) a crosslinking agent having three or more ethylenic polymerizable groups, and development processing the exposed printing plate precursor with an alkali developer having a pH of not more than 12.5. Claims the plate-making method of a printing plate wherein the photopolymerization initiator is a compound selected from (a) an aromatic ketone, (b) an aromatic onium salt compound, (c) an organic peroxide, (d) a thio compound, (e) a hexaaryl-biimidazole compound, (f) a ketoxime ester compound, (g) a borate compound, (h) an azinium compound, (i) a metallocene compound, (j) an active ester compound, and (k) a compound having a carbon–halogen bond. Appl. August 29, 2002.

U.S. 6,649,323. Overcoat for Light-Sensitive Materials Comprising (1-Vinylimidazole) Polymer or Copolymer. Kodak Polychrome Graphics LLC (November 18, 2003). A lithographic printing plate precursor comprises a substrate, a free radical polymerizable photosensitive layer comprising a light-sensitive composition on the substrate, and a water-soluble overcoat layer on the photosensitive layer, wherein the overcoat layer comprises polyvinyl alcohol, and a further component that is not amphoteric and is poly(1-vinylimidazole) or a copolymer of 1-vinylimidazole and at least one further monomer. The photosensitive layer comprises a free radical polymerizable component and a photoinitiator. Claims: a lithographic printing plate precursor comprising a substrate, a free radical polymerizable photosensitive layer comprising a light-sensitive composition, and a water-soluble overcoat layer coated onto the photosensitive layer, wherein the overcoat layer comprises polyvinyl alcohol and a component that is poly(1-vinylimidazole) or a copolymer consisting of units of 1-vinylimidazole and at least one monomer selected from the group consisting of vinylpyrrolidone, vinyl alcohol, vinyl acetate, vinylalkylether, hydroxyalkylacrylate, vinyl acetamide, vinyl formamide, acrylonitrile, acrylamide, methacrylamide and vinylamine and wherein the photosensitive layer comprises a free radical polymerizable component and a photoinitiator and wherein the photoinitiator is selected from the group consisting of acetophenones, benzophenones, (trichloromethyl)-1,3,5-triazines, benzoin compounds, xanthones, thioxanthones, acridines, and hexaarylbisimidazoles Appl. January 21, 2000.

15.7 HOLOGRAPHY

U.S. 5,096,790. Process of Forming Hologram and Polymeric Holographic Recording Medium with Sensitizer. E. I. Du Pont de Nemours and Company (March 17, 1992). A new class of sensitizers for photopolymerizable compositions is disclosed derived from cyclic ketones and tricyclic aminoaldehydes. A preferred compound is cyclopentanone, 2.5-bis[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)methylene].



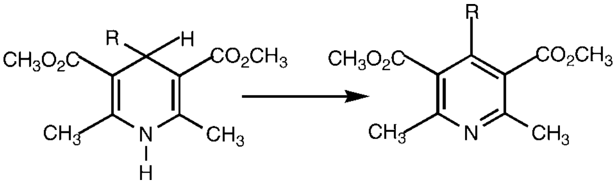
Appl. July 16, 1990. Coating recipe contains Polyox®, WSRN-3000, TMPTA 21.00, TMPEOTA, Poly(methyl methacrylate/ethyl acrylate/methacrylic acid) (51/29/20), Benzophenone, o-Cl-HABI, Leuco Crystal Violet, N-Phenyl glycine, Sensitizer (JAW).

16

PHOTOTACKIFICATION

The concept of generating a tacky surface by exposure has intrigued a number of scientists for many years. The discovery that various coatings containing acrylate monomers could be converted from tacky to non-tacky by light exposure, which was found to be useful for DuPont's CROMALIN® proofing system occurred in the 1960s. Systems in which the exposed area did not accept toner are positive-working, and a matching negative working system was considered to be useful in a range of applications, including proofing, manufacture of color television tubes, preparation of electronic components, etc.

DuPont scientists, primarily at the Company's Neu Isenburg (Germany) laboratory investigated the reaction between HABIs and dihydropyridine (DHP) derivatives, and found that HABIs oxidized DHP readily.



The photooxidized areas became tacky relative to the unexposed areas. As can be seen from the accompanying tables, in which typical recipes are compared, the coatings are relatively simple; the inclusion of a binder is optional.

The recipes appear to be quite simple, and it appears as though phototackification proceeds over quite a range of HABI:DHP concentrations (Table 16.1).

Preparation of the critical dihydropyridine is accomplished according to the Hantzsch synthesis is performed as follows: acetoacetaldehyde, acetoacetic acid *t*-butyl ester and ammonia are mixed to give the corresponding dihydropyridine in good yield. It can readily be seen that many related dihydropyridine derivatives can be easily prepared.

The reaction, identified as the PT-process, was discovered by Drs. W. Abele and M. Grossa. It offered a potentially attractive route toward a negative proofing system, with the advantage that a single coating. The perceived chemistry involved the change in the surface properties of the coating resulting from the oxidation of the dihydropyridine derivative. The author is not convinced that this is the correct explanation, as it was observed that under some conditions, with the same ingredients in different ratios, the system goes from tacky to non-tacky on exposure.

The system was conceived and developed as a negative proofing system. It offered the possibility to eliminate the multiple layers of photopolymer that were deposited in order to make a positive CROMALIN® surprint. Simply speaking, the areas that were exposed through

Table 16.1. Phototackification recipes

	U.S. 4,243,741			U.S. 4.271,260	U.S. 4,292,394	U.S. 4,346,162				U.S. 4,358,529					U.S. 4,461,822	U.S. 4,698,293	U.S. 4,716,095	U.S. 5,399,458
Patent example	1	2	3		3	1a	1b	2a	2b	1a	1b	1c	2a	2b	5	6		1a
Dihydropyridine compound	1	2	1	2	42.36	1.5		5		1		0.5	1	0.8	20.4	9	9	19
Hexaarylbis-imidazole compound(s)	2	3	2	2	90.43	3	3	2.8	2	2	2	2	2.5	2.5	43.5	22	4	37
Poly(ethyl acrylate)																		35
Stabilizer																		2
Polystyrene																		7
Polyepichloro-hydrine	7																	
Methacrylic acid ethyl ester–methacrylic acid copolymer		1.5						1.5	1.5									
Polyglycol hexadecyl ether		0.5						0.5	0.5									
Styrene/maleic acid anhydride copolymer			5															
Triethylene glycol diacetate			2															
Ethylacrylate copolymer of Degussa						2												
DEGALAN® copolymer							2											
Thiopropionyl anilide							1.5											
Benzophenone					6.5			0.3	0.3						3.13			

Table 16.1. (Continued)

	U.S. 4,243,741			U.S. 4.271,260	U.S. 4,292,394	U.S. 4,346,162				U.S. 4,358,529					U.S. 4,461,822	U.S. 4,698,293	U.S. 4,716,095	U.S. 5,399,458
Patent example	1	2	3		3	1a	1b	2a	2b	1a	1b	1c	2a	2b	5	6		1a
Thiopropionyl-*p*-ethoxyanilide									2.5					0.3				
ω-Thiocaprolactam									0.5									
Plexisol® B 372 (polyethylacrylate)										1	1	1	1.5	1.5				
Thiopropionyl-anilide											1	1						
Polystyrene																4		
Copolymer of methylacrylate and butylacrylate																20		
Phenolformaldehyde resin (Alnovol®)				10														
Cl Basic Blue 81				0.2														
Polymethylmethacrylate, of very high M.W.					42857													
Hydroquinone					1										0.48			
Polyoxyethylene-(4)-monolauryl-ether					15													
Triethylene glycol diacetate					8.57													
Polyethylene oxide					1										0.48			
Triethylene glycol diacetate															4.13			
Polymethylmethacrylate															20.6			
Polyoxyethylene-(4)-monolauryl-ether															7.22			

the lithographic negative became tacky on exposure, and could be toned; the toner would not adhere to the unexposed areas.

Comparison of the phototackification approach to a proofing product inevitably invited comparison with the established CROMALIN® proofing system, in which exposure to light effected detackification of the photopolymer layer.

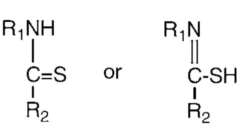
The difference in tackiness between exposed and unexposed areas in the PT system was found to be lower than that in the photopolymer system. PT systems are re-imageable in unexposed areas, making a single layer structure possible. Where images of color separations are overlapping, as is generally the case in, photosensitive PT toners or special PT-toners must be employed. Another option was to employ four laminates; however this resulted in slightly yellow background color. Additionally, there appeared to be a need for a fixing step with the higher speed PT systems; this could be obviated by the application of a protective laminate.

U.S. 4,243,741. Negative Tonable Systems Containing Dihydropyridines and Photooxidants. Abele, Werner; Grossa, Mario. E. I. Du Pont de Nemours and Company (January 6, 1981). Appl. December 21, 1978. A photosensitive element for preparing negative tonable images which comprises a support bearing a layer of a photosensitive composition comprising a thermoplastic binder, at least one dihydropyridine compound and at least one hexaarylbiimidazole compound. Optionally softeners and sensitizer can be present in the photosensitive layer. The photosensitive element is useful in preparing negative tonable images.

U.S. 4,292,394. Process for Preparing Multicolor Toned Images on a Single Photosensitive Layer. Chu, Victor F.H.; Riesenfeld, James (E. I. Du Pont de Nemours and Company). September 29, 1981. Process for preparation of multicolor images on a single negative-working photosensitive layer which comprises imagewise exposing the layer through a transparency to form tacky image areas; toning the tacky image areas with a toner which becomes swollen or solubilized upon contact with the tacky areas; buffing or rubbing the toned image areas until glossy; and repeating the exposing, toning and buffing or rubbing using a different image-bearing transparency and appropriate toner. The process is useful in preparing multicolor proofs, e.g., maps, textile and wall covering design proofs and samples, etc. Appl. December 31, 1979.

The inclusion of certain thio derivatives improved sensitivity of the system.

U.S. 4,358,529. Photosensitive Reproduction Elements for Forming Negative Tonable Images. Abele, Werner (E. I. Du Pont de Nemours and Company). November 9, 1982. A nonsilver photosensitive reproduction element which comprises a support bearing a layer of a photosensitive composition which comprises (1) at least one thermoplastic binder, (2) a photosensitive system consisting essentially of (a) a hexaarylbiimidazole compound and (b) a dihydropyridine compound; and optionally (3) a plasticizer, and (4) a thioamide, thiolactam or thiocarbanilic acid ester of the formula



$$R_1NH{-}C(=S){-}R_2 \quad \text{or} \quad R_1N{=}C(SH){-}R_2$$

The photosensitive element is useful in preparing negative tonable images. Appl. June 17, 1981.

Improved image density was achieved by modification of toners.

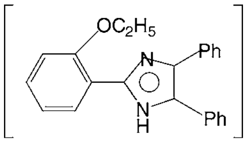
U.S. 4,461,822. Process for Toning Image-Wise Modified Surfaces. Abele, Werner (E. I. Du Pont de Nemours and Company). July 24, 1984. Process for toning imagewise tacky surfaces by multiple application of at least two toners containing different low melting compounds having a polar substituent and melting in the range of 25° to 110°C., which in contact with one another render the toners tacky at room temperature thus yielding higher color density or change of color tone. Appl. September 15, 1983.

In practice, this did not work too well as it was not possible to re-expose an already toned area and deposit another colored toner thereon. Thus, a cyan toned area could not be overtoned with a yellow toner to generate a green image color.

Subsequently, work was undertaken to make the toners themselves tackifiable, and this allowed then toner to be deposited over the previously toned areas.

> **U.S. 5,399,458. Process for Making Images Employing a Toner Which Has a Tackiness That can be Increased by Actinic Radiation.** Grossa, Mario; Tigler, Dieter; Metzger, Bernhard; Gallo, Paola (E. I. Du Pont de Nemours and Company). March 21, 1995. A process for preparing images, particularly color proof prints, in which tacky and non-tacky areas are produced by imagewise exposure of a radiation-sensitive layer is described. The tacky areas are toned with a toner having a tackiness that can be increased by irradiation with actinic radiation. Appl. August 10, 1993.

Another problem was that the original HABI/DHP system had a light yellow background, which was unsatisfactory for color proofing applications. This was resolved by replacing the o-Cl-HABI or CDM-HABI by o-alkoxy-HABIs, e.g., the dimer of (2-*o*-ethoxyphenyl)-4,5-diphenylimidazole.



o-Ethoxy-HABI

The system was also investigated for the manufacture of positive working printing plates and photoresists.

During the early 1990s, DuPont developed toning foils (EUROSPRINT®) for CROMALIN®. These could be successfully employed with the PT process.

> **U.S. 4,806,451. Process for the Production of Multicolor Proofs Using Precolored Toning Films.** Frohlich, Helmut H. (E. I. Du Pont de Nemours and Company). February 21, 1989. The invention relates to a process for producing an image on a light-sensitive tonable layer comprising the steps of: (A) exposing the light-sensitive layer imagewise to produce imagewise tacky and complementary non-tacky areas; (B) bringing the imagewise-exposed layer into surface-to-surface contact with a supported non-photosensitive transfer layer containing at least one finely divided powder and/or a dissolved dye in a binder; and (C) separating the transfer layer from the light-sensitive layer, whereby the transfer layer adheres selectively to the imagewise tacky areas, the improvement wherein, the binder of the transfer layer consists essentially of (a) about 55–97 wt. % of at least one polymer in the form of a powder having a minimum film-forming temperature of above 50°C., and (b) about 3–45 wt. % of at least one thermoplastic and/or one thermoplastic-elastomeric polymer, having a minimum film-forming temperature when used as a latex, or, a glass transition temperature when used as a dissolved polymer, which is at least 10°C. lower than the minimum film-forming temperature of polymer (a), whereby polymer phases (a) and (b) are incompatible. Appl. June 24, 1987.

And later

> **U.S. 5,126,226. Process for the Preparation of Images on Tonable, Light-Sensitive Layers.** Frohlich, Helmut H.; Fryd, Michael (E. I. Du Pont de Nemours and Company). June 30, 1992. A process for preparing images on a tonable, light-sensitive layer in which a transfer layer containing a toner and a core/shell polymer as a binder is used. The core polymer has a glass transition temperature above 50°C. and the shell polymer has a glass transition temperature below 40°C. Such transfer layers are used in proofing processes for high quality printing. Appl. December 3, 1990.

> **U.S. 4,271,260. Positive Nonsilver Washout Systems Containing Dihydropyridines and Photooxidants.** Abele, Werner; Grossa, Mario; Pilz, Otto. E. I. Du Pont de Nemours and Company (June 2, 1981). Appl. April 7, 1980. Process for preparation of positive images which comprises exposing imagewise a supported layer of a photosensitive composition comprising an alkali-soluble polymeric binder, at least one dihydropyridine compound and at least one hexaarylbiimidazole compound and developing by washing out the exposed image areas. Optionally auxiliary layers can be present between the support and photosensitive layer. The photosensitive elements are useful in preparing positive working printing plates and photoresists. Appl. April 7, 1980.

It was also possible to employ the DHP-HABI chemistry to generate positive mode images.

> **U.S. 4,698,293. Process for Forming Positive Tonable Images Using a Photosensitive Material Containing at Least 1,4-Dihydropyridine.** Grossa, Mario (E. I. Du Pont de Nemours and Company). October 6, 1987. A process for the production of patterns that consist of powders and that are positive with respect to the original is described, according to which a light-sensitive layer containing at least one 1,4-dihydropyridine compound is exposed imagewise, treated with a strong acid, post-exposed diffusely to produce tacky areas, and is subsequently toned. Appl. November 12, 1986.

Dr. Mario Grossa, one of the DuPont Neu Isenburg R&D scientists was asked to present a review paper describing the technology at an SPSE meeting in Washington, DC in 1979, and was approached by a research manager of the RCA Corporation, asking if DuPont had ever considered applying this technology to the manufacture of color television monitors. DuPont had not! As a matter of fact, few scientists were aware of how color TV tubes were manufactured: the process involved applying sequentially slurries of phosphors in an aqueous photopolimerizable medium, drying, exposing through masks, washing out the unhardened material and repeating the process until the green, red and blue phosphors had been positioned.

This process was complex, involving a great deal of washing, drying, etc., and RCA had already investigated other technologies to achieve the goal.

DuPont then undertook joint research with scientists at RCA's Sarnoff Laboratory in Princeton, NJ and progress was made until the takeover of RCA by General Electric Corporation caused this program to be terminated.

The program was then returned to Neu Isenburg, where Grossa made improvements, including the use of a novel nitro-dihydropyridine derivative. In order to minimize cross-contamination of phosphors a new invention was needed:

> **U.S. 4,716,095. Method for Reducing Color Cross-Contamination During Re-Imaging of Phototackifiable Materials.** Grossa, Mario (E. I. Du Pont de Nemours and Company). December 29, 1987. A process is described to improve the reproduction quality of multiply exposable negatively tonable light-sensitive reproduction materials containing at least one 1,4-dihydropyridine compound, wherein the light-sensitive layer is treated with a strong acid before the imagewise exposure. Appl. November 12, 1986.

Grossa and others had success in improving the system for the manufacture of colored TV tubes, but ultimately this technology was not commercialized, as the slower, more labor-intensive wet process was by that time fully automated, and tube manufacturers were not interested in establishing a new production path and associated equipment.

17

HABIS IN SILVER-BASED PHOTOGRAPHIC SYSTEMS

HABIs have been considered of primary interest as photo-polymerization initiators and photo-oxidants. It is surprising that over 50 U.S. patents exist that deal with HABIs in silver photographic systems. The first patent which described the use of HABIs in silver photographic system appeared in 1973.

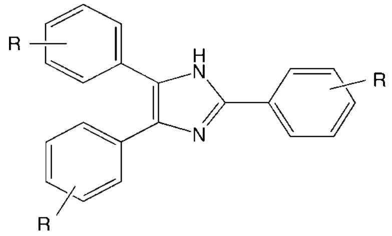
U.S. 3,734,733. Positive Working Photo-Thermographic Materials Containing Bi-Imidazolyl Compounds and Reducing Agents and the Use Thereof in Color Development. Albert Lucien Poot et al. AGFA-Gevaert, N.V. (Mortsel, BE) 5/22/1973. In a component thermog. copying system, 1 sheet is treated with a photosensitive biimidazolyl deriv., which may be spectrally sensitized with a cyanine dye, and a photooxidizable compd., such as a naphthol or a hydroquinone. The image-receiving sheet contains a compd. that will react with the photooxidizable compd. and a heat-sensitive reducing agent. Thus parchment is coated with 40 g/m^2 of a mixt. contg. bis[2-(o-chlorophenyl)-4,5-diphenylimidazole] 10, 4-methoxy-1-naphthol 1, and ethyl cellulose 10 g in 2-butanone 500 ml. After uv exposure through an original transparency the sheet was contacted for 5 sec at 125° with an image-receiving sheet of white paper coated with 0.2 mg/m^2 Ag as Ag behenate, 400 mg/m^2 phthalazinone, and 40 g/m^2 2,6-di-tert-butyl-4-methylphenol in poly(tert-butyl methylate) binder. A copy having a sharp pos. black image was obtained. App. 4/9/1970.

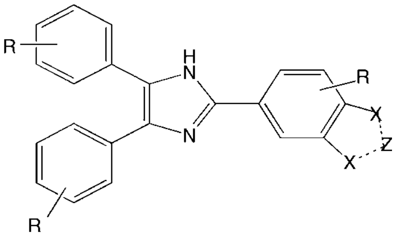
17.1 BLEACHOUT SYSTEMS

Beginning with U.S. 4,196,002, Eastman Kodak has patented photothermographic elements consisting of a heat bleachable material comprising (i) at least one hexaarylbiimidazole with (ii) at least one dye, especially an antihalation or filter dye.

U.S. 4,196,002. Photothermographic Element Containing Heat Sensitive Dye Materials. Levinson, Steven R.; Adin, Anthony. Eastman Kodak Company (April 1, 1980). A photothermographic element can comprise a support and on the support or in the support an antihalation or filter component that comprises a heat bleachable material comprising (i) at least one hexaarylbiimidazole with (ii) at least one dye, especially an antihalation or filter dye, that is reactive with the product of the hexaarylbiimidazole formed upon heating the material to a temperature above about 90°C. This provides an antihalation or filter material that becomes at least 40% colorless within about 20 minutes, typically within about 30 seconds, upon heating to a temperature as described. The antihalation or filter material can be a heat bleachable dye layer of a photothermographic element. Appl. October 23, 1978.

U.S. 5,672,562. Thermal Recording Element. Goswami, Ramanuj; Perry, Robert J.; Zielinski, Paul Anthony. Eastman Kodak Company (September 30, 1997). A thermal recording element comprising a support having thereon a dye layer comprising a polymeric binder containing: (a) a formazan dye that absorbs at from about 400 to about 850 nm, and (b) a hexaarylbiimidazole which is an oxidative dimer of a 2,4,5-triarylimidazole having one of the following formulas:





Filed: Appl. May 8, 1996.

Additionally, HABIs have been found useful in silver based photothermographic systems.

U.S. 6,576,410. High-Speed Thermally Developable Imaging Materials and Methods of Using Same. Zou, Chaofeng; Wilson, Robert D.; Daubendiek, Richard L.; Gersey, Timothy R. Eastman Kodak Company (Rochester, NY) June 10, 2003. High-speed black-and-white photothermographic emulsions and materials comprise chemically sensitized photosensitive silver halide grains, at least 70% of the total photosensitive silver halide projected area being provided by tabular silver halide grains comprising at least 70 mole % bromide (based on total silver halide). The tabular grains have an average thickness of at least 0.02 μm and up to and including 0.10 μm, an equivalent circular diameter of at least 0.5 μm and up to and including 8 μm and an aspect ratio of at least 5:1. These high-speed materials can be imaged in any suitable fashion using ultraviolet, visible, infrared, or X-radiation. In one embodiment, they have one or more thermally developable layers on both sides of the support and can be imaged using X-radiation with or without a phosphor intensifying screen in an imaging assembly. Particularly useful heat-bleachable, acutance, filter, anti-crossover, anti-irradiation, and/or antihalation compositions can include a radiation absorbing compound used in combination with a hexaarylbiimidazole (also known as a "HABI"), or mixtures thereof. Appl. July 11, 2002.

U.S. 6,573,033. X-Radiation Sensitive Aqueous-Based Photothermographic Materials and Methods of Using Same. Simpson, Sharon M., Moore, William E. Eastman Kodak Company (June 3, 2003). Aqueous-based photothermographic materials that are sensitive to visible or X-radiation contain X-radiation sensitive phosphors in association with specific chemically sensitized tabular silver halide grains. The silver halide grains comprise at least 70 mol % bromide, based on total silver halide, have an average thickness of at least 0.02 μm and up to and including 0.10 μm, an equivalent circular diameter (ECD) of at least 0.5 μm and up to and including 8 μm, and an aspect ratio of at least 5:1. These materials can be imaged in any suitable fashion but preferably they have one or more photothermographic layers on both sides of the support and can be imaged using X-radiation with or without an associated phosphor intensifying screen. Particularly useful heat-bleachable acutance, filter, cross-over prevention (anti-crossover), anti-irradiation and/or antihalation compositions include a radiation absorbing compound used in combination with a hexaaryl-biimidazole (also known as a "HABI"). Appl. July 11, 2002.

U.S. 4,499,304. Color-Forming Sulfonamidodiphenylamines and Corresponding Sulfonimide Dyes. Gabrielsen, Rolf S.; Graham, Patricia A.; Klijanowicz, James E.; Stern, Max H. Eastman Kodak Company (February 12, 1985). Color-forming para-sulfonamidodiphenylamines and their corresponding sulfonimide dyes are useful in imaging materials. The color-forming sulfonamidodiphenylamines are prepared by condensation reactions. The corresponding sulfonimide dyes are formed by oxidation of the color-forming sulfonamidodiphenylamines by means of a suitable oxidizing agent, such as the oxidized form of a cross-oxidizing silver halide developing agent. A color-forming compound of was used in an imaging element to provide a negative dye image. The imaging material contained the following composition coated on a poly(ethylene terephthalate) film support at the noted coverages: color-forming compound of and a lophine dimer represented by the formula. Appl. June 8, 1982.

Below, in Table 17.1 are listed U.S. patents containing both HABIs and silver systems.

Table 17.1.

Patent No.	Assignee	Title
3,734,733	AGFA-Gevaert	Positive working photo-thermographic materials containing biimidazolyl compounds and reducing agents and the use thereof in color development
4,196,002	Eastman Kodak Co.	Photothermographic element containing heat sensitive dye materials
4,201,590	Eastman Kodak Co.	Heat sensitive reactive products of hexaarylbiimidazole and antihalation dyes
4,411,984	Eastman Kodak Co.	Dye precursors and their use in photographic materials and processes
4,499,304	Eastman Kodak Co.	Color-forming sulfonamidodiphenylamines and corresponding sulfonimide dyes
4,552,980	Eastman Kodak Co.	Dye precursors and their use in photographic materials and processes
4,579,808	DuPont	Imageable colloidal metal/mercaptan elements
4,584,261	DuPont	Process for etching nonphotosensitive layer under washoff photopolymer layer
4,654,296	DuPont	Process for making lithographic film using photopolymer diffusion modulation layer for pigmented bottom layer
4,764,451	Fuji Photo Film Co., Ltd.	Image-forming method employing light-sensitive material containing silver halide, reducing agent, polymerizable compound and a photopolymerization initiator
4,871,643	Fuji Photo Film Co., Ltd.	Image-forming method employing light-sensitive material and image-receiving material comprising microcapsules and specified paper support
4,876,170	Fuji Photo Film Co., Ltd.	Image-forming method employing light-sensitive material and image-receiving material comprising microcapsules and specified paper support
4,876,173	Fuji Photo Film Co., Ltd.	Light-sensitive material comprising light-sensitive layer containing microcapsules provided on specific paper support
4,879,201	Fuji Photo Film Co., Ltd.	Method of making a lithographic plate comprising microcapsules
4,912,011	Fuji Photo Film Co., Ltd.	Image-recording method comprising heating a light-sensitive material containing microcapsule
4,923,389	DuPont	Negative working low silver wash-off contact film
4,987,050	Fuji Photo Film Co., Ltd.	Light-sensitive transfer material and image-forming process using the same
5,030,541	Fuji Photo Film Co., Ltd.	Image-forming method using a light-sensitive material
5,049,480	DuPont	Photosensitive aqueous developable silver conductor composition
5,089,370	Fuji Photo Film Co., Ltd.	Light-sensitive material comprising light-sensitive layer provided on support
5,118,590	Fuji Photo Film Co., Ltd.	Light-sensitive microcapsule containing polymerizable compound and pigment particles
5,176,981	Fuji Photo Film Co., Ltd.	Light-sensitive transfer material and image-forming method employing the same
5,227,274	Fuji Photo Film Co., Ltd.	Process for preparation of light-sensitive material containing microcapsules
5,254,428	Fuji Photo Film Co., Ltd.	Process for preparation of light-sensitive microcapsule

Table 17.1. (Continued)

Patent No.	Assignee	Title
5,275,927	Minnesota Mining and Manufacturing Company	Photothermographic articles containing novel barrier layers
5,296,331	Fuji Photo Film Co., Ltd.	Image receiving material containing particles of thermoplastic compound
5,498,504	AGFA-Gevaert	Process for the preparation of an image using only dry steps
5,629,130	AGFA-Gevaert	Method for the formation of a heat mode image
5,719,005	AGFA-Gevaert	Method for the formation of an improved photo mode image
6,403,294	Fuji Photo Film Co., Ltd.	Silver halide photographic material
6,548,233	Eastman Kodak Co.	Thermally developable emulsions and imaging materials containing mixture of silver ion reducing agents
6,558,874	DuPont	Photosensitive silver conductor tape and composition thereof
6,573,033	Eastman Kodak Co.	X-radiation sensitive aqueous-based photothermographic materials and methods of using same
6,576,410	Eastman Kodak Co.	High-speed thermally developable imaging materials and methods of using same
6,599,685	Eastman Kodak Co.	Thermally developable imaging materials having improved shelf stability and stabilizing compositions
6,605,418	Eastman Kodak Co.	Thermally developable emulsions and materials containing phthalazine compounds
6,620,577	Eastman Kodak Co.	High speed photothermographic materials containing selenium compounds and methods of using same
6,630,291	Eastman Kodak Co.	Thermally sensitive imaging materials containing phthalazine precursor
6,638,687	Fuji Photo Film Co., Ltd.	Method for preparing lithographic printing plate
6,645,706	Eastman Kodak Co.	Thermally developable materials with improved speed and contrast and methods of use
6,667,148	Eastman Kodak Co.	Thermally developable materials having barrier layer with inorganic filler particles
6,689,546	Eastman Kodak Co.	Thermally developable materials containing backside conductive layers
6,689,547	Eastman Kodak Co.	Thermally developable imaging materials with improved image uniformity
6,699,647	Eastman Kodak Co.	High speed photothermographic materials containing tellurium compounds and methods of using same
6,703,191	Eastman Kodak Co.	Thermally developable emulsions and materials containing tirazine-thione compounds
6,713,240	Eastman Kodak Co.	Black-and-white aqueous photothermographic materials containing mercaptotriazole toners
6,713,241	Eastman Kodak Co.	Thermally developable emulsions and imaging materials containing binder mixture
6,730,461	Eastman Kodak Co.	Thermally developable imaging materials with reduced mottle providing improved image uniformity
6,737,227	Eastman Kodak Co.	Thermally developable emulsions and materials containing heterocyclic disulfide compounds
6,746,831	Eastman Kodak Co.	Thermally developable imaging materials with barrier layer containing a cellulose ether polymer

Table 17.1. (Continued)

Patent No.	Assignee	Title
6,770,428	Eastman Kodak Co.	Photothermographic materials containing high iodide core-shell emulsions
6,803,177	Eastman Kodak Co.	Silver compounds and compositions, thermally developable materials containing same, and methods of preparation
6,841,343	Eastman Kodak Co.	Black-and-white organic solvent-based photothermographic materials containing mercaptotriazole toners
6,844,145	Eastman Kodak Co.	High-speed thermally developable imaging materials and methods of using same
6,849,392	Eastman Kodak Co.	Thermally developable emulsions and materials containing triazine-thione compounds
6,942,960	Eastman Kodak Co.	Photothermographic materials containing doped high iodide emulsions
6,964,842	Eastman Kodak Co.	Black-and-white aqueous photothermographic materials

18

GRAVELL'S CONTRIBUTION TO THE RECORDING OF WATERMARKS

Occasionally a technical development falls into the hands of an artist or scholar who has no interest in the chemistry or physics of the process, but can apply it to an area that challenges his special interests. Thus it was that a scholar, Thomas Gravell, who died in 2004, added immensely to the research of watermarks and paper technology—because he had heard about DYLUX® proof paper. Here is an instance, where HABI, a unique chemical, touches a community of scholars, who know nothing of chemistry!

The digitization of documents generally addresses their informational content, i.e., text and pictorial information, but little attention is paid to the substrate, whether it is paper, parchment, film or other materials. The age of the document can often be better understood by an analysis of the material, but in general this involves costly and complicated chemical and physical investigations.

One useful tool for gaining more insight into the substrate is to analyze watermarks, where these are present. Until the nineteenth century, paper was handmade on molds, wood-framed rectangular grids of brass-wire sieves that captured the plant fibers destined to make up the sheets of paper while allowing the water in which the fibers had been macerated to escape [1].

From the thirteenth century onward, European paper mills identified their products through distinctive watermarks. Watermarks are designs impressed into the paper during its manufacture by wires that are bent into desired shapes and then sewn onto the mould, normally centered in its right half. In addition to watermarks, some manufacturers also used countermarks, smaller designs, words, or initials made in the same way as watermarks and affixed in the center of the left half of the mould. Where the wires of the watermark—and, if present, the countermark—occur, the resulting paper is thinner than it is elsewhere, and the resulting watermark (and countermark), more translucent than its surroundings, and can be seen by holding the paper up to the light. Generations of philatelists dipped stamps into benzene and held the transparentized paper up to bright light—but they had no permanent record.

18.1 TECHNIQUES FOR STUDYING WATERMARKS

Until forty years ago, the only way of recording watermarks for comparative study was through tracing or freehand sketching. Since tracing may harm a document, librarians and archivists objected to this method of reproducing watermarks. In addition, tracings also fail to record some of the minute details in the watermarks that can assist the investigator in making exact matches. The same is true of free-hand sketches, even when the sketcher uses calipers to ensure exact measurements. Moreover, any writing or printing on the paper often obscures the watermark to the naked eye and further limits its accurate reproduction. Several methods of recording watermarks are now available to reproduce them exactly in all their details without damaging the documents in which they occur including β-radiography, the Ilkley technique, and Gravell's DYLUX® method.

Gravell developed the use of DYLUX® 503 proof paper, sold by DuPont as a medium for recording watermarks in the early 1970s. It is by far the simplest and least expensive technique and has thus been widely adopted.

18.2 DYLUX® 503 PROOF PAPER

DYLUX® paper is a light sensitive product, which can be handled in subdued light. It consists of a coating, which contains a complex mixture of chemicals, which can selectively react with ultraviolet light to form a color, or with visible light to stabilize the image. The reaction schemes indicate how these materials function. When visible light impinges on the photosensitive layer, it results in the formation of a reduction product which interacts with any radical that is formed by subsequent ultraviolet light irradiation, and prevents color formation. It is thus possible to form either positive or negative images, depending on the exposure sequence.

The color-forming and deactivation processes have relatively low gamma, showing excellent continuous tone. The imaging process results in the formation of dyes, that are stable under normal storage conditions. DYLUX® proof paper is employed in the printing industry to evaluate the quality of lithographic negatives for pinholes, positioning, text, etc. The paper is exposed with ultraviolet light through a lithographic negative, where it yields a cyan pattern; which when left in ambient light is "fixed". Alternatively, if the lithographic negative is exposed initially to visible light, the exposed areas are desensitized, and the unexposed areas can be converted to color by a flooding ultraviolet exposure, resulting in a positive mode image.

18.3 WATERMARK RECORDING WITH DYLUX® 503 PROOF PAPER

Gravell employed DYLUX® paper to study watermarks of postage stamps [3]. Many stamps printed in the 19th century and early 20th century were printed on watermarked papers on sheet-fed presses. When the paper was inserted incorrectly, the watermark was reversed, making such stamps more rare and more valuable. Gravell simply positioned the stamp over the DYLUX® paper in good contact, and exposed with visible light and "developed" the watermark by a subsequent flooding exposure with ultraviolet light.

Starting about 1975, Gravell shifted his attention to the recording of watermarks of historical documents [4], initially in Delaware, and later all over the United States. He published extensively, and demonstrated his approach to recording of watermarks in many important libraries, such as the Folger Library, the Library of Congress, etc. He published a number of books on the watermarks of European and American papers. Many scholars of paper and documents employed his technique. A DYLUX® film product has also been available, and Gravell showed that watermarks recorded on this film could be superimposed over other film or paper recordings of watermarks, to identify subtle changes.

In Gravell's publications, the contact prints were reproduced for publication photographically, using a red filter to heighten the contrast between the light and dark tones (yellow and blue) in the DYLUX contact print. In this electronic archive, scanning the contact prints in color and saving the red channel accomplished the same effect.

Gravell's studies were primarily qualitative, as he lacked equipment to quantify his work. He donated his collection of watermarks to the University of Delaware and Virginia Technical University, where it can be viewed on a website, identified as the Gravell Archive (http://www.gravell.org). This facile way of recording watermarks was widely used by others. In addition to journal publications he collaborated on three books. The database includes digital images of photographic reproductions of over 6500 watermarks in paper made between 1400 and 1835 which form part of the Thomas Gravell Watermark Collection at the University of Delaware Library.

18.4 EXTENSIONS OF GRAVELL'S WORK

The availability of computer-driven scanners allows the duplication of the DYLUX® image quite easily to form colored images, which are more light stable and permanent than the DYLUX® images, either with laser or ink-jet printers. Additionally, modern electrostatic printers may be employed to make permanent images on film or paper; under some conditions, such exposures can be made so as to increase visual contrast over that of the original DYLUX® image. Here it is also possible to generate a black/white transparency, which may be superimposed over a watermark recorded on DYLUX® paper for comparison purposes.

Gravell's method involves the sequence of imagewise exposure with visible light followed by ultraviolet light to form positive images.

Image formation with UV light, and ambient light stabilization of the image background can also be considered. In this case, the thin part of the watermark reproduces as dark against a light field. In my work of the study of the watermarks of the classic stamps of Bermuda, I have preferred this method. For most stamps, an exposure of 1 minute to an exposure unit containing several black light fluorescent lamps is required. Additionally, it was found that paper thickness of different printing runs of such stamps can be easily compared and differentiated, by measuring the amount of cyan (blue) color formed during the exposure. The measurement of the amount of color generated is easily accomplished with a densitometer, which records the amount of reflected light. DYLUX® 503 is designed to reach a reflectance density of 1.4; differences of 0.1 are readily discernible with the naked eye, or recorded digitally with the densitometer. Different printing runs of a particular stamp, printed on different paper, dyed with different dyes can be readily discerned.

In some cases, as many as ten printings of stamps were made, sometimes using different paper stock, different colored papers and different inks. Naturally, some of these printing runs were very short, and hence, the stamps of these have more value.

REFERENCES

[1] For a discussion of the background of watermarks, I am indebted to publications by Prof. T.-L. Pebworth of the Univ. of Michigan.

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[3] T.L. Gravell, "Wartermarking stamps on cover", in: Stamps, March 20, 1971, p. 646.

[4] T.L. Gravell, "A safe, inexpensive way to make prints from glass negatives", Restaurateur 2, 185–190, (1978); "Reproducing watermarks for study", Restaurateur 2, 95–104 (Copenhagen, Denmark); T.L. Gravell and G. Miller, A Catalogue of American watermarks 1690–1835, Garland Reference Library of the Humanities, vol. 15, Garland Publishing, Inc., New York and London, 1979; Catalogue of foreign watermarks found on paper used in America 1700–1835, Garland Reference Library of the Humanities, Garland Publishing, Inc., New York and London, 1979.

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THE ROLE OF PATENTS IN THE DEVELOPMENT OF HABI TECHNOLOGY

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The United States Constitution gives Congress the power "To promote the Progress of Science and the useful Arts, by securing for limited Times to Authors and Inventors the exclusive Right to their respective Writings and discoveries." Rather than exercise this power itself, Congress has delegated the power to grant patents to the Patent and Trademark Office, which grants patents within a statutory framework established by Congress. To fully appreciate the role that patents played in the development of HABI technology, some basic understanding of the patent law is necessary. In addition, it is important to understand what a patent is, and, equally important, to understand what a patent is not.

Patents may be granted for compositions of matter, processes, machines, and articles of manufacture. Thus, a single "discovery" can produce more than one patent. If the discovery is a new material, for example, a composition of matter patent might be obtained on the material itself. In addition, patents might be obtained on a process for making the material, a process for using the material, and an article of manufacture containing the material. If an improved process for making or using the material is discovered later, additional patents might be obtained on the improved process. If a new process for making the material or a new use for the material is discovered later, additional patents might be obtained on the new processes for making the material, the new use for the material, and/or new articles of manufacture containing the material. Thus, a single discovery can produce a patent estate containing a large number of patents, each directed to a different aspect of the discovery, as well as patents on improvements and new uses for the discovery. In the typical situation, the basic patent or patents, such as composition of matter patents that dominate all uses of the claimed compounds, are obtained first or at least early in the life of the technology. Then the life of the patent estate is extended by later obtained improvement patents, article of manufacture patents, and method patents.

An example of this is the discovery of a previously unknown dye for use in a conventional silver halide photographic film. This discovery could produce a patent on the dye itself (composition of matter), a patent on a process for making the dye, a photographic film containing the dye (article of manufacture), and a process for making an image by exposing and developing the photographic film containing the dye. If it were later discovered that the dye was also useful in photopolymerizable compositions, additional patents might be obtained on photopolymerizable compositions that contain the dye as well as on a process for making an image by exposing and developing the photopolymerizable composition containing the dye. If the resulting image had a number of uses, for example as a photoresist, as a color proof, as a holographic image, and as a printing plate, patents might be obtained on each of these uses.

Contrary to popular belief, a patent does *not* give the patent owner the right to practice the invention. A patent only gives the patent owner the right to exclude others from making, using, selling, or offering for sale the patented invention in the United States or importing the patented invention into the United States. Performance of any of these acts without permission from the patent owner is an infringement of the patent. The patent owner may seek damages from the infringer in Federal Court and may ask the court to order the infringer to stop its infringing activities.

Further, a patent is not necessary for an inventor to practice an invention. Although a patent would protect the invention, the inventor need not go to the time and expense to obtain a patent if he or she has no desire to prevent others from practicing the invention. Provided the invention does not infringe someone else's patent and provided practice of the invention is not prohibited by some other law, such as a product safety law, an inventor can begin to practice an invention immediately, without applying for, or obtaining, a patent.

Because a patent does not give the owner of a patent the right to practice the invention, a patent owned by another party may prevent an inventor from practicing his or her own invention. In the example given above, the composition of matter patent on the dye would dominate all uses of the dye. If the composition of matter patent on the dye were owned by one party and the patents on the use of the dye in photopolymerizable compositions were owned by a different party, neither could practice the invention without the consent of the other. The owner of the patents on the use of the dye in photopolymerizable compositions would be unable to practice the invention without infringing the composition of matter patent. And the owner of the composition of matter patent would be unable to use the dye in photopolymerizable compositions without infringing the patent on the use of the dye in photopolymerizable compositions.

Only the inventor or inventors may receive a patent, so the application for a patent must be made either by the inventor or, in cases in which the invention is owned by someone else such as an employer, in the name of the inventor. At the time the original HABI applications were filed, the law required that every inventor named in a patent application have made a contribution to every claim of the patent. Because a patent was invalid if the inventorship was incorrect, attorneys were reluctant to name more than one inventor, even when the invention had been developed by a team of researchers. Consequently, most of the early HABI patents list only a single inventor even though most were the result of the efforts of a research team.

By the 1980's, Congress finally realized that the notion of the lone inventor working in his or her garage to solve some problem no longer applied to a large amount of research. Many inventions were the product of the collaborative inventive endeavors of a number of people working together in large corporate research organizations, a phenomenon that had begun about a century earlier with Thomas Edison's research laboratory. The law was changed so that anyone who made a contribution to one claim of the patent was a coinventor of the patent. The law was also changed to allow mistakes in determining inventorship to be corrected, provided the original inventorship determination had been made in good faith.

To obtain a patent, the inventor files a patent application with the United States Patent and Trademark Office and pays the appropriate fees. The application contains a specification, in which the applicant is required to describe the invention, enable a person familiar with the technology to which the invention pertains or is most nearly connected to practice the invention, and disclose the "best mode" contemplated by the inventor for practicing the invention. Drawings may be included to aid in an understanding of the invention. The application must also contain one or more claims that "particularly point out and distinctly claim" what the inventor regards as the invention. Typically, an application contains a number of claims of varying scope.

The claims define the invention. They delineate the scope of protection granted to the patent owner. Claims are sometimes compared to the legal description in a deed. Like the legal description in the deed, they define the metes and bounds of the property right granted to the patent owner. The patent owner has the right to exclude others from practicing the invention defined by the claims, and only from the invention defined by the claims.

Because the applicant must describe how to make and use the invention, patents often contain extensive amounts of information that is well known. In the example discussed above, for example, the patent that claims a photographic film containing the dye would contain an extensive description of how to make and use photographic film. And the patent that claims a photopolymerizable composition containing the dye would contain an extensive description of how to make and use photopolymerizable compositions. Someone who read the specification without reading the claims might conclude that the patent covered considerably more than it actually did or might wonder how the inventor had succeeded in obtaining a patent on so much that was well known.

Once the application has been received by the Patent Office, it is assigned to a patent examiner, who determines if the application and the claims satisfy the statutory requirements for a patent. To be patentable, an invention must be new, must be useful, and must not be obvious to an individual familiar with the area of technology to which the invention pertains. The examiner conducts a search of the relevant literature and renders an opinion, known as an Office Action, as to whether the invention satisfies these requirements. If the examiner finds that the application and the claims that define the invention satisfy the statutory requirements, the application is allowed. The applicant pays an issue fee and the patent is granted.

However, patent examiners almost invariably reject the application in the initial Office Action. This typically starts a dialog between the examiner and the applicant. The applicant can amend the claims, argue the rejection, and/or present additional evidence as to why the invention is patentable. If no agreement is reached, the applicant can appeal the examiner's action, first to an appeal board within the Patent Office, and eventually to the courts.

After the application is filed, it may be a year or more before the initial Office Action. The applicant may take up to six months to respond to each Office action, and the examiner may take several months to respond to each of the applicant's responses. Therefore, it is typically two to four years between the filing date of an application and the issue date of the patent.

At the time the original HABI patent applications were filed, the term of a patent was seventeen years from the issue date of the patent. When the patent term ends, the patent owner's right to exclude others from practicing the invention expires. The invention is now in the public domain and anyone may practice it, provided, of course, that practice of the invention does not infringe some other patent and is not prohibited by some other law. Consequently, for inventions that were likely to become more valuable as time progressed, the applicant had an incentive to delay the Patent Office proceeding in order to delay the issue date of the patent and, thus, delay the date that the patent rights would expire. Applicants were typically able to delay a few months by not taking any required action, such as responding to an Office Action or paying an issue fee, until its due date.

However, the system was open to abuse. By taking advantage of a number of Patent Office procedures, some applicants were able to delay their issue dates for years so that basic patents issued well after the technology to which they related had been developed commercially by others. Because pending applications were held in secret by the Patent Office, others in the industry did not know about the applications until the patent issued. In one notorious case, a series of basic patents issued nearly four decades after the original application was filed. These patents were referred to as “submarine patents” because they remained hidden until they “surfaced” unexpectedly and surprised the entire industry. In 1995, Congress changed the law so that patents expire twenty years from their filing date, rather than seventeen years from their issue date. In addition, most pending applications are published eighteen months after their filing date. Consequently, applicants can no longer extend their patent rights or conceal their pending applications by delaying prosecution of their applications.

There were also some applications that had prolonged prosecutions through no fault of the applicant. Appeals, for example, typically took at least a year, and sometimes several years, to be decided. Sometimes the Patent Office would request additional information about the invention that might take the applicant some time to assemble. More recent changes in the law have provided for an extension of the patent terms to account for delays in prosecution caused by the Patent Office. However, the length of the extension is reduced by the delays caused by the applicant, encouraging the applicant to expedite prosecution.

The application that eventually matured into the basic HABI patent was filed March 21, 1962. The application listed Lawrence Cescon, who had begun the investigation of hexaphenylbiimidazoles and prepared a number of substituted hexaphenylbiimidazoles, as the inventor. The claims were composition of matter claims that broadly claimed 2,4,5-triphenylimidazoyl radicals and their dimers, 2,2′,4,4′,5,5′-hexaphenylbiimidazoles. Because the dimers of the unsubstituted triphenylimidazole had previously been reported in the literature, the broad claims were limited to compounds in which the phenyl group bonded to the carbon atom in the 2-position of the imidazole ring (the carbon atom between the two nitrogen atoms) had a substituent in the *ortho*-position with a sigma value below 0.7. Preferred groups were alkyl, alkyoxyl, chloro, bromo, and fluoro. Each of the three phenyl groups could also be optionally substituted with up to three other substituents. There were also claims to nine specific hexaphenylbiimidazoles, among which were: 2,2′-bis(*o*-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole [“o-chloro-HABI”]; 2,2′-bis(2,4-dichlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole, and 2,2′-bis(*o*-methoxyphenyl)-4,4′, 5,5′-tetraphenyl-1,2′-biimidazole.

The original application was filed before the HABI-containing imaging systems had been discovered. Photochromic systems were the contemplated use. The application disclosed that “The [2,4,5-triphenylimidazoyl] radicals and the dimers are stable and form a photochromic system, finding utility as components in sun shields or shades.” Specific uses mentioned were automobile windshields and spectacle lenses.

In the initial prosecution, the examiner indicated that the compounds were not patentable over known materials. According to Dr. Dessauer, “The examiner told us that similar imidazoles had been reported to give off light when heated, and what we had showed no novelty over the prior art. I replied that the phenomenon that we had invented was photochromism, a color change induced by light, as in certain organisms like salamanders, while what he cited was chemiluminescence, a phenomenon attributed to fireflies. Since fireflies are different from salamanders, a patent should be granted."

Following this lucid explanation of the subtle difference between photochromism and chemiluminescence, the examiner withdrew this rejection. However, the examiner indicated that a patent could be granted only if the 2,4,5-triphenylimidazoyl dimer could be chemically identified. At the time, the only way to do this was by X-ray crystallography. Although X-ray crystallography is now essentially a routine method of structure determination, at the time it was a long and tedious process. A single crystal had to be grown, and numerous reflections recorded on photographic film. Each film had to be individually read with a densitometer. Then the structure was calculated with the help of a mechanical calculator. An entire Ph.D. thesis, experimental work of several years, might be devoted to the determination of a structure of a single molecule.

The Patent Office suspended prosecution of the application for several years while a structure determination was carried out. The structure of the *o*-bromophenyl dimer [2,2′-bis(*o*—bromophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole] was subsequently determined and submitted to the Patent Office, and the claims of the application were allowed. Consequently, the basic HABI patent, U.S. Patent 3,784,557 (to Lawrence Anthony Cescon), "Phototropic 2,4,5-Triphenylimidazolyl Radicals and Dimers Thereof," did not issue until January 8, 1974, nearly *twelve years* after the filing of the initial application.

Because of the examiner's request for a chemical identification of a dimer, prosecution of the basic application lasted eight or nine years longer than that for a typical application. This meant that the basic composition of matter patent, which would dominate all uses of the claimed *ortho*-substituted 2,4,5-triphenylimidazoyls and their dimers, did not expire until January 8, 1991. Until that date, DuPont could exclude others from making, using, selling, or offering for sale in the United States or importing into the United States any of these *ortho*-substituted hexaphenylbiimidazoles as well as any product containing any of these *ortho*-substituted hexaphenylbiimidazoles, regardless of its use. Because a patent does not give the patent owner the right to practice the invention, even if others discovered and patented other uses for these *ortho*-substituted hexaphenylbiimidazoles, they would be unable to practice their inventions in the United States until the basic composition of matter patent expired.

By the time the basic patent issued, imaging products using HABI chemistry had been on the market for five years. No competitors were forced out of the market when this patent issued, however, because DuPont had patented HABI-containing imaging systems in a number of other patents. Before the basic patent issued, DuPont had already obtained almost fifty other patents on various aspects of HABI technology. These patents were derived from applications that had been filed years after the basic HABI patent had been filed, but which had issued before the basic HABI patent issued. This was just the reverse of the usual situation in which the basic composition of matter patent is obtained early in the patent program and the life of the patent estate is extended by later obtained article of manufacture and method patents. In this case, the basic patent issued after a considerable patent estate had been assembled.

The first DuPont HABI-related patent to issue was U.S. Patent 3,383,212 (to Alexander Maclachlan), "Photographic Process Utilizing Composition Comprising an Oxidatively Activatable Color Generator, Thermally Activatable Oxidant and a Redox Couple" issued May 14, 1968, nearly six years earlier, from an application filed April 29, 1964, more than two years after the basic HABI application was filed. This patent claimed a two-step process for forming a visible image. In one step, a colored image was formed by oxidizing a leuco dye using a thermally activated triphenylimidazoyl radical. In the other step, the dimer not used to form the image was photochemically deactivated by a reductant. The first step, which could be either the thermal or the photochemical step, was carried out in imagewise fashion. Depending on which step was carried out first, either a positive image or a negative image could be obtained. No product based on this patent was ever introduced.

The second HABI patent, U.S. Patent 3,390,994 (to Lawrence Anthony Cescon), "Photodeactivatable Light-Sensitive Color-Forming Composition," issued July 2, 1968, from an application filed February 17, 1966. This patent also claimed a two-step imaging process in which the sense of the image could be reversed by reversing the order of the steps. However, one step was irradiation with ultraviolet light, and the other step was irradiation with visible light.

This patent was one of several patents on an image formation process in which a photochemically generated triphenylimidazoyl radical oxidized a leuco dye. This technology was commercialized by DuPont as the DYLUX® proofing system. The patent issued before another patent on leuco dye oxidation, U.S. Patent 3,445,234 (to Lawrence Anthony Cescon and Rolf Dessauer), "Leuco Dye/Hexaarylbiimidazole Image-Forming Composition," which had been originally filed earlier, October 31, 1962, but did not issue until May 20, 1969. Although these patents expired July 2, 1985, and May 20, 1986, respectively, the DYLUX® proofing system was still protected for another four and a half years by the basic HABI patent, which, as noted above, did not expire until January 8, 1991, and dominated all uses of the *ortho*-substituted hexaphenylbiimidazoles recited in the claims.

As the time the HABI technology was being developed, DuPont was also developing photopolymer technology and building a photopolymer-related patent estate. The first patent to claim the use of hexaphenylbiimidazoles in photoinitiator systems for photopolymer imaging systems was U.S. Patent 3,479,185 (to Vaughan Crandall Chambers, Jr.), "Photopolymerizable Compositions and Layers Containing 2,4,5-Triphenylimidazole Dimers," issued November 18, 1969, from an application filed March 4, 1966. This was the tenth HABI-related patent to issue. The claims of this patent were generally directed to compositions containing a polymerizable monomer and a photoinitiator system comprising a 2,4,5-triphenylimidazolyl dimer and a free-radical-producing hydrogen donor, and to a process for imagewise irradiating the composition to form an image. Because the only use for the previously known, unsubstituted HABI was in photochromic systems, this patent, as well as a number of the other use patents, was able to claim use of a broader range of hexaphenylbiimidazoles than was recited in the basic composition of matter patent. The first claim of this patent recited an imaging system that contained "a 2,4,5-triphenylimidazoyl dimer consisting of two lophine [2,4,5-triphenylimidazoyl] radicals bound together by a single covalent bond." Not only was use of the unsubstituted 2,4,5-hexaphenylbiimidazole in photoinitiator systems included in the claim, the claim covered the use of all possible 2,4,5-triphenylimidazolyl dimers in these photoinitiator systems.

Despite its efficiency, the HABI photoinitiator system had several disadvantages. The original hexaphenylbiimidazoles had little absorption in the visible region of the spectrum, so imaging had to be carried out with ultraviolet radiation. And the system did not absorb as strongly as could be desired. Solutions to these problems led to a whole series of "improvement patents" which rounded out the patent estate and extended its life.

An important discovery was that other materials, which absorbed the imaging radiation and sensitized the dissociation of the dimer to triphenylimidazoyl radicals, could be added to improve the efficiency of the imaging reaction. U.S. Patent 3,549,367 (to Catherine Tehlin Chang and Roxy Ni Fan), issued November 22, 1970, "Photopolymerizable Compositions Containing Triarylimidazolyl Dimers and *p*-Aminophenyl Ketones Compositions," and U.S. Patent 3,552,973 (to David S. Fishman), issued January 5, 1971, "Light Sensitive Hexaarylbiimidazole/*p*-Aminophenyl Ketone Compositions" claimed imaging systems in which *p*-aminophenyl ketones, such as Michler's ketone and its ethyl analog, were used in imaging systems. Because *p*-aminophenyl ketones absorbed strongly in the ultraviolet and were efficient sensitizers of HABI disassociation, much less HABI was required for efficient imaging.

Another important extension of the HABI patent estate was the discovery that certain compounds in which the phenyl groups in the 4- and 5-positions of the imidazole ring (the two adjacent carbon atoms) had different substituents were sensitive to longer wavelengths of the spectrum and, thus, improved imaging speed. This led to two patents on the "unsymmetrical HABIs," U.S. Patent 4,252,887, issued February 24, 1981, and U.S. Patent 4,311,783, issued January 19, 1982 (both to Rolf Dessauer), both entitled "Dimers Derived from Unsymmetrical 2,4,5-Triphenylimidazole Compounds as Photoinitiators" and both derived from an original application filed August 14, 1979. The preferred compound was 2,2′,4,4′-tetrakis(*o*-chlorophenyl)-5,5′-bis(*m,p*-dimethoxyphenyl)-biimidazole. A further extension was provided by the discovery that a mixture of dimers prepared by the oxidative coupling of two different imidazoles provided further improvements in imaging speed. This discovery was the subject of U.S. Patent 4,622,286 (to Thomas M. Sheets), "Photoimaging Composition Containing Admixture of Leuco Dye and 2,4,5-Triphenylimidazolyl Dimer," issued November 11, 1986.

The versatility of the HABI photoinitiator system was further increased by the discovery that it could be sensitized to visible radiation. U.S. Patent 3,652,275 (to Martin D. Baum and Cyrus P. Henry, Jr.), issued July 9, 1972, the seventeenth HABI-related patent to issue, "Hexaarylbiimidazole Bis(p-Dialkyl-aminophenyl-α,β-unsaturated) Ketone Compositions," was the first of a series of patents on visible light sensitizers for the HABI photoinitiator system. Later patents by Tom Dueber (U.S. Patents 4,162,162; 4,454,218; and 4,565,769), by Bruce Monroe (U.S. Patent 4,987,230), and especially by Bill Smothers (U.S. Patents 4,917,977; 5,147,758; and 5,204,467; among others) extended the range of the HABI photoinitiator system even further into the visible region of the spectrum, eventually to the red region. This technology became more important when visible lasers began to replace ultraviolet lights as the sources of imaging radiation.

Although the discovery that the combination of a hexaphenylbiimidazole and a free-radical-producing hydrogen donor made an excellent photoinitiator system led to large number of HABI-related patents, many of these patents were not, strictly speaking, "HABI patents." They were directed to some aspect of photopolymer technology and listed the HABI photoinitiator system as one of a number of possible photoinitiator systems. However, HABI-containing photoinitiator systems were used in a number of DuPont photopolymer products even though a number of other possible photoinitiator systems were also listed in the patents.

As the HABI technology became more widely known, the hexaphenylbiimidazole/free-radical-producing hydrogen donor initiator system became part of a "standard list" of photoinitiator systems that was included in practically every photopolymer-related patent, not only by DuPont but by others, even though, because a patent does not give the patent owner the right to practice the invention, no one but DuPont could use the initiator system in the United States until after January 8, 1991. According to Dr. Dessauer's database of United

States patents, as of November 22, 2005, there were 1188 HABI-related issued United States patents. There were also an additional 453 published United States patent applications, some of which had issued as United States patents and thus may be counted twice, that mention HABI technology.

The Japanese patent literature contains even more published patent applications that mention HABI technology. However, under Japanese patent law, patent claims have a very narrow scope. Consequently, a whole series of related applications might be filed in Japan when only a single application would be filed in the United States. In addition, in Japan patent applications are published at eighteen months but are not examined until the applicant requests examination and pays an examination fee. Examination formerly had to be requested within seven years of the filing date, since shortened to three years, or the application is considered abandoned. Examination is never requested for a large number of applications so they act as defensive publications.

Starting from an initial, unsuccessful attempt to develop a commercially viable photochromic system, HABI technology developed into two important imaging applications, the DYLUX® proofing system and an important photoinitiator system for a number of photopolymer products. These imaging applications were not even contemplated when the initial patent application was filed. However, the initial application contained composition of matter claims, which dominated all uses of the claimed compounds, even uses that had not been discovered when the application was filed. Because the patent examiner requested a structural determination for one of the dimers, which required several years of experimental work to accomplish, the basic composition of matter patent did not issue until nearly twelve years after the filing of the initial application. By this time, not only had the imaging applications been discovered, a considerable patent estate had been assembled. And products based on these discoveries had already been on the market for five years. Because of the Patent Office's delay in considering the basic application, when the patent finally issued, it dominated all uses of the claimed *ortho*-substituted triphenylimidazoyls and their dimers in the United States until January 8, 1991.

This is not to say that DuPont did not have any competition; there were numerous competitors. However, the competitors had to "invent around" DuPont's technology, that is, develop their own technology, instead of copying DuPont's. This patent gave DuPont an important competitive position in the photoresist market and in the proofing and printing market during this period.

20

PHOTOPOLYMERS—AN ENABLER OF INDUSTRIAL INNOVATION

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ABSTRACT

Photopolymer science and technology are now over fifty years of age. In the time since the initial invention of photo-induced crosslinking and polymerization, major innovations have occurred in several industries as a direct result of the application of the new technology. In several cases, it can be unequivocally stated that the adoption of photopolymer technology in those industries has revolutionized the way the industry approaches manufacturing its products. In addition to lowering costs of manufacture and saving time and labor, the manufacturing processes in general have become safer for workers' health and more environmentally benign as a result of these changes.

20.1 INTRODUCTION

During the late 1940's and into the early 1950's, photochemistry was an unkempt science. Progress in the field was unusually empirical and observational. However, several scientific trends were coming to fruition which would accelerate the development of photochemistry and of its applications. One of these was progress in gas phase free radical chemistry, where pioneering work was done to understand the role of light in the decomposition of certain classes of molecules, especially azo compounds, to yield highly reactive fragments, recognized as free alkyl radicals. Another was insights developed during studies of gas phase reactions of olefins, which often exhibited extremely bad mass balances. It was recognized that these materials were being converted to high molecular weight materials as oligomers of the monomeric olefin. These insights, as well as other concepts percolating through the physical chemistry community at this time, created an environment ripe for invention.

As in many such instances, invention occurred simultaneously (or nearly so). Louis Plambeck of DuPont, and Louis Minsk of Eastman Kodak each had an insight at about the same time. Interestingly, each had as their industrial target, new imaging technology.

Minsk recognized that photoreactions of many olefinic compounds, especially cinnamates and related aromatic unsaturated esters and carboxylic acids, which had been known since the days of early Italian and German chemical inquiries, could be induced to photodimerize. Minsk attached these photosensitive entities to the chains of soluble polymers. Irradiation of the solutions with ultraviolet light formed photodimers, which now possessed a molecular weight twice that of the original material. Under appropriate choices of solvent and starting molecular weight of the original polymer, Minsk showed he could cause the new materials to separate from solution as insoluble, higher molecular weight material. In a viscous liquid formulation, held for example in a Petrie dish, Minsk showed that he could irradiate areas of the dish, and keep other areas in darkness, and then rinse the dish with a solvent capable of removing the soluble region, while not dissolving the insoluble regions generated by irradiation. Minsk had created a photoimage via his light-induced dimerization of the cinnamate containing oligomers. See Minsk (1948) [1].

Plambeck had exactly the same idea, and chose a very different manifestation to demonstrate his concept. Plambeck irradiated mixtures of monomers containing acrylate based functionality, in the presence of azo and benzoin containing small molecules. He, too, produced light-struck regions which became insoluble to solvents which would remove the regions not irradiated with ultraviolet light. Plambeck showed that he had induced acrylate polymerization to produce high molecular weight, insoluble materials by the action of the light. This technology was used during WW II to produce topographical maps from aerial photographs. Plambeck later improved the technology by adding solid binders to the formulation so that the mixtures could be cast as films on supports. See Plambeck (1956) [2].

Each researcher patented their experimental discoveries. Photoimaging technology was born in the early 1950's. Much has transpired in the intervening 50-odd years since these inventions were published, and yet many new applications of this now "ancient" technology are being developed even today.

This paper will illustrate how photopolymer technology has helped to revolutionize two industries, printing and publishing, and the manufacture of electronic circuits and devices. Several new, developing applications will be described as well.

20.2 FUNDAMENTALS OF PHOTOPOLYMERIZATION AND PHOTOIMAGING

The term photopolymerization is used in a generic way to designate the creation, using light as a trigger, of high molecular weight material from smaller, lower molecular weight starting materials. For an excellent introduction to photopolymerization and other photoimaging concepts see Reiser (1989) [3]. Several methods can be used to cause this transformation. The most common is the free-radical induced oligomerization of monomers. In this process (eqs. (1)–(3)), light is used to create a free radical (eq. (1)). Next, the free radical ($R^{\bullet}$) adds to an unsaturated monomer to create a new radical, which propagates (eq. (2)) with other monomers until terminated by some event (hydrogen extraction, dimerization, etc.) (eq. (3)).

The Minsk route using photodimerization is now called "photocrosslinking," but is often referred to as a class of photopolymerization (eq. (4)).

$$R{-}R \rightarrow 2R^{\bullet} \tag{1}$$

$$R^{\bullet} + M{-}CH{=}CH_2 \rightarrow R(M{-}CHCH_2)_n^{\bullet} \tag{2}$$

$$R(M{-}CHCH_2)_n^{\bullet} + H{-}N \rightarrow R(M{-}CHCH_2)_nH \tag{3}$$

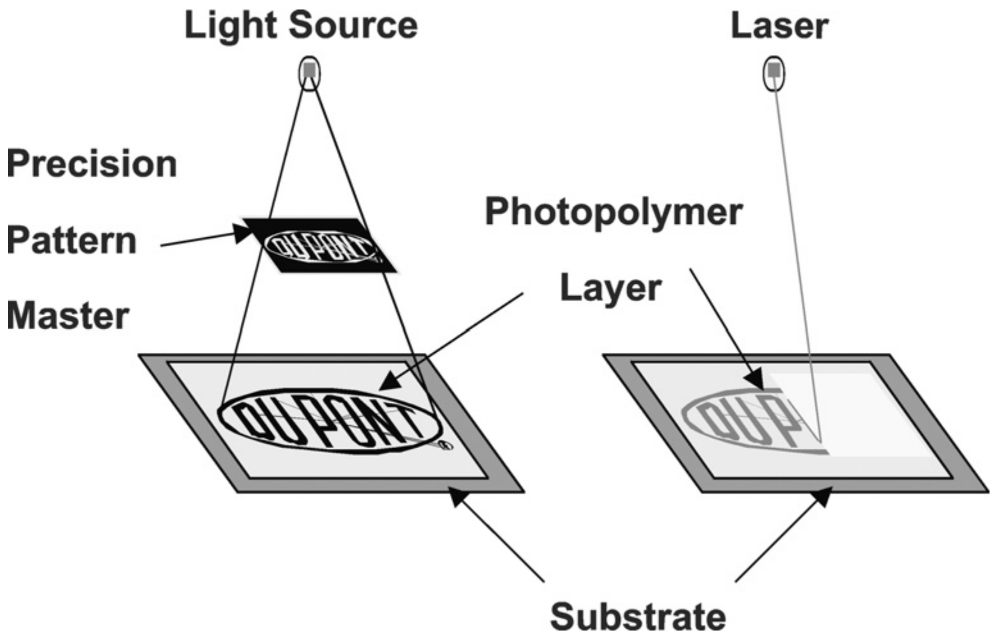
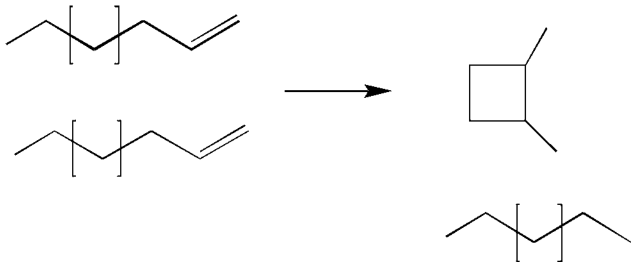


Figure 20.1. Photopolymer imaging. In this figure, light impinges on a polymeric layer, supported on a rigid or flexible substrate, and causes physical change that can be subsequently developed to reveal the image. The light is modulated either directly, by the laser source (on right), or via the light and dark patterned regions of the photomask (on left).


(4)

In industrial practice, these methods (and others) are used to create image-wise patterns of photopolymers using either direct (often laser-based) writing, or using imposition masks to delineate light and dark regions (Fig. 20.1).

The advance in technology that was created by the inventions of Minsk and Plambeck, and all those who followed them, was one that revolutionized several industries. The advance was one which promulgated the idea that an image could be used to replicate a structure over and over again in a predictable and cost-saving manner. The concept is referred to as “photolithographic replication,” or simply “photolithography.” This concept will be discussed in the next section.

20.3 REPLICATION AS AN INDUSTRIAL PARADIGM FOR INNOVATION

In the period around 1960, printing of documents, books and journals was accomplished by type setting operations. At the same time, electronic devices, such that they were, were constructed by hand wiring individual functional elements (capacitors, resistors, vacuum tube based diodes, etc.) into a chassis. Each of these industries was hampered by these labor intensive, slow and costly unit operations. Demand for radios, televisions, washers, driers, dishwashers and other electronic devices was growing, but costs were not falling rapidly enough to allow the average consumer access to these new appliances. In the printing and publishing realm, hand type setting had been replaced by use of large, automated type setting machines such as linotype equipment, but the costs of these were too high to allow small printers to thrive. Large publishers became the norm in the printing industry. The history of how these two industries evolved over the time from about 1965 through the 1990's exemplifies the paradigm of photopolymers as enablers of change.

20.3.1 The printing industry

In 1958 the DuPont Company introduced a photopolymer-based printing plate called Dycril™. This printing plate was imaged using ultraviolet light through a photomask which contained information related to the content to be printed. This content could be letters (lines, spaces, type fonts, etc.) or graphical information as represented by dots of different gray scale content (that is, pictures derived from photographs). An early (1957) advertisement of this newly introduced printing plate is shown in Fig. 20.2.

The effect of the light exposure is to render the imaged areas insoluble in a solvent that will dissolve the unexposed regions. "Development" of the exposed printing plate then reveals the image as a raised relief, made of organic polymeric material, supported on the metal base. The structure is then mounted on a printing press, and ink applied to the raised surface of the image, and the image transferred to paper (or other receiving layer). This kind of printing process is called "letterpress" printing, and it is exactly analogous to the use of a stamp to transfer images.

Many other kinds of printing plates for other kinds of printing were developed using this new photopolymer paradigm. For example lithographic plates, in which the very thin photopolymer image is barely thick enough to see visually, prints by allowing the hydrophilic ink

DU PONT PROGRESS REPORT

Better Things for Better Living . . . through Chemistry

WILMINGTON, DEL. MARCH 13, 1958 No. 2a Mid-Atlantic Edition

DU PONT DISPLAYS PLATE AT NEWSPAPER CONFERENCE

Photorelief plates for rotary and flat bed use.

Plans Three Types of Photopolymer Plates

PITTSBURGH, Pa., Mar. 13 — The Photo Products Department of E. I. du Pont de Nemours & Co., Inc., exhibited samples of experimental photopolymer printing plates today to the newspaper production men attending the Mid-Atlantic Newspaper Mechanical Conference.

These plates are composed of a layer of photosensitive plastic (termed photopolymer) bonded to a metal support. As described in a progress report in October, 1957, ultra-violet light exposure of the plate through a high contrast negative (right reading from the emulsion side) causes the plastic to harden throughout its entire depth. Subsequent "wash out" with a dilute alkaline water solution removes the unexposed and unhardened photopolymer leaving the text and art at proper printing height. The exposure and wash out steps can be completed in about 15 minutes.

A Du Pont Photo Products spokesman, W. H. Vinton, Manager, New Products Development, stated that current plans are to market three types of plates — a steel-supported plate about .060 inch thick with .030 inch relief; a steel-supported plate about .090 inch

expected to be available in about two years, the time required to construct production facilities. Sizes up to 20 by 24 inches are contemplated initially.

Present indications are that early use of photopolymer printing plates in newspaper production may be most attractive in direct printing of R.O.P. color, photocomposed advertising and similar areas where quality considerations and the availability of a photographic negative offer many distinct advantages.

This entire page was printed direct from a photorelief plate on a rotary press as an example of present status of the project, but Du Pont personnel stress that final product characteristics have not been firmly established and that considerable developmental work still remains to be done prior to commercialization.

Printing Development Laboratory Established

WILMINGTON, Del., Mar. 13 — The Du Pont Photo

Figure 20.2. A photopolymer-based printing plate.

to adhere to the aluminum support. The function of the thin photopolymer image is to repel the ink from the organic regions. These kinds of printing plates are widely used in newspaper and magazine printing.

For printing on flexible polymeric films (for example the package material for many frozen vegetables), or on corrugated board stock, very thick photopolymer printing plates have been developed and are used today to print colorful packages that entice customers to grab them off the shelves in the grocery store.

As the printing industry transitioned from the “photographic” era to the digital era we are in today, the process of making printing plates became more and more dependent on computer technology. Digital cameras created digitized images that could now be sent to a central printing plant by satellite links. Computer programs were used to write stories and to compose the printed page. Output of this digitized image of an entire page, ready to send to the press, could now be accomplished using laser sources, eliminating the need for film negatives (photomasks). In addition, using photopolymer films sensitive to laser light, intermediate images (“proofs”) of the final printed page could be viewed by the customer, e.g., an advertiser, who could give permission to print based on this sneak-preview of how the final printed page would appear.

All of these advances contributed to faster, more efficient, more accurate, and lower cost processes for producing printed matter for use in commerce. According to the US Bureau of Labor Statistics [4], which tracks productivity gains in many industrial sectors of the US economy, productivity in the printing and publishing industry, as measured by output per worker hour, doubled during the period from 1987 (the first year in which statistics were initiated) to 2002. During that fifteen year period, the average annual gain in productivity was 4%. It is possible that substantial additional productivity gains were realized in the period between 1960, just after DuPont and other companies introduced photopolymer materials to the printing industry, and 1987, when statistical data gathering was begun.

20.3.2 The electronics industry

The year 1968 was a revolutionary year for the electronics industry. In fact, one can contend that this was the year when the appliance industry evolved into what we know recognize as the electronics industry. The transistor had been invented by Bardeen, Brittain and Shockley at Bell Laboratories in 1948, but the true value of this technology was not demonstrated to the commercial world until Texas Instruments produced the first transistor radio in 1954. This product, the TR1, contained three transistors. Those junction transistors were made by laborious vacuum deposition techniques. The true advance of the TR1, however, was that it could fit into a shirt pocket. This created a tremendous demand for portable electronics that continues into today. See a recent review by Simcoe (2004) [5].

In 1958, Kilby, again at Texas Instruments, invented the integrated circuit, effectively monolithically putting transistors and other electronic devices on a single chip. In 1998, on the fortieth anniversary of the invention, TI celebrated on the Internet [6]. The first chip was made by cumbersome masking and evaporation methods. Over time, photolithographic methods produced tremendous productivity advances and cost reductions. Photoresists played a major role in that process change.

It took some time to develop new processes to adopt the advantages of integration. In 1968, DuPont, working closely with IBM, developed a photopolymer based process for delineating

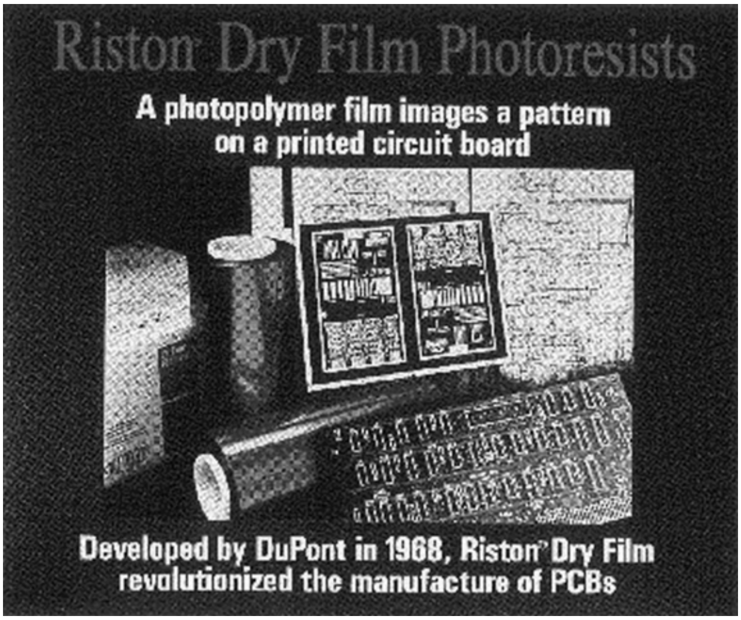


Figure 20.3. Photopolymer films used to create printed circuit boards were introduced in 1968.

Table 20.1. Productivity gains (output/worker-hour) in printing and publishing (P&P) and semiconductor and electronic components (S&EC) industries, 1987–2002. All data are referenced to 1997 as 100

Industry	Year		
	1987	1997	2002
P&P	62	100	115
S&EC	16	100	221

conductive copper traces on an insulating fiber-glass based substrate to create a printed circuit board (see Fig. 20.3). The Riston™ dry film photoresist and the lamination processes developed to use it, made it possible to eliminate the electrical chassis used for many years in the manufacture of electrical appliances. Now, electrical interconnections could be produced reprographically, and electronic components could be placed directly onto the board and soldered in automated equipment.

The advances in productivity that have occurred in the semiconductor and electronics component industries since the introduction of the integrated circuit, the printed circuit board, advanced wafer processing equipment, and many other innovations, many of them driven by the paradigm of photolithographic replication, are astounding. The US Bureau of Labor Statistics (US BLS, 2004 [4]) states that productivity increased almost fourteen times over the period 1987 through 2002, with every single year showing productivity gains of from 4–46%, averaging over 20% per year.

The US BLS data for both the printing and publishing industry and the semiconductor and electronic components industry, the official BLS nomenclature for these industrial segments are shown in Table 20.1.

The data shown here are some of the few hard data available to assess the effect that the introduction of new technology has on an industry. It is not the present thesis that all of the productivity gains that were realized in printing and electronics are due only to the introduction of photopolymer lithographic principles to the industry. Many other factors certainly contributed too. However, it is the thesis of this work that without the advances in cost reduction and productivity that were possible because of photolithographic principles, the gains would have been smaller and the industries might not be as efficient as they are today—and we consumers would not be awash in magazines, books and electronic devices! As an example, partly because of photolithography, the marginal cost of adding one more transistor to a chip is now estimated at $\$0.01 \times 10^{-6}$, one millionth of a US penny.

20.4 WHAT IS ON THE HORIZON IN PHOTOPOLYMERS?

Is it possible that photopolymer technology could revolutionize other industries in the future? If so, which ones?

Photopolymerization is used today in a myriad of new applications. It is not possible to comprehensively cover all of them. Some possible interesting applications are discussed here.

Three dimensional modeling (rapid prototyping, for example) can now be accomplished both by conventional UV curing of liquid monomers, and in new developments in several laboratories around the world, by two-photon direct imaging using intersecting laser beams. Both methods can be used to make faithful replicas of objects from digital data. Now we can each have an exact replica of our healthy hip joint made in polymer, and converted into a ceramic or titanium hip joint for placement in our bodies. This will make hip replacement surgery a personal experience, and may make it safer, too. Photopolymers with material property gradients built into them, for example, subtle changes to index of refraction profile across a plastic ocular lens, could lead to new lens implant techniques to correct vision.

Photopolymers and rapid curing are beginning to change the way dentistry is practiced. Mercury amalgams are eliminated, tooth replicas can be made to replace teeth lost to aging, and laser based processes can be used to eliminate mechanical drilling. Truly painless dentistry may be around the corner.

Photopolymer based optical chips are being introduced into telecommunications applications, replacing hand assembled glass fiber based optical components. The scalability of photopolymer technology promises lower costs and better reliability.

Photopolymers are used today to make holograms. In the near future, volume holograms in multilayer materials will lead to optical data storage of unprecedented storage capacity.

20.5 CONCLUSIONS

While photopolymer technology and the principle of application of the scalability of lithographic replication are now over 50 years old, there are many fresh ideas that will lead to exciting new applications for photopolymer technology. The new millennium will see advances in electronics, down to nanometer feature size; in optics, as polymers displace glass in applications closer and closer to the ultimate home user of high bandwidth; and in biomedical applications where increasing use of truly custom materials and designs will demand direct write materials that will produce personalized implantables. It is a bright and interesting future for those who work in materials science and photoscience.

ACKNOWLEDGMENTS

The author worked in photoscience and photoimaging for thirty years in various capacities for the DuPont Company. Many of the ideas and concepts presented here were developed as a direct consequence of the interactions with fellow workers in DuPont. The author acknowledges this debt with gratitude. The author also appreciates several conversations about the future of photopolymer science with Dr. Edwin Chandross and Dr. George Hammond.

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PHOTOTROPIC 2,4,5-TRIPHENYLIMIDAZOLYL RADICALS AND DIMERS THEREOF

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No Drawing. Continuation-in-part of application Ser. No. 388,010, Aug. 6, 1964, which is a continuation-in-part of application Ser. No. 181,475, Mar. 21, 1962, both now abandoned. This application Mar. 10, 1967, Ser. No. 622,085
Int. Cl. C07d *47/36*
U.S. Cl. 260—309 **33 Claims**

ABSTRACT OF THE DISCLOSURE

2,4,5-triphenylimidazolyl radicals and their dimers (2,2′,4,4′,5,5′ - hexaphenyl biimidazoles) having on the phenyl groups from 1 to 10 substituents free from a hydrogen atom capable of reacting with methyl magnesium iodide, one such substituent being in the ortho position on the 2-phenyl group and having a sigma value below 0.7. The 2-phenyl group can contain up to four substituents, while the 4 and 5 phenyl groups can contain up to three substituents each.

The radicals and the dimers are stable and form a photochromic system, finding utility as components in sun shields or shades.

They are prepared by oxidizing the corresponding substituted 2,4,5-triphenylimidazole to form the biimidazole which is dark stable. The radical forms upon exposure of the biimidazole to a light source and is stable in the presence of the light radiation.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 388,010, filed Aug. 6, 1964, and now abandoned which was a continuation-in-part of now-abandoned application Ser. No. 181,475, filed Mar. 21, 1962.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to novel imidazolyl and biimidazole compositions of matter. More particularly, it concerns selectively substituted 2,4,5-triphenylimidazolyl radicals and their dimers.

(2) Description of the prior art

Substances which change color upon exposure to light and return to their original color after the light source is removed are called phototropic substances. An example is the oxidation product of lophine (2,4,5-triphenylimidazole) which upon exposure to actinic radiation changes color from a light lemon yellow to a reddish purple. This and other phototropic materials have not been widely used, however, because they possess certain disadvantages, e.g., they are slow in reverting back to their original color; the color is fixed, i.e., no variation in color can be obtained; only a comparatively low number of color reversals is attained before compound failure; or they are adversely affected by heat.

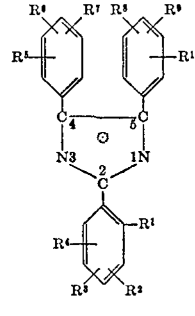
The foregoing deficiencies of known phototropic materials are overcome by the novel compositions of this invention.

SUMMARY OF THE INVENTION

The novel compositions of matter of this invention are 2,4,5-triphenylimidazolyl radicals having certain substituents in at least the ortho position of the 2-phenyl ring,

and their dimers. These novel compositions are represented by the formulas:

(I)



wherein

R¹ is a substituent free from a hydrogen atom capable of reacting with methyl magnesium iodide, and has a sigma value below 0.7;

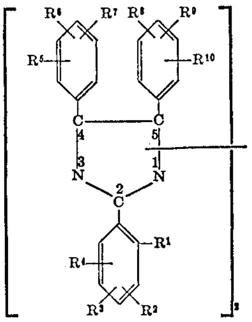
R² through R¹⁰ are each selected from the class consisting of hydrogen and a substituent free from a hydrogen atom capable of reacting with methyl magnesium iodide;

with the proviso that any two R¹ through R¹⁰ substituents in adjacent positions on the same phenyl ring can be joined together to form a benzo group; and

with the proviso that only one of R⁵ through R⁷ and only one of R⁸ through R¹⁰ can be in a position ortho to the phenyl carbon that is attached to the imidazolyl group;

and

(II)



wherein

R¹ through R¹⁰ are defined as above; and wherein the two imidazolyl rings are joined through a single bond and the remaining valences of the 3 carbon atoms and the 2 nitrogen atoms of each ring are satisfied by two conjugated double bonds.

It is an essential limitation that the novel compositions of this invention contain the R¹ substituent in the ortho position of the 2-phenyl group. For it is the presence of this group in the ortho position that distinguishes said compositions of this invention over art imidazoles and biimidazoles by imparting one or more of the following properties to said compositions: (1) the dissociation temperature is raised; (2) they exhibit a surprisingly fast color change when exposed to or removed from light; (3) they can be subjected to a high number of color reversals; (4) they are surprisingly stable.

Thus, the compositions of this invention are useful as automatic sun shades or shields in coating glass or other transparent objects, in the inner layer of laminated glass, or as solutions in solvents to give decorative effects.

DESCRIPTION OF THE INVENTION

(1) Introduction

The relationship between the imidazolyl radicals and the biimidazole compounds of the invention lies in the fact that together they comprise a photochromic system. That is, the biimidazoles, on exposure to activating light radiation, such as sunlight or ultraviolet light, dissociate to form the radicals which are stable in the presence of the radiation; and the radicals dimerize to reform the biimidazoles when the radiation is removed. The photochromic properties of the system arise because the biimidazoles and the corresponding imidazolyls are differently colored. The following equation illustrates the reversibility of the system, wherein $L—L$ is the biimidazole (dimer) and $L\cdot$ is the imidazolyl radical monomer):

$$L-L \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2L\cdot \tag{1}$$

(2) Preferred embodiments

Representative substituents free from a hydrogen capable of reacting with methyl magnesium bromide include alkyl, alkoxy, alkoxycarbonyl, alkylthio, dialkylcarbamoyl, dialkylsulfamoyl, alkanoyloxy, N-alkylalkanamido, aryl, aryloxy, arylthio, benzo, halo or cyano groups. The alkyl and alkoxy groups above, whether alone or as a part of another group, e.g., alkylthio, can be of any chain length but are preferably lower alkyl or lower alkoxy, i.e., of 1–6 carbon atoms. Examples of such groups include methyl, ethyl, propyl, butyl, isobutyl, sec.-butyl, tert.-butyl, pentyl, isopentyl, hexyl, ethoxy, pentoxy, isobutyloxy, and the like. The alkanoyl and alkanamido-containing substituents can also be of any chain length, but are preferably lower alkanoyl or alkanamido, i.e., of 1–6 carbon atoms. Representative groups range from formyl to caproyl and from formamido to caproamido, respectively. The aryl and aryl-containing groups preferably contain 6–10 carbon atoms and are exemplified by phenyl, 1-naphthyl, 2-naphthyl, and the like. Halo substituents include bromine, chlorine and fluorine.

The definition of R^1 specifies a sigma value below 0.7. By the term "sigma value" or "constant is meant the value obtained for the substituent in the para position of benzoic acid and its derivatives as discussed and illustrated by H. H. Jaffe, Chem. Rev. 53, 191 (1953), particularly pp. 219–223 and column 5 of Table 7 on p. 222. Preferred R^1 substituents are alkyl, alkoxy, chloro, bromo or fluoro. In addition, R^1 taken together with any one of R^2 through R^4 appearing ortho to R^1 can be benzo, i.e., —CH=CH—. These same immediately foregoing groups that are preferred as R^1 groups are also preferred groups for R^2 through R^{10}; however, more preferably the R^2 through R^{10} groups are hydrogen; most preferably, R^2 through R^{10} are alkoxy, especially lower alkoxy in the meta-position of the 4- and 5-phenyl rings.

Preferably, also, the 2-phenyl ring carries only one ortho-substituent; namely, the R^1 substituent.

Substituents having a hydrogen capable of reacting with the Zerewitinoff reagent, called an active hydrogen, should be avoided because compositions containing them are either non-phototropic, have a low order of phototropism, or are readily converted to non-phototropic substances. Examples of these undesirable groups include hydroxyl, thiol, carboxyl, amino and alkylamino.

The biimidazole dimers of the invention comprise two imidazolyl radicals connected at the 1-1′, 1-2′, 1-4′, 2-2′, 2-4′ or 4-4′ positions. The imidazolyl radicals can combine to form the dimer linked at any one of the above-listed positions, the particular position being dependent upon the thermal conditions under which dimerization occurs. Because of its thermal stability at room temperatures, e.g., 20–27° C., the 1-2′ dimer is preferred.

(3) Preparation

The biimidazoles of this invention are prepared by oxidatively coupling the corresponding triphenylimidazole.

One suitable oxidation method utilizes the procedure described by Hayashi et al. in Bull. Chem. Soc. Japan, 33, 565 (1960) wherein the substituted triphenylimidazole in ethanolic potassium hydroxide is treated with aqueous potassium ferricyanide. The dimeric product precipitates and is isolated by filtration and washed free of ferricyanide with water.

Another method involves oxidation with halogen such as chlorine, bromine or iodine in the presence of alkali; for example, treating the potassium salt of the imidazole with iodine in ether as disclosed for other imidazoles by Zimmerman et al., Angew. Chem., 73, 808 (1961).

A third oxidation method is the anodic oxidation of the imidazole in dimethylformamide or acetonitrile containing a supporting electrolyte such as alkali metal chlorate.

Difficulty may be encountered in the dimerization if the triphenylimidazole contains more than two substituents having sigma constants of 0.7 and above. The dimers obtained, however, are phototropic compounds.

It should be noted that where the preparative method involves realtively low temperatures and the biimidazole (dimer) is substantially insoluble in the reaction medium as in the above Hayashi et al. procedure, the product precipitates as formed. Sometimes the crude product comprises mixtures of biimidazoles and may contain one or more biimidazoles that are relatively easily dissociated by heat, such as, for example, the 4,4′-isomer. Such thermal instability is, in general, more readily apparent in the liquid, e.g. in solution, than in the solid. Thus whereas the solid dimer may be essentially uncolored, i.e. undissociated at room and ordinary storage temperatures, it may become extensively colored, i.e. dissociated to imidazolyl radicals, almost immediately on being dissolved in an inert solvent such as benzene. As the radicals in solution are in equilibrium with all possible dimeric structures, in time, in the absence of exciting light radiation, the radical color fades as the radicals dimerize to biimidazoles that are not thermally dissociable at that temperature in the particular solvent used. In other words, on equilibration, the system tends to produce biimidazoles that are thermodynamically stable at the temperatures employed. Thus no matter which of the above methods is used to oxidize a particular imidazole, substantially the same dimeric product is obtained on recrystallization under the same conditions. The 1,2′-isomer is such a product, obtained under the conditions described in Example 1.

If it is desired to recrystallize the product, suitable solvents include benzene, ethyl ether, methanol, ethanol, cyclohexane, and the like. In general, allowing the biimidazole product to crystallize at ordinary, e.g., room temperatures from the recrystallization solvent yields a product which comprises at least one isomer, such as the 1,2′-dimer, which is thermally stable at the solution temperatures employed. Prior workers in the art assigned the 1,1′-structure to the various dimers prepared in the above chemical oxidation methods. They gave no structure proof, however, so that the 1,1′ designation is arbitrary and seems based on the following argument: That starting imidazole hydrogen is normally positioned on nitrogen (though it is known that it may also tautomerically exist on anyone of the three imidazole ring carbons). Therefore, since this hydrogen is lost in the oxidative coupling (dehydrogenation) to dimer, it seemingly follows that two imidazole nitrogens which formerly bore the hydrogens are joined to each other in the dimer. In contrast, however, the crystallographic study described herein under Example 6 indicates that the present products obtained by the ferricyanide oxidation method and subsequently purified as described have the 1,2′ structure. Thus it is reasonable to conclude that the prior art products, having been made by essentially the same method, also have the 1,2′ rather than the disclosed 1,1′ structure, or both. The position of the bond joining the imidazole rings in the invention compounds is, however, immaterial to the broad aspect of this invention in that the fast radical recombination rate is independent of such bonds as discussed below.

The imidazolyls of this invention are prepared by subjecting the corresponding biimidazole to photolyzing light. This procedure is described in further detail below.

Dimers that differ in how the imidazole rings are joined may be interconverted photolytically, for example, by irradiating a particular dimer, e.g. the 1,2′-isomer discussed above, in solution, with photolyzing light, and allowing the imidazolyl radicals to recombine in the dark at another (higher or lower) temperature (Equation 1 above). This other temperature should, of course, be below the dissociation temperature of the isomer to be recovered. For example to prepare dimers which may have relatively low thermal stability in solution, e.g. dissociate in the dark at room temperatures under proper conditions, a thermally more stable, but photochromic, dimer solution is cooled to a lower temperature, e.g. −80 to +10° C., and irradiated to effect dissociation. The resulting radicals are then allowed to recombine in the dark at such low temperature. The process can be repeated on the same solution as may be necessary, to eventually build up substantial proportions of the new dimer. Isomers thus produced may be recovered at temperatures at which they are thermally stable using techniques well known to those skilled in the art of preparative chemistry; for example, the dimer may be precipitated from the carrier solvent containing it by adding one or more other solvents, e.g. petroleum ether, which is miscible with the carrier solvent but which is essentially a non-solvent for the biimidazole; or the dimer may be allowed to crystallize from the solvent at the indicated or still lower temperatures; or the solvent may be removed from the biimidazole, as by distillation, including at reduced pressures where necessary. The product may be characterized by the methods mentioned below. As indicated above the dissociation temperature for a particular dimer is generally higher for the solid than the liquid state so that quite often even the so-called thermally unstable dimers may be stored and used solids at room temperature.

Similarly triarylimidazolyl radicals formed by dissociating a particular dimer at one temperature can be warmed to higher temperature in a suitable inert solvent, which temperature is above the theraml dissociation temperature of the starting dimer but below the thermal dissociation temperature of another, more thermally stable isomer, then the radicals are allowed to recombine at said higher temperature, to produce the more stable isomer.

The substituted triphenylimidazoles used in the oxidation procedures to prepare the biimidazoles of this invention can be prepared by refluxing, in glacial acetic acid containing ammonium acetate, benzil with an appropriately substituted benzaldehyde or a benzil and benzaldehyde which are both suitably substituted, then drowning the reaction mass, e.g., in water, in an ammonium hydroxide solution, etc., filtering and purifying the product by recrystallization, as described by Davidson, et al. in J. Org. Chem., 2, 319 (1937); or by refluxing a benzoin and a benzaldehyde in methanol in the presence of copper acetate and ammonia, an adaptation of the procedure of Wiedenhagen et al., Ber. 70, 570 (1937); or by heating a benzil and a benzaldehyde at 180° to 190° C. in formamide as disclosed in Belgian Pat. 589,417.

(4) Specific illustrations

The invention is further illustrated by the following examples which are not intended to be limiting but which describe in detail the novel compositions and their preparation. Parts are given by weight unless otherwise stated.

EXAMPLE I

To 2.1 parts of benzil (0.01 mole) dissolved in 50 parts of glacial acetic acid containing 6 parts of ammonium acetate (0.078 mole) was added 1.4 parts of o-chlorobenzaldehyde (0.01 mole), and the solution was refluxed for 2 hours. The solution was then drowned in 200 parts of cold water whereupon 3.1 parts of reaction product precipitated. The product was isolated by filtration and purified by recrystallizing twice from ethanol. The product, 2-(o-chlorophenyl)-4,5-diphenylimidazole, is a white crystalline solid having a melting point of 196° to 197° C. and the following analysis:

Calculated (percent): C=76.3; H=4.6; N=8.5. Found (percent): C=76.7; H=4.7; N=8.2.

To 1.1 parts of the above prepared imidazole dissolved in 100 parts of ethanol containing 12 parts of potassium hydroxide was added 450 parts of a 1% by weight water solution of potassium ferricyanide at a rate of 5 parts per minute for 1.5 hours with continuous stirring. The oxidation reaction product in an amount of 1.0 part precipitated from the reaction mixture, was isolated by filtration, and was washed with water until free from ferricyanide. The porduct was dried at 56° C. for eight hours at 0.1 mm. mercury pressure after predrying overnight in a vacuum oven at 50° C. It was solvated with two moles of ethanol for every three moles of biimidazole. The product 2,2′-bis(o-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole is a pale yellow crystalline solid which softens at about 90° C. and melts to form a yellow gel at 95° to 110° C. The compound turns lavender at 170° C., becomes red-brown at 190° C. and at 220° C., it becomes red.

Analysis for the solvated biimidazole.—Calculated (percent): C=75.4; H=4.7; N=8.1. Found (percent): C=75.9; H=4.7; N=8.1.

A portion of the ethanol-solvated product was dried azeotropically with cyclohexane to produce non-solvated material. Recrystallization from ether also yields the non-solvated product, M.P. 205° C.

The biimidazole, after recrystallization from methanol, has the following crystallographic characterization:

Monoclinic elementary cell with *a*=33.742 A., *b*=11.438 A., *c*=35.444., *β*=93.5°.

Space group *I2/a*.

An X-ray density of 1.283 g./cm.^{3} is calculated for 16 dimer molecules per elementary cell.

X-ray powder diffraction data for the product is found in the following Table I.

TABLE I

Interplanar spacings, *d* (A.), and estimated intensities, I_o, of the power diffraction pattern of $C_{42}H_{28}N_4Cl_2$ after recrystallization from methanol

d (A.):	I_o
9.891	41
9.158	57
8.864	100
8.412	51
8.070	34
7.682	7
7.433	33
6.788	11
6.626	25
6.306	48
5.960	38
5.798	31
5.641	26
5.451	10
5.220	28
5.125	36
5.046	38
4.892	43
4.809	28
4.720	39

TABLE I—Continued

d (A.):	I_o
4.630	70
4.390	20
4.246	25
4.190	48
4.050	21
3.963	61
3.756	49
3.677	38
3.562	36
3.463	34
3.357	28
3.278	16
3.245	16
3.139	18
3.084	16
3.035	7
3.004	7

A colorless 0.5% benzene solution of this biimidazole turned purple immediately on exposure to sunlight and the color faded within a minute after shutting out the light. A control solution of the art dimer of 2,4,5-triphenylimidazolyl radical required 15 minutes to fade after the light exposure. In another measurement for color life, the benzene solution was irradiated in a quartz cell 1 cm. thick for 1 minute supported 3½ inches from a 275-watt sun lamp (General Electric RS) and placed in a spectrophotometer for a recording of the change with time in the optical density (D) of the maximum absorption band at 545 mμ. A reading was also obtained after the solution had been kept in the dark overnight and used as an "infinity" reading (D_∞). A plot of $1/(D-D_\infty)$ vs. time (minutes) gave a line whose slope represented the color fading rate of the phototrope and provided a reproducible quantitative value of this property for comparison with a control compound not having an ortho-substituent in the 2-phenyl ring and other phototropes. The value obtained for the 2-(o-chlorophenyl)-4,5-diphenylimidazolyl radical of this example, i.e., the slope of the above graph, was 7.3 compared with 0.46 for the art unsubstituted triphenylimidazolyl radical, that is, the radical from the new compound fades about 16 times as fast as the radical from the unsubstituted compound.

EXAMPLE II

By the procedure of Example I, 1.75 parts of 2,4-dichlorobenzaldehyde (0.01 mole) was reacted with benzil to produce 3.5 parts of 2-(2,5-dichlorophenyl)-4,5-diphenylimidazole, a white, crystalline solid having a melting point of 174.5–175°C. and the following analysis:

Calculated (percent): C=69.0; H=3.9; N=7.7. Found (percent): C=69.0; H=4.0; N=7.4.

1.2 parts of the imidazole was oxidized to 2,2′-bis(2,4′-dichlorophenyl)-4,5′,5,5′-tetraphenyl-1,2′-biimidazole by treatment with potassium ferricyanide as described in Example I. The product was obtained in 81% yield as a pale yellow phototropic solid. It softens at 90° C., forms a gel at 115° C., becomes a yellow liquid at 133° C., turns red at 210° C., becomes orange at 250° C., and decomposes at 262° C. Analysis for the unsolvated biimidazole was:

Calculated (percent): S=69.2; H=3.6; N=7.7. Found (percent): C=69.3; H=4.2; N=7.4.

A 0.5% benzene solution of the above product turned purple on exposure to sunlight, the color fading in 45 seconds. From optical density measurements of the 558 mμ absorption band obtained as described in Example I, the color fading rate value was 17, indicating a fading rate of about 35 times that of the art 2,4,5-triphenylimidazolyl radical with a value of 0.46 taken as a control.

The solid material turns purple on exposure to light and reverts to the original pale yellow color when taken from the light.

EXAMPLE III

o-Anisaldehyde in an amount of 1.4 parts was reacted with 2.1 parts of benzil as described in Example I to produce 2.9 parts (90% yield) of 2-o-anisyl-4,5-diphenylimidazole. This imidazole is a white, crystalline solid having a melting point of 207.5–208.5° C. and the following analysis:

Calculated (percent): C=81.0; H=5.6; N=8.6. Found (percent): C=80.8; H=5.6; N=8.5

When 1.1 parts of the imidazole was oxidized with potassium ferricyanide according to the procedure of Example I, 0.96 part of a pale green phototropic 2,2′-di(o-anisyl) - 4,4′,5,5′ - tetraphenyl-1,2′-biimidazole was produced. On heating, this material softens at 160° C., remaining pale green. On continued heating it darkens to brown and turns red when the temperature reaches 210° C. On exposure to light at room temperature the biimidazole turns a weak blue. Identity of the product was confirmed by the following analysis for a material solvated on the average with 2 moles of ethanol for every 3 moles of biimidazole:

Calculated (percent): C=80.0; H=5.6; N=8.2. Found percent): C=79.8; H=5.4; N=8.6.

A 0.5% benzene solution turned weak blue when irradiated with sunlight. The color fading rate value by optical density measurement of the maximum absorption band at 612 mμ obtained as described in Example I was 7.7 vs. 0.46 for the art unsubstituted triphenylimidazolyl radical, indicative of a fadeout in less than a minute.

EXAMPLE IV

2,4-dimethoxybenzaldehyde (1.7 parts) was reacted with benzil as in Example I to give 3.2 parts as a 90% yield of 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole. This compound is a white solid melting at 164–165° C. and show the following analysis:

Calculated (percent): C=77.5; H=5.7; N=7.9. Found (percent): C=77.9; H=5.8; N=8.0.

Upon oxidation with potassium ferricyanide the imidazole was converted in 91% yield to 2,2′-bis(2,4-dimethoxyphenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole, a pale green phototropic solid. Analysis of a portion of the product which was isolated in an unsolvated state was:

Calculated (percent): C=77.7; H=5.4; N=7.9. Found (percent): C=77.2; H=5.8; N=7.8.

The solid turned blue-green when exposed to light and reverted to a pale green when removed from the light. A benzene solution also turned blue-green on light exposure and exhibited a color fading rating value of 0.82 by measurement of the change of the optical density of the 611 mμ absorption band in the spectrophotometer within a time range as described in Example I. Such a value indicates a color fading rate essentially two times that of the unsubstituted triphenylimidazolyl radical.

EXAMPLE V

1-naphthaldehyde (1.6 parts) was condensed with benzil in the presence of ammonium acetate as described in Example I to produce in 99% yield 2-(-naphthyl)-4,5-diphenylimidazole as a white crystalline solid having a melting point of 289.5–290° C. and an analysis:

Calculated (percent): C=86.7; H=5.2; N=8.1. Found (percent): C=87.0; H=5.2; N=8.2.

By treatment with potassium ferricyanide the imidazole was oxidized to 2,2′-di(1-naphthyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole, a pale green solid phototrope having in the unsolvated state the following analysis:

Calculated (percent): C=86.9; H=5.0; N=8.1. Found (percent): C=86.6; H=5.2; N=8.1.

With heating this biimidazole exhibits at 85° C. a brightening of the green color. At 130° C. the color fades to a yellow. The compound softens at 153° C. and forms a yellow gel at 165° C. On cooling the material to room temperature and reheating these changes may be repeated.

The solid material turns orange on exposure to sunlight and reverts to a pale yellow-orange when withdrawn from the light. A dilute colorless benzene solution turns green when radiated and gives a color fading rating value of 1.2 when the change in the optical density of the 467 mμ band is measured as described in Example I. Such a value indicates a color fading rate which is over 2.5 times that of the unsubstituted triphenylimidazolyl radical with a value of 0.46.

EXAMPLE VI

When 1.9 parts of o-bromobenzaldehyde was used in place of the o-chlorobenzaldehyde in Example I, 3.6 parts (97% yield) of 2-(o-bromophenyl)-4,5-diphenylimidazole was produced. This produce is a white crystalline solid melting at 205.5°–206.5° C. and having the following analysis:

Calculated (percent): C=67.2; H=4.0, N=7.5. Found (percent): C=67.8; H=4.4; N=7.4.

1.3 parts of the imidazole was oxidized with potassium ferricyanide as described in Example I, the compound being converted to 2,2′ - bis(o - bromophenyl)-4,4′-5,5′-tetraphenyl-1,2′-biimidazole, in 90% yield. This dimer is a pale yellow solid which softens at 106° C. and forms a yellow gel at 120° C. Its identity was confirmed by the following analysis of the material isolated as a product solvated on the average with 2 moles of ethanol for every 3 moles of biimidazole:

Calculated (percent): C=66.8; H=4.1; N=7.2. Found (percent): C=68.8; H=4.0; N=7.2.

The biimidazole, after recrystallization from methanol, has the following crystallographic characterization:

Monoclinic elementary cell with *a*=13.215 A., *b*=20.143 A., *c*=15.996 A., *β*=122.0°.
Space group *P*2$_1$/*c*.
An X-ray density of 1.376 g./cm.^{3} is calculated for 4 dimer molecules per elementary cell.

X-ray powder diffraction data is set forth in the following Table II.

TABLE II

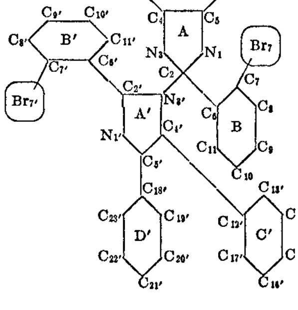
Interplanar spacings *d* (A.) and estimated intensities (I$_0$) of the powder diffraction pattern of $C_{42}H_{28}N_4Br_2$ after recrystallization from methanol

d (A.):	I$_0$
11.19	15
10.56	7
10.12	100
9.840	51
8.041	5
7.818	12
7.334	23
6.189	11
5.923	23
5.758	16
5.615	16
4.782	11
4.651	33
4.619	28
4.393	18
4.300	18
4.266	17
4.106	16
4.035	48
3.911	22
3.863	17
3.793	20
3.750	32
3.682	5
3.568	8
3.509	17
3.465	9
3.384	33
3.373	30
3.320	9
3.268	7
3.226	14
3.190	41
3.081	20
3.006	27
2.968	9
2.816	34
2.666	7
2.615	13
2.591	5
2.576	4
2.523	8
2.502	5
2.489	6
2.428	5
2.358	5
2.324	12
2.309	8
2.200	5
2.189	8

Irradiation of the solid biimidazole under a sun lamp gave a purple coloration. A purple solution formed at once when an essentially colorless 0.5% benzene solution of the phototrope was similarly irradiated, and the color faded in about a minute when the light was turned off. A measurement, as described in Example I, of the rate of color fading by recording the change in the optical density of the 550 mμ absorption band following the irradiation gave a value of 7.4, which is about 16 times the fading rate of the unsubstituted triphenylimidazolyl radical.

The above dimer of 2-(o-bromophenyl)-4,5-diphenylimidazolyl radical recrystallized from methanol is linked in the 1,2′ positions and the compound is, therefore, 2,2′-bis(o-bromophenyl) - 4,4′,5,5′ - tetraphenyl - 1,2′ - biimidazole. The molecular configuration was determined by X-ray crystal structure analysis. The measured atomic coordinates are given in Table III, the bond lengths in angstrom units and bond angles are listed in Table IV and dihedral angles between various planes of the dimer molecule are stated in Table V.

The individual atoms of the biimidazole referred to in the tables are identified for a biimidazole having a 2–3′ linkage as shown in Formula III which follows since this structure and corresponding nomenclature were used in treating the crystallographic data set forth. It will be recognized, however, that this 2–3′ linkage is identical with the 1,2′-linkage which has been used throughout the present specification to name the biimidazoles having this structure.



FORMULA III

This dimer was chosen for structure analysis because it has a relatively small elementary cell with four molecules. The data in Tables III, IV, and V were obtained as follows:

After recrystallization from methanol the dimer of 2-(o-bromophenyl)-4,5-diphenylimidazole retains varying amounts of solvent. Heating to 100° C. and high vacuum are required to remove totally the occluded methanol. However, since powder diffraction diagrams of this dimer before and after removal of the solvent are identical, the methanol forms no stoichiometric solvate. Electron density diagrams computed during the subsequent structure analysis show no additional peaks indicative of the presence of methanol in crystallographic positions. Therefore, it follows that methanol occupies random positions between the dimer molecules.

A single crystal was mounted on top of a glass fiber on a goniometer and three-dimensional X-ray data were recorded on film using the equi-inclination Weissenberg technique. CuKα radiation was used throughout. Three exposures of 9.6, 96, and 960 minutes were made for each layer along the <010> axis from the equator ($h0l$) to the twelfth layer (h:12:l). Subsequent exposures three weeks later showed that the crystal was stable in air and ordinary light and no special protection of the crystal was required.

The X-ray intensities were estimated visually by use of calibration strips. Out of a total of 5346 theoretical reflections, 3573 reflections with 2θ angles less than 157° were measured; 1773 reflections could not be observed because their intensity was too small.

An IBM 7040 computer was used for applying the Lorentz-polarization correction to the observed intensities, as well as for all other crystallographic computations. No absorption correction was made.

A sharpened three-dimensional Patterson synthesis was prepared for the dimer. Since this compound contains 4 molecules with 8 bromine atoms per elementary cell in space group $P2_1/c$, there is a total of 64 symmetry-related Br-Br vectors. All Br-Br vectors were identified by the following atomic coordinates:

$$\mathrm{Br}(7)\,x=0.350_3\,y=0.25\,z=0.236_0$$
$$\mathrm{Br}(7')\,x=0.035_1\,y=0.25\,z=0.274_6$$

The positions of the carbon and nitrogen atoms which form the organic molecule were not derived from these vector diagrams. Instead, the positions of the bromine atoms were used for two independent mathematical operations which produce electron density diagrams: Fourier synthesis and minimum functions. A Fourier synthesis calculated with about 90% correct signs was obtained by using only Br atoms. This showed the approximate atomic positions in the electron density diagrams as well as spurious peaks.

Minimum functions $M_2Br(7)$ and $M_2Br(7')$ were based upon superpositions of the two independent Br atoms and were combined to an M_4Br (7,7′) minimum function. Although the superposition function is a mathematical operation different from the Fourier synthesis, the resulting electron density diagram showed the same adventitious pseudo-mirror planes which cause the doubling of all peaks.

The subsequent location of carbon and nitrogen positions was determined by combining the electron-density diagrams obtained from the Fourier-synthesis and the minimum function M_4. Since only peaks coinciding on both three-dimensional diagrams represent true atomic positions, all noncoincident peaks were omitted. Each peak was fitted into either a hexagon or a pentagon. In this way it was possible to locate, on both electron-density diagrams, three coinciding hexagons and one pentagon, in addition to the two bromine atoms.

A new cycle of structure factor calculations based on one half of the organic molecule which had been located together with the two bromine atoms was followed by another three-dimensional Fourier-synthesis. One more hexagon and one pentagon were located from this diagram and two more structure-factor calculations and subsequent Fourier-syntheses were required to locate the positions of all carbon and nitrogen atoms in the dimer molecule.

Refinement of the atomic positions in the dimer molecule as located in electron density diagrams was made by least-squares analysis. All structural parameters, isotropic thermal parameters, and scale factors were varied to bring the difference between observed and calculated structure factors compared with the sum of the observed structure factors to a minimum according to:

$$R=\frac{\Sigma||F_o|-|F_o||}{\Sigma|F_o|}$$

The refinement was terminated after several cycles of structure factor calculations and least-square analysis when the parameter changes became insignificant and the final R-value was 0.109.

This value is well below the internationally accepted standard of 0.15 for this reliability index.

TABLE III

Atomic coordinates, standard deviations and temperature factors of 2,2-bis(o-bromophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole ($C_{42}H_{28}N_4Br_2$) follow:

	X	Y	Z	σ(ax)	σ(by)	σ(cz)	B
Br(7) [1]	0.3484	0.2369	0.7377	0.002	0.002	0.002	5.463
N(1)	0.1189	0.1660	0.5344	0.010	0.010	0.010	2.886
C(2)	0.2254	0.1497	0.5306	0.012	0.013	0.012	2.986
N(3)	0.1893	0.1054	0.4456	0.010	0.010	0.010	3.128
C(4)	0.0805	0.0934	0.4097	0.013	0.013	0.012	3.118
C(5)	0.0317	0.1306	0.4634	0.012	0.012	0.012	2.813
C(6)	0.3143	0.1154	0.6266	0.013	0.014	0.013	3.250
C(7)	0.3706	0.1443	0.7179	0.012	0.012	0.012	2.794
C(8)	0.4542	0.1130	0.8067	0.014	0.015	0.014	4.016
C(9)	0.4740	0.0463	0.8007	0.018	0.018	0.018	5.593
C(10)	0.4197	0.0133	0.7116	0.017	0.016	0.017	5.202
C(11)	0.3398	0.0484	0.6245	0.016	0.016	0.016	4.937
C(12)	0.0141	0.0421	0.3308	0.014	0.014	0.014	3.750
C(13)	0.0451	0.0329	0.2620	0.015	0.014	0.015	4.262
C(14)	0.0163	0.4799	0.3088	0.019	0.018	0.019	6.272
C(15)	0.0985	0.4455	0.3076	0.021	0.019	0.021	7.317
C(16)	1.1341	0.4539	0.2414	0.017	0.016	0.017	5.515
C(17)	0.9240	0.0059	0.3315	0.016	0.016	0.016	4.927
C(18)	0.9139	0.1398	0.4437	0.012	0.012	0.012	2.835
C(19)	0.8171	0.1444	0.3440	0.014	0.014	0.014	3.855
C(20)	0.7042	0.1605	0.3271	0.015	0.014	0.015	4.273
C(21)	0.6820	0.1747	0.4003	0.016	0.015	0.016	4.660
C(22)	0.7804	0.1693	0.4997	0.016	0.015	0.016	4.950
C(23)	0.8935	0.1502	0.5189	0.015	0.014	0.015	4.191
Br(7′)	0.0346	0.2491	0.2740	0.002	0.002	0.002	6.323
N(1′)	0.3011	0.3183	0.5056	0.010	0.010	0.010	2.966
C(2′)	0.2256	0.2767	0.4974	0.013	0.014	0.013	3.306
N(3′)	0.2745	0.2127	0.5167	0.010	0.010	0.010	2.938
C(4′)	0.3877	0.2190	0.5354	0.012	0.013	0.012	2.855
C(5′)	0.4016	0.2889	0.5289	0.012	0.013	0.012	2.848
C(6′)	0.0990	0.2925	0.4672	0.014	0.014	0.014	3.978
C(7′)	0.0075	0.2857	0.3715	0.015	0.015	0.015	4.422
C(8′)	0.8881	0.3035	0.3417	0.017	0.016	0.017	5.421
C(9′)	0.8713	0.3295	0.4080	0.018	0.107	0.018	5.774
C(10′)	0.9608	0.3385	0.5033	0.018	0.016	0.018	5.491
C(11′)	0.0808	0.3191	0.5379	0.016	0.015	0.016	4.843
C 12′)	0.4728	0.1637	0.5541	0.012	0.013	0.012	2.878
C(13′)	0.5653	0.1523	0.6480	0.014	0.014	0.014	3.813
C(14′)	0.6470	0.1014	0.6572	0.017	0.017	0.017	5.538
C(15′)	0.6294	0.0629	0.5790	0.018	0.017	0.018	5.651
C(16′)	0.5320	0.0771	0.4849	0.009	0.017	0.019	6.110
C(17′)	0.4513	0.1262	0.4723	0.015	0.015	0.015	4.537
C(18′)	0.5070	0.3203	0.5439	0.013	0.014	0.013	3.278
C(19′)	0.5107	0.3931	0.5600	0.015	0.015	0.015	4.333
C(20′)	0.6140	0.4257	0.5741	0.018	0.017	0.018	5.583
C(21′)	0.7100	0.3982	0.5770	0.015	0.015	0.015	4.328
C(22′)	0.7027	0.3268	0.5630	0.015	0.016	0.015	4.546
C(23′)	0.6046	0.2932	0.5467	0.014	0.014	0.014	3.948

[1] The specific atoms are identified in Formula III.

TABLE IV

Bond lengths and bond angles in 2,2′-bis(o-bromophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole

	A.
N(1)[1]–C(2)[1]	1.477
C(2)–N(3)	1.480
N(3)–C(4)	1.258
C(4)–C(5)	1.518
C(5)–N(1)	1.319
C(2)–C(6)	1.517
C(6)–C(7)	1.369
C(7)–Br(7)	1.940
C(7)–C(8)	1.405
C(8)–C(9)	1.381
C(9)–C(10)	1.380
C(10)–C(11)	1.412

See footnotes at bottom of table.

TABLE IV—Continued

	A.
C(11)–C(6)	1.397
C(4)–C(12)	1.501
C(12)–C(13)	1.376
C(13)–C(14)	1.451
C(14)–C(15)	1.298
C(15)–C(16	1.399
C(16)–C(17)	1.448
C(17)–C(12)	1.401
C(5)–C(18)	1.556
C(18)–C(19)	1.388
C(19)–C(20)	1.406
C(20)–C(21)	1.378
C(21)–C(22)	1.429
C(22)–C(23)	1.412
C(23)–C(18)	1.297
C(2)–N(3′)	1.495
N(1′)–C(2′)	1.255
C(2′)–N(3′)	1.401
N(3′)–C(4′)	1.367
C(4′)–C(5′)	1.430
C(5′)–N(1′)	1.316
C(2′)–C(6′)	1.508
C(6′)–C(7′)	1.364
C(7′)–Br(7′)	1.923
C(7′)–C(8′)	1.431
C(8′)–C(9′)	1.303
C(9′)–C(10′)	1.358
C(10′)–C(11′)	1.430
C(11′)–C(6′)	1.383
C(4′)–C(12′)	1.498
C(12′)–C(13′)	1.363
C(13′)–C(14′)	1.441
C(14′)–C(15′)	1.382
C(15′)–C(16′)	1.397
C(16′)–C(17′)	1.389
C(17′)–C(12′)	1.403
C(5′)–C(18′)	1.429
C(18′)–C(19′)	1.487
C(19′)–C(20′)	1.421
C(20′)–C(21′)	1.363
C(21′)–C(22′)	1.451
C(22′)–C(23′)	1.359
C(23′)–(C18′)	1.380

	Degrees
N(1)–C(2)–N(3)	108.8
C(2)–N(3)–C(4)	105.6
N(3)–C(4)–C(5)	111.9
C(4)–C(5)–N(1)	108.4
C(6)–C(7)–C(8)	125.4
C(7)–C(8)–C(9)	116.3
C(8)–C(9)–C(10)	121.7
C(9)–C(10)–C(11)	119.1
C(10)–C(11)–C(6)	121.6
C(11)–C(6)–C(7)	115.7
C(12)–C(13)–C(14)	116.3
C(13)–C(14)–C(15)	120.6
C(14)–C(15)–C(16)	125.0
C(15)–C(16)–C(17)	117.2
C(16)–C(17)–C(12)	117.4
C(17)–C(12)–C(13)	123.4
C(18)–C(19)–C(20)	112.5
C(19)–C(20)–C(21)	124.5
C(20)–C(21)–C(22)	116.9
C(21)–C(22)–C(23)	119.7
C(22)–C(23)–C(18)	117.6
C(23)–C(18)–C(19)	128.7
N(1)–C(2)–C(6)	107.7
N(3)–C(2)–C(6)	110.8
C(2)–C(6)–C(7)	125.3
C(2)–C(6)–C(11)	118.9
N(3)–C(4)–C(12)	122.2
C(5)–C(4)–C(12)	125.5

TABLE IV—Continued

	Degrees
C(4)–C(12)–C(13)	118.5
C(4)–C(12)–C(17)	118.2
N(1)–C(5)–C(18)	118.0
C(4)–C(5)–C(18)	133.3
C(5)–C(18)–C(19)	112.9
C(5)–C(18)–C(23)	117.9
C(6)–C(7)–Br(7)	122.6
C(8)–C(7)–Br(7)	111.9
N(3′)–C(2)–C(6)	111.9
N(1)–C(2)–N(3′)	108.4
N(3)–C(2)–N(3′)	109.3
C(2′)–N(3′)–C(2)	128.9
C(4′)–N(3′)–C(2)	123.8
N(1′)–C(2′)–N(3′)	110.0
C(2′)–N(3′)–C(4′)	106.6
N(3′)–C(4′)–C(5′)	104.1
C(4′)–C(5′)–N(1′)	110.9
C(6′)–C(7′)–C(8′)	121.0
C(7′)–C(8′)–C(9′)	117.6
C(8′)–C(9′)–C(10′)	123.0
C(9′)–C(10′)–C(11′)	121.7
C(10′)–C(11′)–C(6′)	115.3
C(11′)–C(6′)–C(7′)	121.4
C(12′)–C(13′)–C(14′)	114.7
C(13′)–C(14′)–C(15′)	123.7
C(14′)–C(15′)–C(16′)	118.5
C(15′)–C(16′)–C(17′)	120.1
C(16′)–C(17′)–C(12′)	119.2
C(17′)–C(12′)–C(13′)	123.9
C(18′)–C(19′)–C(20′)	115.1
C(19′)–C(20′)–C(21′)	128.0
C(20′)–C(21′)–C(22′)	114.4
C(21′)–C(22′)–C(23′)	120.2
C(22′)–C(23′)–C(18′)	126.1
C(23′)–C(18′)–C(19′)	116.1
N(1′)–C(2′)–C(6′)	125.4
N(3′)–C(2′)–C(6′)	124.6
C(2′)–C(6′)–C(7′)	120.8
C(2′)–C(6′)–C(11′)	117.6
N(3′)–C(4′)–C(12′)	126.4
C(5′)–C(4′)–C(12′)	129.4
C(4′)–C(12′)–C(13′)	119.0
C(4′)–C(12′)–C(17′)	117.1
N(1′)–C(5′)–C(18′)	126.6
C(4′)–C(5′)–C(18′)	125.1
C(5′)–C(18′)–C(19′)	114.0
C(5′)–C(18′)–C(23′)	129.9
C(6′)–C(7′)–Br(7′)	120.8
C(8′)–C(7′)–Br(7′)	118.2

[1] The specific atoms are identified in Formula III.

TABLE V

The dihedral angles between intramolecular imidazolyl and phenyl group planes in 2,2′-bis(o-bromophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole follow.

Planes:	Angle, degrees
A–A′	121
A–B	67
A–C	33
A–D	38
A′–B′	101
A′–C′	103
A′–D′	164

EXAMPLE VII

2-(o-fluorophenyl)-4,5-diphenylimidazole was made in 99% yield by reacting 1.2 parts of o-fluorobenzaldehyde with benzil as described in Example I. The product is a white crystalline solid melting at 205.5–206° C. It gave the following analysis:

Calculated (percent): C=80.2; H=4.8; N=8.9. Found (percent): C=80.0; H=4.9; N=8.9.

When 1.0 part of the imidazole was reacted with potassium ferricyanide in an ethanol solution of potassium hydroxide as was done in Example I, 2,2'-bis(o-fluorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole was produced in a 78% yield. This biimidazole is a pale yellow solid which softens at 139°–149° C., forms a gel at 158° C., and changes to a yellow-brown liquid at 165° C. Recrystallization from ethyl ether gives unsolvated dimer, M.P. 216.5–217° C.

The phototropic biimidazole containing one mole of water per mole of compound analyzed as follows:

Calculated (percent): C=78.3; H=4.7; N=8.7. Found (percent): C=78.6; H=4.8; N=8.6.

Upon irradiation by direct or indirect (through window glass) sunlight or by a sun lamp the pale yellow compound in the solid state turns purple, and the color fades when the radiation is stopped. An essentially colorless benzene solution of 0.5% concentration is also colored purple when it is exposed to this radiation and soon reverts to the colorless condition when the solution is removed from the light or the light is shut off. A quantitative measurement, as described in Example I, of the rate of color fading by recording the change in optical density of the maximum absorption band for the colored solution at 548 mμ gives a rate value of 6.2 which shows the imidazolyl radical having a fluorine substituent in an ortho position of the 2-phenyl group to have a color life about 1/13 that of the unsubstituted compound, the latter having a fading rating of 0.46.

By using the procedure described in Example I above with the appropriate substituted benzaldehyde or 9-phenanthrene carboxaldehyde, the following substituted biimidazoles were prepared:

2,2' - bis(o - ethoxyphenyl) - 4,4',5,5' - tetraphenyl-1,2'-biimidazole.—This compound is a light yellow solid which softens at 138° C., and becomes a green gel at 140° to 145° C. and a clear green liquid at 154° C. A further effect is observed when the green liquid turns brown between 165 and 180° C. and orange at 218° C. On light exposure at room temperature a benzene solution of the compound turns blue, and the color decays in about 5 minutes in the dark. The identity of the compound was confirmed by the following analysis of unsolvated material:

Calculated (percent): C=81.4; H=5.64; N=8.25. Found (percent): C=80.8; H=5.65; N=8.15.

2,2' - bis(2,3 - dimethoxyphenyl) - 4,4',5,5' - tetraphenyl-1,2'-biimidazole.—This is a light yellow solid which softens at 95° C. and becomes a yellow gel at 104° C., a yellow liquid at 140° C., orange at 160° C., red-orange at 180° C., and brown at 200° C. An irradiated benzene solution of the compound turns purple and loses its color in the dark in about 6 minutes. A chemical analysis was as follows:

Calculated for the material solvated on the average with one mole of ethanol for every two moles of compound (percent): C=77.0; H=5.63; N=7.64. Found (percent): C=76.95; H=5.70; N=7.68.

2,2' - bis(9 - phenanthryl) - 4,4',5,5' - tetraphenyl - 1,2'-biimidazole.—This biimidazole is a pale pink solid which turns yellow and softens at 165° C. and becomes a yellow gel at 180° C. and a yellow liquid at 230° C. In a benzene solution the compound turns yellow-orange when irradiated and loses the color in the dark in less than two minutes. An analysis of the material solvated on the average with one mole of ethanol for every two moles of compound:

Calculated (percent): C=87.2; H=4.91; N=7.00. Found (percent): C=87.2; H=4.6; N=7.00.

2,2' - bis(o - chlorophenyl) - 4,4',5,5' - tetrakis(m-methoxyphenyl)-1,2'-biimidazole.—This compound is a light yellow solid with a melting point of 175–178.5° C. and having the following characteristics:

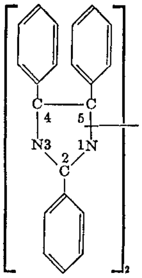
Analysis.—Calc'd for $C_{46}H_{36}N_4O_4Cl_2$ (percent): C, 70.87; H, 4.65; N, 7.18; Cl, 9.09. Found (percent): C, 70.84; H, 4.66; N, 7.25; Cl, 8.97.

M.W.: Calc'd 780. Found 806.

$\lambda_{max.}$: 260 mμ, ε=28,000.

Additional dimer compounds prepared by the procedure of Example I include 2,2'-bis(o-methylphenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, M.P. 120° C., giving a violet radical with a 3.5 color fading value as measured in benzene by the procedure described in Example 1; 2,2'-bis-(2,4,6 - trimethylphenyl) - 4,4',5,5' - tetraphenyl-1,2'-biimidazole giving a violet color, having a color life of about 7 minutes and a fading rate of 1.0; 2,2'-bis(o-methoxyphenyl) - 4,4' - bis(p - methoxyphenyl) - 5,5' - diphenyl-1,2'-biimidazole giving a blue color having a color life of about 4 minutes and fading rate of 1.61; 2,2'-di(1-naphthyl) - 4,4',5,5' - tetrakis(p - methoxyphenyl) - 1,2'-biimidazole giving a green color, having a color life of about 7 minutes and a fading rate of 1.01 as measured at 660 mμ; and 2,2' - bis(o-methoxyphenyl)-4,4',5,5'-tetrakis(p-methoxyphenyl)-1,2'-biimidazole which gives a blue color and has a fading rate of 0.50.

Additional substituted dimers of 2,4,5-triphenylimidazolyl radicals of this invention, prepared as described in Example I, are set forth in he following Table VI wherein the substituents are present on the phenyl groups as designated in the formula. It is understood that upon irradiation, the corresponding imidazolyl forms:



It is understood that in the above formula conjugated double bonds exist in the heterocyclic rings in accordance with the positions of the linkage between these rings.

TABLE VI

Substituents of phenyl rings attached to imidazolyl radical at—

2-position	4-position	5-position
o-Acetoxy		
o-Benzyl		
2,3-benzo(1-naphthyl)		
2,3-benzo	2,3-benzo	
Do	do	2,3-benzo.
Do	p-Methoxy	p-Methoxy.
3,4-benzo-2-methoxy-(2-(1-methoxy) naphthyl).		
4,5-benzo-2-methoxy-(2-(3-methoxy) naphthyl).		
o-Benzylthio	o-Benzylthio	o-Benzylthio.
o-Bromo		
Do	p-Bromo	
Do	o-Methoxy	o-Methoxy.
2-bromo-4-phenyl		
o-Butoxy		
o-N-butyl		
N-butylacetamido		
o-Butylthio		
o-Butyryloxy		
o-Chloro		
Do	o-Chloro	
Do	p-Chloro	
Do	o-Chloro	o-Chloro.
Do	3,4-dichloro	
Do	m-Pentyloxy	
Do	p-Methoxy	p-Methoxy.
Do	o-Methoxy	o-Methoxy.
Do	m-Methyl	m-Methyl.
Do	m-Methoxy	m-Methoxy.
Do	m-Ethoxy	m-Ethoxy.
Do	m-(β-Phenoxyethoxy)	m-(β-Phenoxyethoxy).
Do	p-Propionyloxy	
2-chloro-4-phenyl		

TABLE VI—Continued

Substituents of phenyl rings attached to imidazolyl radical at—

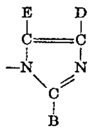
2-position	4-position	5-position
o-Cyano		
Do	p-t-Butyl	
Do	do	p-t-Butyl.
Do	p-Cyano	p-Cyano.
Do	p-Methoxy	p-Methoxy.
2, 3, 4, 5-dibenzo(9-phenanthryl).		
2, 3-dibromo		
2, 4-dibromo		
2, 6-dibutyl		
o-Dibutylsulfamoyl		
2, 4-dichloro		
Do	o-Bromo	
2, 6-dichloro		
Do	p-Butoxy	p-Butoxy.
2, 4-dicyano	p-Cyano	p-Cyano.
2, 6-dicyano		
2, 4-diethoxy		
o-Diethylsulfamoyl		
2, 5-difluoro	p-Cyano	
Do	do	Do.
2, 3-dimethoxy		
2, 4-dimethoxy		
Do	o-Chloro	
Do	do	o-Chloro.
Do	2, 4-dimethoxy	
Do	do	2, 4-dimethoxy.
Do	o-Methoxy	
Do	p-Methoxy	
Do	m-Phenylthio	
Do	do	m-Phenylthio.
o-Dimethylcarbamoyl		
2,4-dinaphthylthio		
2,4-dipentyl	2,4-dipentyl	2,4-dipentyl.
Do	3,4-benzo(2-naphthyl)	3,4-benzo.
2,4-dipropoxy		
Do	o-Diethylcarbamoyl	
o-Dipropylcarbamoyl		
o-Ethoxy		
o-Ethoxycarbonyl		
o-Ethyl		
o-N-ethylbutyramido		
o-N-ethylpropylamino		
o-ethylthio		
o-N-ethylvaleramido	p-t-Pentyl	p-t-Pentyl.
o-fluoro		
Do	o-Methoxy	o-Methoxy.
o-Methoxy		
Do	p-Chloro	
Do	p-Methoxy	
Do	o-Methoxy	Do.
Do	p-Methoxy	p-Methoxy.
Do	o-Methylthio	o-Methylthio.
Do	p-Nitro	
Do	do	p-Nitro.
Do	p-Phenylsulfonyl	
Do	do	p-Phenylsulfonyl.
o-Methoxycarbonyl		
Do	3, 4-benzo	
Do	p-N-ethylphenylsulfamoyl.	
2-Methoxy-4-phenyl		
o-Methyl		
Do	p-Benzoyloxy	p-Benzoyloxy.
o-N-methylacetamido	o-N-ethylbutyramido	o-N-ethylbutyramido.
Do	o-N-methylacetamido	
Do	do	o-N-methylacetamido.
o-N-methylpropionamido.		
o-Methylthio		
o-1-naphthyl	p-Phenoxy	
o-2-naphthyl		
o-Pentyloxy		
o-Pentyloxycarbonyl		
Do	3,4-benzo	3,4-benzo.
o-Phenoxy		
Do	3,4,5-trimethoxy	3,4,5-trimethoxy.
o-Phenyl(2-biphenyl)		
o-Phenyl	p-Methoxycarbonyl	p-Methoxycarbonyl.
Do	m-Pentyloxycarbonyl	
Do	do	m-Pentyloxycarbonyl.
Do	p-Phenyl	p-Phenyl.
o-Phenylthio	p-1-Naphthylthio	p-1-Naphthylthio.
o-Propoxy		
2,4,6-tribromo		
2,4,6-tributyl		
2,3,5-trichloro		
2,4,5-trichloro		
Do	o-butylthio	
2,4,6-tricyano	p-Cyano	p-Cyano.
2,4,6-triethoxy		
2,4,6-trimethoxy		
2,4,6-trimethyl		
2,4,6-tripropoxy		

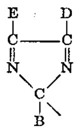
(5) Properties

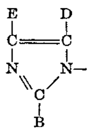
The triarylimidazolyls of this invention are relatively long-lived free (paramagnetic) radicals, which can exist for long periods of time under the influence of the light stimulus required to dissociate the photochromic dimers thereof. They have finite lifetimes in the absence of such stimulus and are characterized by their color, light absorption spectra, electron spin resonance spectra utilizing known methods [Ingram, Free Radicals as Studied by Electron Spin Resonance, Academic Press (1958)] and dimerization rate.

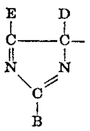
Their color and their longevity (which reflects their inherent stability) can be attributed to the extensively delocalized character of the odd electron, demonstrable by electron spin resonance spectroscopy. Thus in analogy to the pentaphenylcyclopentadienyl radical in which the unpaired electron can be written on 20 different carbon atoms [Hine, Physical Organic Chemistry, p. 382, McGraw-Hill Book Co., Inc. (1956)] the odd electron in a 2,4,5-triphenyl imidazolyl radical can exist on at least 14 positions in a delocalized charge and spin distribution. In short the radical is actually a hybrid of all the schematically possible position isomers wherein the electrons involved are delocalized. The dotted circle in Formula I in the section entitled "Summary of the Invention" is a well-known convention for simply depicting such hybrids with delocalized electrons. Specifically, the dotted circle stands for 5 electrons which satisfy the valencies of the carbon and nitrogen atoms of the imidazolyl ring, 4 of said electrons being paired in the form of two conjugated double bonds, with the fifth electron being odd (that is, unpaired) and thereby characterizing said compounds as radicals.

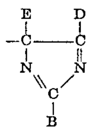
In contrast to the radicals, the dimers are essentially diamagnetic and are normally colorless or substantially so, owing undoubtedly to the fact that the odd electron that characterizes the radical is no longer free and delocalized but is paired and localized in the bond joining the two imidazole rings of the dimer. Structures (a) through (e) below schematically represent the structure of the imidazole rings and the points at which they can be joined. The letters B, E and D represent the substituted phenyl groups in the 2, 4 and 5 positions of the imidazolyls of this invention.

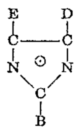

(a)


(b)


(c)


(d)


(e)


(hybridized radical)

Those skilled in the art will appreciate that schematic structures (a)–(e) can also be used to illustrate canonical forms that contribute to but singly do not represent the overall resonance-hydrid structure of the free triarylimidazolyl radical. The localized structures (a) through (e) relate to the delocalized radical structure as follows: When a particular dissociable (e.g. photochromic) and substantially colorless dimer, say (a)–(a) (i.e. the $1,1'$-isomer) absorbs energy (e.g. light energy) sufficient to rupture the localized bond linking the two imidazole rings, the two radicals that simultaneously form correspond initially, at the moment of bond rupture, to radicals having structure (a) wherein the free electron is still localized at the original site, i.e. the nitrogen atom at the 1-position. Such radicals are expected to have substantially the same color as the original dimer and also to be at a substantially higher energy (less stable) than the hybridized, colored radical with its delocalized electrons. But because the original bonding electron is now free to delocalize and this process inherently represents a considerable driving force towards greater radical stability (Hine, loc. cited), such radicals are expected to rearrange substantially instantaneously to the resonance-stabilized hybrid. In the same way, momentarily formed radicals (b), (c), (d) and (e) stabilize themselves by rearranging their electrons to the same hybrid state. Thus, all dimers that differ only in how the imidazole rings are joined will, upon dissociation, form an identical hybrid radical. This radical will be in equilibrium with all possible dimeric forms, as summarized by Equation 1 above where L—L stands for (a)-(a), (a)-(b), (a)-(c), (a)-(d), (a)-(e), (b)-(b), (b)-(c), (b)-(d), (b)-(e), (c)-(c), (c)-(d), (c)-(e), (d)-(d), (d)-(e) and (e)-(e); and L· is their common intermediate with its delocalized electron structure. Where the substituents at the 4 and 5 positions of the imidazole ring (designated (d) and (e) above) are the same, then positions (a) and (c) become identical, also (d) an (e), and the number of possible isomeric dimers reduces to 6.

These dimers as a class absorb in the ultraviolet. All show a maximum in the 2350 to 2850 A. region; some have a second maximum in the 3000 to 3750 A. range. Therefore to photo-dissociate the dimers into the colored triarylimidazolyl radicals, it is preferable to use light rich in such wavelengths. Photolysis can be effected by irradiating the solid dimer or preferably a solution in a suitable medium which should be substantially inert to the dimer, the imidazolyl radicals and to the photolyzing radiation. Suitable solvents include nitriles such as acetonitrile, hydrocarbons such as benzene and toluene, sulfoxides and sulfones such as diethyl sulfoxide and sulfolane, esters and polyesters such as ethyl acetate and poly (methyl methacrylate), esters and acetals such as tetrahydrofuran, polyethyleneglycol, and poly vinyl butyral, and (less preferably alcohols or other such substances having potentially abstractable hydrogens such as ethanol, 2-propanol and butanol.

Under photolyzing conditions favoring dimer dissociation, the Equation 1 equilibrium moves to the right and color appears. When the light stimulus is removed, the radicals recombine and the color fades. Normally in the absence of light the equilibrium position is so far to the left that the characteristic radical color is not evident. (Occasionally, however, the dimers themselves will show some color attributable to presence of uncombined radicals.)

The composition of the dimer or dimers in the photochromic compositions depends on such prevailing conditions as the solvent, the dimer concentration, and the temperature. For example in a sun screen containing a photochromic system of this invention, one or more dimers in equilibrium with the corresponding radicals as defined may predominate at summer or tropical temperatures, while other isomeric dimers (differing only in how the imidazole rings are joined as discussed above) may be favored at winter or arctic temperatures. The triarylimidazolyl species responsible for the phototropic system's characteristic color in activating light and its fading rate in the dark will, however, be the same under all conditions.

Of course mixtures of the photochromic dimers, which may differ not only in how the imidazole rings are joined therein but also in how the phenyl groups of the imidazole rings are substituted, can also be used in formulating photochromic systems and devices of this invention.

Since the structures of the novel triarylimidazolyl radicals, and therefore their properties such as color and recombination (color fading) rate, do not depend on how the imidazole rings are joined in the various possible corresponding dimers thereof, the dimers need only be photolytically dissociable to the corresponding triarylimidazolyl radicals for the purposes of this invention.

The biimidazoles are normally solids, and can be characterized by elemental analysis, molecular weight, melting point, color; infrared, visible, and ultraviolet adsorption spectra; phototropism, thermotropism and piezotropism

(response to change in pressure) when such properties exist for a particular compound. Infrared spectroscopy, among other physical methods, may be used to determine how the imidazole rings are joined in the dimer, if this is desired, owing to differences in absorption among the carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen bonds. X-ray diffraction analysis is also useful in determining biimidazole crystal form and molecular configuration. Different biimidazoles, including dimeric isomers, may differ in their phototropic and thermotropic properties, that is, in how easily they are dissociated by light and heat. Also, as discussed previously, the standard preparative procedures generally yield dimers that are thermally stable at ordinary temperatures. The biimidazoles can also be characterized by the properties of the corresponding imidazolyl radicals such as the color, absorption spectra, and recombination rate, i.e., color life, the time to revert to natural state after shutting off the source of radiation.

The triarylimidazolyl radicals of this invention, though relatively long-lived and capable of existing for long periods of time under the influence of light, combine (dimerize) at a surprisingly rapid rate, so that in the absence of the dissociating light stimulus the characteristic radical color fades rapidly at a characteristic rate, a property highly useful in sun shield applications. Such rapid color fading, attributable to the presence of an ortho-substituent in the 2-phenyl ring, is surprising since it was expected that a substitutent more bulky than hydrogen at a position so close to the imidazole ring would sterically retard rather than accelerate radical dimerization.

The ortho substitutent which characterizes all these novel compositions exerts important beneficial effects both in the biimidazoles and in the imidazolyl radicals formed therefrom on dissociation. For example such substituent raises the temperature required to thermally dissociate the dimer to the corresponding radicals. Thus in sun screens, for example, the invention dimers are more resistant to forming unwanted color due to thermal dissociation in the dark than corresponding dimers without the ortho substituent. Moreover, in the imidazolyl radicals such ortho substituent provides for rapid color fading. Thus sun screens or glasses based on such colored radicals as light filters will, in passing from brightly to dimly lighter areas, revert rapidly to their original uncolored state. Varying the substituents in positions other than ortho in the 2-phenyl ring provides still other advantages, for example, desirable variations in color or alterations in color shade obtained on exposure to light, changes in melting point, changes in solubility in solvents, etc.

For most rapid color fading it is preferred that the 2-phenyl ring contain no more than one ortho-substituent since in general a second ortho-substituent tends to oppose the color fading enhancement effected by the first ortho-substituent. A second ortho-substituent however is quite often valuable in that it tends to further increase the thermal stability of the dimeric form.

The followng examples illustrate the effect of temperature upon the formation of a particular isomer, and illustrate the effect the ortho substituent on the 2-phenyl group has in determining the properties of the novel compositions.

EXAMPLE VIII

A toluene solution of 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole was photolyzed at −85° C. and the relative radical concentration determined by electron spin resonance. The photolysis was stopped after the radical concentration had reached steady state, and the sample was then allowed to warm as the radical concentration was being continually monitored. The radical concentration at first increased and reached a maximum after 2 minutes. A thermocouple next to the sample tube read −20° C. The radical concentration then decreased to a minimum after 3 minutes (T=5° C.) and after passing through another maximum at 6 minutes (T=+12° C.), the concentration decayed to zero as the sample approached room temperature.

The data indicate that three different isomers of 2,2'-bis(o-bromophenyl) - 4,4',5,5'-tetraphenylbiimidazole are formed. One isomer is formed by photolysis at −85° C., a second isomer is formed between −20° and 12° C. and a third isomer is formed above 12° C. The isomer stable at room temperature is 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole.

Except for slight differences in the time and temperatures, similar results are obtained with

2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-fluorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-methoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole and
2,2'-bis(2,4-dimethoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole.

The isomers thus produced may be recovered and characterized by the techniques and methods outlined above.

EXAMPLE IX

A dilute, approx. 0.7% wt., ether solution of 2,2'-bis (o-fluorophenyl - 4,4',5,5'-tetraphenyl - 1,2'-biimidazole) (prepared as in Example VII) contained in a UV-transparent glass vessel was cooled to −78° C. and irradiated with 3000–4000 A. UV light from a high intensity tensor type lamp having a rating of 200 foot candles 12 inches from the bulb and placed 12 inches from the vessel. The irradiated solution developed the purple color characteristic of the 2-orthofluorophenyl - 4,5-diphenyl imidazolyl. After 4 minutes the lamp was turned off, and a nitrogen stream passed through the solution for 4 hours at −78° C. or until substantially all the ether evaporated. During the evaporation the solution was twice more irradiated—once at ½ volume for 4 minutes, again at ¼ volume for 2 minutes. To remove last traces of ether and any water that may have accumulated in the product, the vessel was placed in a vacuum desiccator and pumped at 0.1 mm. Hg pressure for 1 hour. The product, a light yellow solid, was evidentally a mixture of biimidazoles as evidenced by the following: (1) the infrared spectrum of a dispersion in KBr differed from that of the starting 1,2'-dimer and indicated the presence of at least one other biimidazole along with the starting 1,2'-dimer. For example the shoulder at 6.22 mμ, absent in the original (1,2') spectrum is considered to indicate the presence of the 4,4' isomer. (2) Rubbed with a spatula, a sample developed the purple imidazolyl radical color. In contrast the starting 1,2'-dimer was not so piezochromic, yielding no color under these conditions. (3) Also in contrast to the starting 1,2'-isomer, the above product dissolved in benzene with immediate color formation. The solution was essentially identical in its visible absorption spectrum and color fading value to the colored benzene solution obtained on photolyzing the 1,2'-dimer as described in Example VII, showing that the different biimidazoles dissociate to the the same imidazolyl radical.

The proportion of the above biimidazole product that dissociates to radicals in solution at room temperature and that is considered to be the 4,4'-isomer was determined to be 8.4% as follows: 2 mg. (3.2×10^{-6} mole) was added to 10 ml. of ethanol containing 4×10^{-6} moles of the leuco dye, tris (4-N,N-diethylamino - 2 - methylphenyl) methane, and 1.05×10^{-5} moles of p-toluenesulfonic acid. Color characteristic of triarylmethane dye (D^+ in the equation below) formed immediately. The amount produced from the leuco (DH) was determined spectrophotometrically and was related to the amount of biimidazole (LL) that dissociated into imidazolyl radicals (L) according to the stoichiometry

$$LL \rightarrow 2L\cdot$$
$$2L\cdot + DH + H^+ \rightarrow 2LH + D^+$$

In contrast, the starting 1,2'-isomer which does not dissociate spontaneously in ethanol produces no color during 24 hours under the same conditions.

Substantially similar results were obtained in the above experiments on replacing the o-fluoro compound with other biimidazoles, namely

2,2'-bis(o-methylphenyl) 4,4',5,5'-tetraphenyl-1,2'-biimidazole;
2,2'-bis (o-chlorophenyl)-4,4'-5,5'-tetra(m-methoxyphenyl)-1,2'-biimidazole;
2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole.

In each case, there was obtained a mixture of biimidazoles which contained at least one other isomer in addition to the 1,2'-isomer, including the 4,4'-isomer (thermally dissociable at room temperature in solution).

EXAMPLE X

This example further illustrates the surprisingly fast color fading of the ortho-substituted imidazolyl radicals of this invention. Various invention compounds, as listed below and prepared as in the preceding examples, were compared in the color fading test procedure described under Example I with analogously substituted position isomers, also prepared by the Example I method. The results are tabulated below in Table VII.

TABLE VII.—COLOR FADING OF SUBSTITUTED TRI PHENYL IMIDAZOLYL RADICALS IN BENZENE AT ROOM TEMPERATURE

2-phenyl	4-phenyl	5-phenyl	Color fading value
None	None	None	.46
o-Methyl			3.5
p-Methyl			.22
o-Chloro			7.3
p-Chloro			.41
	o-Chloro		.20
o-Bromo			7.4
p-Bromo			.36
o-Fluoro			6.2
p-Fluoro			.46
o-Methoxyl			7.7
p-Methoxyl			.092
o-Methoxyl	p-Methoxyl		1.61
p-Methoxyl	do		.043
o-Methoxyl	do	p-Methoxyl	.50
p-Methoxyl	do	do	.0077
o-CH_3O, m-CH_3O			3.42
o-CH_3O, p-CH_3O			.82
m-CH_3O, p-CH_3O			.091
o-, m-Benzo			1.2
m-, p-Benzo			.81

Table VII shows that with respect to the important color fading rate property the ortho-substituted products of this invention outperform analogously substituted isomers which essentially differ only in the position of the substituent on the indicated phenyl group of the imidazolyl radical.

EXAMPLE XI

This example illustrates the comparatively high resistance to thermal color change of representative invention dimers. All the compounds tabulated below in Table VIII were prepared by the method described in Example I so that they essentially differed only in being isomers with respect to the position of the indicated substituent in the 2-phenyl group of the imidazolyl radical. The procedure involved heating the biimidazole under test to 110° C. and observing its color

TABLE VIII.—THERMOTROPY OF SUBSTITUTED 2-PHENYL-4,5-DIPHENYL IMIDAZOLYL DIMERS

2-phenyl substituent	Original dimer color	Color change on heating to 110° C.
o-Methoxy	Pale green	None.
o,m-Dimethoxy	Light yellow	Do.
o,p-Dimethoxy	Pale green	Do.
p-Methoxy	Light green	Dark green.

The data show that the invention compounds containing an ortho-methoxy group undergo no color change while the para-methoxy compound is thermotropic and rapidly darkens on heating under the conditions of the test. The o-methoxy's stabilizing effect is particularly remarkable in the o,p-dimethoxy compound wherein the o-methoxy completely suppresses the p-methoxy's inherently adverse effect.

UTILITY

As previously stated, all the compositions of this invention are useful in sun shield or shade applications, either dispersed in a solid or liquid, or as the interlayer of a laminate. Preferably the binder, solvent or laminate is transparent, as for example clear glass or plastic. Specific applications include automobile windshields, spectacle lenses, and the like.

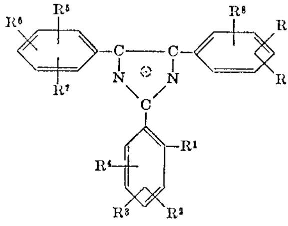
For example, a solution of dimethyl formamide containing 10% by weight of cellulose acetate (essentially completely acetylated) and 0.1% by weight of 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2' - biimidazole prepared as described in Example I was spread on a glass plate and dried by the application of mild heat from an infrared heat lamp utilizing sufficient ventilation. The glass plate was placed in a window frame and when illuminated in the sunlight a pleasing pink color quickly developed. The glass plate reverted to its essentially colorless state in a matter of seconds when the source of illumination was not present.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition of matter selected from the class consisting of

(A) a light-stable imidazolyl maintained under the influence of ultraviolet light represented by the formula



wherein

R¹ has a sigma value below 0.7 and is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)-carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl-lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

R² through R¹⁰ are each individually, selected from hydrogen lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl) carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl-lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

and any two R¹ through R¹⁰ substituents in adjacent positions on the same phenyl ring of the above formula can be joined together to form a —CH=CH— group; and

with the proviso that only one of R⁵ through R⁷ and only one of R⁸ through R¹⁰ can be in a position ortho to the phenyl carbon that is attached to the imidazolyl nucleus of the above formula;

said imidazolyl having an unpaired delocalized electron and having four electrons paired; and said imidazolyl being maintained upon the surface of an inert substrate or in solution in a solvent that is inert to said imidazolyl;

and

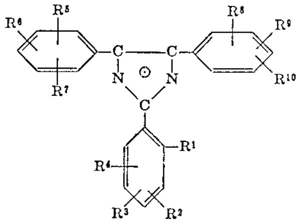
(B) dimers thereof, said dimers having the property of forming color in solution in an inert solvent upon exposure to ultraviolet radiation corresponding to the ultraviolet light absorption spectrum of the dimer, which color fades upon removal of the radiation.

2. A composition of matter consisting essentially of

(A) a light-stable imidazolyl; and

(B) an inert substrate or a solvent inert to said imidazolyl;

said composition being maintained under the influence of ultraviolet light and said imidazolyl being maintained upon the surface of said substrate or in solution in said solvent; said imidazolyl being represented by the formula



wherein

R¹ has a sigma value below 0.7 and is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower akylthio, di(lower alkyl)-carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl-lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

R² through R¹⁰ are each individually selected from hydrogen, lower alkyl, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di(lower alkyl) sulfamoyl, lower alkanoyloxy, N-lower alkyl-lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano; and

any two R¹ through R¹⁰ substituents in adjacent positions on the same phenyl ring of the above formula can be joined together to form a —CH=CH— group; and

with the proviso that only one of R⁵ through R⁷ and only one of R⁸ through R¹⁰ can be in a position ortho to the phenyl carbon that is attached to the imidazolyl nucleus of the above formula; and

said imidazolyl having an unpaired delocalized electron, and having four electrons paired.

3. The light-stable imidazolyl of claim 2 wherein R¹ is selected from the class consisting of lower alkyl, lower alkoxy, chloro, bromo and fluoro; and R² through R¹⁰ are each selected from the class consisting of R¹ and hydrogen.

4. The light-stable imidazolyl of claim 3 wherein R² through R¹⁰ are each hydrogen.

5. The composition of matter of claim 2 having the chemical name 2-(o-chlorophenyl)-4,5-diphenyl imidazolyl.

6. The composition of matter of claim 2 having the chemical name 2-(2,4-dichlorophenyl)-4,5-diphenyl imidazolyl.

7. The composition of matter of claim 2 having the chemical name 2-(o-methoxyphenyl)-4,5-diphenyl imidazolyl.

8. The composition of matter of claim 2 having the chemical name 2-(o-bromophenyl)-4,5-diphenyl imidazolyl.

9. The composition of matter of claim 2 having the chemical name 2-(o-fluorophenyl)-4,5-diphenyl imidazolyl.

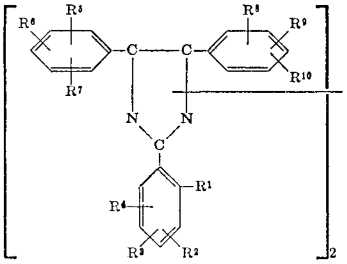
10. The composition of matter of claim **2** having the chemical name 2-(2,3-dimethoxyphenyl)-4,5-diphenyl imidazolyl.

11. The composition of matter of claim **2** having the chemical name 2-(o-chlorophenyl) - 4,5 - bis(m-methoxyphenyl) imidazolyl.

12. The composition of matter of claim **2** having the chemical name 2-(o-chlorophenyl)-4,5-bis(m-methylphenyl) imidazolyl.

13. The composition of matter of claim **2** having the chemical name 2-(o-methoxyphenyl)-4,5-bis(p-methoxyl) phenyl imidazolyl.

14. A composition of matter represented by the formula



wherein

R^1 has a sigma value below 0.7 and is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

R^2 through R^{10} are each individually selected from hydrogen, lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di-lower alkyl) sulfamoyl, lower alkanoyloxy, N-lower alkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

any two R^1 through R^{10} substituents in adjacent positions on the same phenyl ring of the above formula can be joined together to form a —CH=CH— group;

with the proviso that only one of R^5 through R^7 and only one of R^8 through R^{10} can be in a position ortho to the phenyl carbon that is attached to the imidazolyl nucleus of the above formula; and

wherein the two imidazolyl rings are joined through a single bond and the remaining valences of the 3 carbon atoms and the 2 nitrogen atoms of each ring are satisfied by 2 conjugated double bonds; and

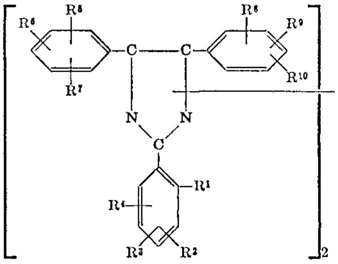
wherein said composition has the property of forming color in solution in an inert solvent upon exposure to ultraviolet irradiation corresponding to the ultraviolet light absorption spectrum of the composition, which color fades upon removal of the radiation.

15. The composition of claim **14** wherein R^1 is lower alkyl, lower alkoxy, chloro, bromo or fluoro; and R^2 through R^{10} are each selected from R^1 or hydrogen.

16. The composition of claim **15** wherein R^2 through R^{10} are each hydrogen.

17. The composition of claim **15** wherein R^1 is defined as in claim **15**; R^2–R^6 and R^9–R^{10} are each hydrogen, and R^7 and R^8 are each meta-alkoxy groups of 1–6 carbon atoms.

18. A composition of matter represented by the formula



wherein

the two imidazolyl rings of the above formula are joined at either the 1–2′ or 4–4′ positions of said rings, and the remaining valences of the 3 carbon atoms and the 2 nitrogen atoms of each ring are satisfied by 2 conjugated double bonds;

R^1 is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-loweralkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

R^2 through R^{10} are each individually selected from hydrogen, lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di-lower alkyl)sulfamoyl, lower alkanoxyloxy, N-lower alkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;

any two R^1 through R^{10} substituents in adjacent positions on the same phenyl ring of the above formula can be joined together to form a —CH=CH— group;

with the proviso that only one of R^5 through R^7 and only one of R^8 through R^{10} can be in a position ortho to the phenyl carbon that is attached to the imidazolyl nucleus of the above formula; and

wherein said composition has the property of forming color in solution in an inert solvent upon exposure to ultraviolet irradiation corresponding to the ultraviolet light absorption spectrum of the composition, which color fades upon removal of the radiation.

19. The composition of claim **18** wherein R^1 is lower alkyl, lower alkoxy, chloro, bromo or fluoro; and R^2 through R^{10} are each selected from R^1 or hydrogen.

20. The composition of claim **19** wherein R^2 through R^{10} are each hydrogen.

21. The composition of claim **18** wherein the two imidazolyl rings are joined at the 1–2′ positions of said rings.

22. The composition of claim **21** wherein R^1 is lower alkyl, lower alkoxy, chloro, bromo or fluoro; and R^2 through R^{10} are each selected from R^1 or hydrogen.

23. The composition of claim **22** wherein R^2 through R^{10} are each hydrogen.

24. The composition of matter of claim **21** having the chemical name 2,2′ - bis(o - chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole.

25. The composition of matter of claim **21** having the chemical name 2,2′ - bis(2,4 - dichlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole.

26. The composition of matter of claim **21** having the chemical name 2,2′-bis(o-methoxyphenyl) - 4,4′,5,5′-tetraphenyl-1,2′-biimidazole.

27. The composition of matter of claim **21** having the chemical name 2,2′-bis(o-bromophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole.

28. The composition of matter of claim **21** having the chemical name 2,2′-bis(o-fluorophenyl) - 4,4′,5,5′ - tetraphenyl-1,2′-biimidazole.

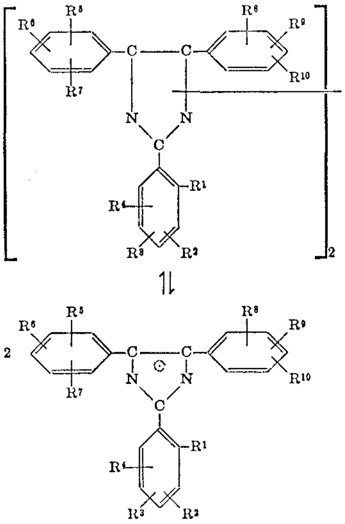
29. The composition of matter of claim 21 having the chemical name 2,2'-bis(2,3-dimethoxyphenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole.

30. The composition of matter of claim 21 having the chemical name 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis (m-methoxyphenyl)-1,2'-biimidazole.

31. The composition of matter of claim 21 having the chemical name 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis (m-methylphenyl)-1,2'-biimidazole.

32. The composition of matter of claim 21 having the chemical name 2,2'-bis(o-methoxyphenyl)-4,4',5,5'-tetrakis (p-methoxyphenyl)-1,2'-biimidazole.

33. A phototropic composition comprising the photodissociable imidazolyl dimer and the light-stable imidazolyl radical in reversible equilibrium in an inert solvent according to the equation and structures set forth as follows:



wherein

- R^1 has a sigma value below 0.7 and is selected from lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano;
- R^2 through R^{10} are each individually selected from hydrogen, lower alkyl, lower alkoxy, lower alkoxycarbonyl, lower alkylthio, di(lower alkyl)carbamoyl, di(lower alkyl)sulfamoyl, lower alkanoyloxy, N-lower alkyl lower alkanamido, phenyl, naphthyl, phenyloxy, naphthyloxy, phenylthio, naphthylthio, halo or cyano; and
- any two R^1 through R^{10} substituents in adjacent positions on the same phenyl ring in the above formulas can be joined together to form a —CH=CH— group;
- with the proviso that only one of R^5 through R^7 and only one of R^8 through R^{10} can be in a position ortho to the phenyl carbon that is attached to the imidazolyl nucleus of the above formulas;
- and wherein the two imidazolyl rings of said dimer are joined through a single bond and the remaining valences of the 3 carbon atoms and the 2 nitrogen atoms of each ring are satisfied by 2 conjugated double bonds;
- and wherein said radical has an unpaired delocalized electron and four electrons paired;
- and wherein said composition has a characteristic color when irradiated with dissociating irradiation which color disappears on cessation of the irradiation.

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NATALIE TROUSOF, Primary Examiner

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65—30, 60; 117—33.3, 124 D; 252—300

22

COULD WE HAVE DONE BETTER?

Research is a costly exercise. If it is exploratory, one knows little of what will happen, and frequently, the conclusion is that it is wiser to spend money in improving existing products and processes, where the rewards may be smaller, but more predictable. Of course, for a company like DuPont, that had an enormous overhead in the 1960s, the need is for new products, which offer a high return on investment, so as to support all the staff and accompanying expenses.

In the 1960s, the question inevitably was, is this going to be a $50,000,000 business?—if not, forget it. Well, it is hard to think of many business opportunities that may bring in that kind of money in a few years.

DuPont during the immediate post-war period hired many excellent scientists; the ones with the best academic records inevitably wound up in the company's elite Central Research Department, and after some years there, frequently were transferred to research management positions in operating departments. In some cases, they were even put in charge of sales organizations, without ever having been in field sales! In my experience, many of these people had a fine appreciation for science, but little for markets or emerging businesses. They had little enthusiasm for unfamiliar technology or business areas. For example, Chester Carlson reputedly tried unsuccessfully to interest DuPont (and dozens of other companies) in electrophotography and the potential of a new copying system. Surely, there were wise people at DuPont and other companies that would have supported such new opportunities, but their daily assignments were to keep the existing businesses running, and not to dream of new products that were years away, which would be a fulltime assignment. I always found it easy to talk to people in sales groups, who were often interested in new products, but regrettably, they seldom had the funds to support new programs, which were the province of research management.

Through my early years at DuPont there was a healthy effort on the part of managements to enthuse young chemists to invent things outside of their programs. They were told that they should spend 10% of our time doing just that. Regrettably, our management also was anxious for results of our research, and those 10% seldom were used. There were Idea Committees, planning sessions, etc., but while these could discuss new concepts, they could not implement research. Occasionally someone like the late A.B. Cohen was in a position to innovate very effectively, but he was an exception. And many of his coworkers found that while he had many great ideas, he paid little heed to theirs.

One definite disadvantage that the Organic Chemicals Department had was that during the 1960s it was involved in several totally unrelated businesses (fluorocarbons, petroleum additives, dyes and chemical intermediates). When people were transferred from one area to another, they brought little useful experience with them. There was reputedly some cross-fertilization, but it did not do much for moving businesses along. DuPont then was reluctant to hire experts at high salaries to manage new businesses, and consequently, people who had little expertise were put in charge of new programs. I used to ask some of my management friends why it was that in professional sports, the managers never switch from baseball, to football and then to basketball—after all a good manager could manage anything! The answer inevitably is that experience does count in professional sports, where the results can be seen quickly. So here too—we would have done better and faster if we had had management with background in the areas that we were researching.

Rewards—the inevitable reward at DuPont in the 1960s and 1970s was that highly regarded scientists would best advance their careers by being shifted around. We lost some of our ablest chemists because after a few years their careers were put before the programs they were working on. Naturally, some were replaced with able people—but without experience. Our first leader, George Coraor, who was entirely responsible for getting the HABI project started and going, was transferred away, because things did not get commercialized fast enough! Without the solid work done under his supervision, our patent position as well as our ultimate success would not have occurred. The author, who persisted in keeping this program going until 2000, did receive a sizable cash reward some 25 years after the research was initiated and ten years after retirement was honored with two prestigious DuPont awards. No one else of the original team that put things together, with the exception of Dr. Alexander Maclachlan was recognized; Maclachlan deservedly became the Company's Senior Vice President for Research before retiring. Had the original team of Coraor, Cescon, R.L. Cohen, and Dessauer, Maclachlan, Strilko and Yembrick been kept together beyond 1964, more innovative chemistry would surely have resulted.

Another problem was that once DYLUX® proof paper was commercialized; it became a part of the Graphic Arts business section. Any improvements, even if it were to go to other business areas would need to be funded by this group. Naturally, in order to maximize return on investment, their interest was exclusively in the business areas that they served. Hence, no great enthusiasm for branching out into related fields.

An aside: I have always wondered whether a small company, say an automobile dealership, wants to go into a new business, say, selling motorcycles. Would they re-assign the best automobile salesman to this, and risk losing his automobile-selling skills, or would they deal from the bottom, and hope that a less successful salesman would perhaps develop new skills? At least, his reassignment would not significantly reduce their automotive sales.

The answer regrettably is obvious, and that was to some extent what was the trouble with the Venture approach. A Venture Manager, a Marketing Head and a Manufacturing Head, all of whom had been recruited from the successful FREON business, supervised the UVI program. They had been effective there, but they possessed no background in the imaging technology that the research group was developing. In one or two cases one meets geniuses or quick studies, as was William S. Wartell, but it is risky business to place your hands on which your future depends on inexperienced leadership. Subsequent to the demise of the Venture concept in 1971, the author conferred with Robert Gee, who was assigned to find out what went wrong. He confided that with one or two exceptions, none of the Venture Managers possessed the entrepreneurial spirit, skill, or technical background to make their assignments successful. A notable exception was Dr. A.B. Cohen, of Photo Products Department, who championed RISTON® and CROMALIN® .

People said what was needed was a product-champion. Someone in a high place, who has faith in his staff, and who will move mountains because he believes in the product and will get his reward if there is success. Philip Botsolas, during the period from 1976 to 1978 tried to help, but he was in the Sales Group, and had limited resources to support the program. Surprisingly, Dr. Philip Wingate, who was the Photo Products General Manager and Vice President in the 1970s, was quite supportive of much of our work, but he appeared reluctant to cross paths with his Director of Research, Dr. Robert Upson. The one time he did, sparks did fly. But even Wingate could not really help—he had too much else on his plate.

Well, we made it big, but it could have been bigger!

BIOGRAPHIES

Rolf Dessauer was born in Germany, came to the United States in 1939, attended public schools in New York City, enlisted in the United States Army in 1944, obtained his BS and MS degrees at the University of Chicago and his PhD in organic chemistry at the University of Wisconsin in 1952. He joined the research division of DuPont's Organic Chemicals Department in 1952 and initially worked on dyes and ultraviolet screening agents. In 1958 he initiated work on photochromic compounds. This work led to DuPont's dominant position with hexaaryl biimidazoles (HABIs), a unique class of photo-oxidants and photo-initiators, which are used in DYLUX®, CROMALIN® and CROMACHECK® proofing products, RISTON® photoresists, OMNIDEX® holographic films, etc. His work was instrumental in developing proofing as a major activity in the Photo Products Department. After retirement, Dessauer has been active as a consultant and was a co-inventor of the near infrared sensitive THERMAL DYLUX® proof paper. He is the author or co-author of about 30 U.S. patents and several scientific publications. In 2001, Dessauer was awarded the Plambeck Lifetime Achievement Award for his contributions to photopolymerization technology, and the Pedersen Technical Excellence Award for his work with hexaaryl biimidazole photoinitiators. He is a member of the Joseph Priestley Society of the Chemical Heritage Foundation, the Society for Imaging Science and Technology and an Emeritus Member of the American Chemical Society and the American Philatelic Society.

Bruce L. Booth received a PhD in solid-state physics from Northwestern University in June 1967, and a BA in physics from Dartmouth College in 1960. He joined DuPont in 1967 and worked there for 31 years with a variety of research and management assignments involving optical measurements and product characterization, holography, bioassay and clinical instrumentation. He was on the team that set up the joint venture with British Telecom called BT&D and had a lead role in the team that developed the designs and manufacturing process for fiber connected diode laser sub modules for telecom applications. BT&D was ultimately sold to Agilent. He was the prime inventor of the Polyguide™ polymer waveguide forming process and related connectorization technology. From 1993 to 1997 Bruce led the DuPont effort for the successful DARPA funded Parallel Optical Link Organization (POLO) program, which included HP, AMP, SDL and USC as team members where Polyguide was the VCSEL/PD optical link to MT style connectors. With his team he left DuPont in 1998 with the license to practice the Polyguide™/GuideLink™ technology and set up Optical CrossLinks. Bruce currently is founder, chairman and CTO of Optical CrossLinks, Inc. with a focus on establishing high volume manufacturing processes to exploit the growing interest and business opportunities for polymer waveguide and optical fiber based circuitry and interconnect. He has over 36 publications in a broad range of media, and over 11 patents plus additional patent applications. He is affiliated with the American Physical Society, Optical Society of America, and the Society for Photo-optical Instrumentation Engineers (SPIE).

David F. Eaton was educated at Wesleyan University (AB, 1968) and Caltech (PhD, organic chemistry, 1972). He has worked in several areas of photochemistry and photoimaging during his career with DuPont: dye sensitized photopolymerization, electron transfer photochemistry, aqueous photoinitiators, organometallic photochemistry, silver halide sensitization chemistry, semiconductor particle photoredox chemistry, materials for nonlinear optics as well as photochemistry and photophysics of guest-host inclusion compounds. He acted as Coordinator for the Corporate Center for Imaging Applications, a cooperative research endeavor among DuPont's Electronics, Imaging Systems and Central Research Science and Engineering sectors. He moved to DuPont Electronics in 1999, after spending four years as Technology Director for DuPont's Cyrel® Packaging Graphics Products business. Eaton is the author of 86 research publications and reviews and has been granted 11 US patents. He is a Fellow of the Society for Imaging Science and Technology (IS&T), and a member of the American Chemical Society (ACS), American Association for the Advancement of Science (AAAS) and Inter-American Photochemical Society (IAPS); he was chairman of the 1991 Organic Photochemistry Gordon Conference. Before leaving DuPont, Eaton was Technology Director, New Business Initiatives, within DuPont's Electronic Technologies strategic business unit with responsibility for identifying and implementing new business opportunities in Photonics. Eaton became Vice President, Technology and Business Development with PrecisionCure, LLC in early 2005. He founded Light Insights, LLC, a technology-based business development service on retirement from DuPont in 2003. Light Insights provides clients with "understanding of technology for business growth."

Thomas Felder obtained a PhD in physical chemistry from the University of Pennsylvania in 1983 and joined DuPont later that year. He has worked in the fields of silver halide chemistry, xerographics, lithographic printing, fluorochemistry, NIR-induced thermal transfer, and holographics, and holds a number of patents in these fields. He was a member of DuPont Holographics from 1996–2002. He is a research associate working on novel imaging materials in the DuPont Displays Division.

Bruce M. Monroe received his undergraduate education at Wabash college and a PhD in organic chemistry from the University of Illinois (Urbana). After a post-doctoral research fellowship at the California Institute of Technology with Professor George S. Hammond, he joined the DuPont company, where he spent twenty-three years in various aspects of chemical research, primarily in the area of non-silver photoimaging. After retiring from DuPont in 1993, he received a J.D. from the Widener University School of Law. He is now a partner in the Wilmington, Delaware, and Berwyn, Pennsylvania, offices of the intellectual property law firm of RatnerPrestia, LLP. Since 1995, he has been an adjunct professor at the Wilmington campus of the Widener University School of Law, teaching courses in patent law and patent practice. He is the inventor or a coinventor of twelve issued United States patents and the author or coauthor of over thirty technical papers and reviews.

Peter Strilko received an A.B. from the University of Pennsylvania, M.S. from Drexel University and PhD in physical organic chemistry from the University of Delaware. His career with DuPont included 7 years with Dylux® products where he worked principally with photodeactivation and practical light sources and filtering for imaging and deactivation. He spent 20 years with the Riston® group working in a variety of assignments, the last being regulatory affairs and product stewardship.