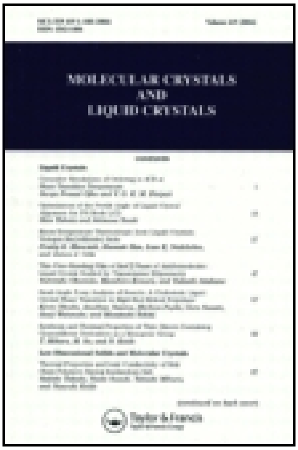

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reminiscences About Organic Photochromics

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Version of record first published: 24 Sep 2006.

To cite this article: Robert C. Bertelson (1994): Reminiscences About Organic Photochromics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 1-8

To link to this article: http://dx.doi.org/10.1080/10587259408037778

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 1–8
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Printed in the United States of America

REMINISCENCES ABOUT ORGANIC PHOTOCHROMICS

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Abstract The history of organic photochromics for potential military and commercial applications, especially the efforts at NCR Corp. during 1955–1972, is recalled. Impractical then because of "fatigue," organic photochromics are now useful for ophthalmic lenses, optical information processing, and photocontrol of physical properties and biological activity of polymers, because of the development of fatigue-resistant dyestuffs and a better understanding of the interactions between the dyestuff and its matrix.

I had mixed emotions when asked to present a "historical review," rather than "recent advances" or "future trends," since "historical review" often means that an elderly scientist near the end of his career tells the young folks how tough it was in the good old days without all the modern equipment. I will take "history" to mean "up until this morning." At least I'm still here to reminisce; at the IUPAC Photochemistry conference in Warwick in 1990, I met people who thought that I was long dead!

The early observations of photochromism were serendipitous. A solid is drying on a benchtop, the sun shines on it for a while, and its color changes; after sitting overnight in the dark the solid is found to be its original color. This process can be repeated. The photocoloration was not so unusual; the reversibility of the color changes was the unusual phenomenon. The first report in the scientific literature appeared in 1876, and concerned the potassium salt of dinitromethane. The so-called leucocyanides and bisulfites of triarylmethane dyestuffs were studied from about 1918, but I have no doubt that 100-year-old reports of the dyestuff industries contain much information observed during attempts to improve the light fastness of these dyes. Some other classes of compounds examined in the period up to about 1940 were the fulgides, aryl disulfides, and carbonyl derivatives such as semicarbazones, osazones, phenylhydrazones and anils of aryl aldehydes. The literature of this period discussed whether photochromism was a chemical or purely physical phenomenon, and recognized photoionization as responsible for the coloration of the triarylmethane derivatives. Several reviews are available summarizing this early work and tabulating photochromic compounds.

In the period from about 1946–55 the entire field of organic photochemistry developed, from the practical standpoint because of the availability of light sources and instrumentation, and from the conceptual standpoint because of a better understanding of molecular spectroscopy. Extensive studies began of the cis-trans photoisomerization of stilbenes, azo compounds, indigoid dyestuffs, and related compounds. The spirobipyrans, known since the 1920s to be nicely thermochromic, were found in 1952 to be photochromic also. Indolinospirobenzo- and naphthopyrans, as well as spiropyrans having several other heterocyclic "left-hand sides," were first prepared in 1940 and their thermochromism and solvatochromism studied; they were not then recognized as photochromic. Later some of these were found to also exhibit photochromism under appropriate conditions. Probably the most significant publication in this period is the thesis of Odile Chaudé, which addresses almost every aspect of spiropyran thermochromism: thermodynamics; kinetics; solvent effects; and the nature of the colored forms.

After 1955 both military and commercial interests motivated greatly increased activity in photochromism. The potential applications each group envisioned overlapped to a considerable extent, so the government R & D contracts available to industry and academe were eagerly sought. One major interest of the military was an instant image, self-developing photographic system for aerial and space surveillance. The lack of photosensitivity to the visible region and the monomolecular nature of the coloration (giving it a photographic speed of *ca*. 0.0001) eliminated photochromic film for simple in-camera picture taking. Another major interest of the military was protection of personnel and optical equipment against flash blindness from the fireball of a nuclear detonation. Goggles, helmet visors, vehicle windshields, aircraft canopies, and other optical filters were obvious hardware items to incorporate photochromic materials. A third major interest was camouflage fabrics and paints. Research and development efforts on these military applications, especially eye protection for pilots, were not confined to the US, of course. Very similar work was underway in both the UK and France, and undoubtedly in the former Soviet Union also.

One major commercial interest also was an instant, self-developing, dry photographic system, but for different reasons. Obviously, no monomolecular in-camera photographic system could compete with Polaroid. However, if you control the spectral distribution and intensity of the light source, and the exposure time, you can "take pictures." In particular, you may be able to easily photocopy documents in an office, an application the ultimate magnitude of which was not realized at that time. In those days before practical xerography, copying an existing document meant photostats, or diazos with ammonia fumes, or Verifax with its tray of sloshing caustic solution and peeling off and disposing of that slimy negative sheet, or the flimsy, waxy Thermofax. The original interest of the National Cash Register Co. was not in office copy systems, but in "high-speed printing." Accounting and banking machines spewed out large amounts of human-readable hard copy directly, and clearly future computers would create data faster than machinery could print it. And so in 1954 the Fundamental Research Department of NCR embarked on a study of photosensitive materials usable for self-developing, instant photography as a means of high-speed printing.

A second major commercial interest in photochromics arose at the end of 1955 when Hirschberg and Frei at the Weizmann Institute pointed out that a photochromic system had two stable states, switchable from one state to the other reversibly, and the state of the system is identifiable; thus in principle a photochromic could be a binary switch for a digital computer having a chemical memory. This concept initiated vigorous research in industrial firms and their academic consultants. A third major commercial interest was the non-nuclear version of the eye-protection problem, *viz.*, photochromic glasses for humans, and windows for vehicles and buildings. Systems that did not meet the stringent military requirements might be useful for protection against sunlight. Finally, many other commercial applications were proposed: these included toys (suntanning dolls); paints and crayons; UV dosimeters (sunburn monitors); color-changable clothing (first predicted in 1912) and its military counterpart, camouflage; and microimage information storage.

With all these promising applications, all this economic motivation, what actually happened? What was successful, and what was not, and why?

Let me now reminisce on photochromic history in the US from about 1956, and in particular at the National Cash Register Co. (NCR). I'm quite certain that very similar histories unfolded elsewhere in the world. Nearly all companies, large and small, began with a thorough review of the published literature, and experimentally with as many different photochromics as were conveniently available, qualitatively compared in the way the compound would actually be used. Since at that time nearly every application desired a large change in optical density or a maximal color contrast when perceived by a human eye, useful photochromics appeared to be limited to organic dyestuffs. The spiropyrans and the leuco derivatives of the triarylmethane, cyanine, and closely related cationic dyes seemed especially useful because of the very high extinction coefficients of the colored forms, quantum yields of 0.5–1.0 for color formation, and a change from colorless or yellow to purple or blue. The indigoid compounds and the metal dithizonates, though generally less photosensitive, showed some promise for applications involving a change from one visible color to another. For nuclear flash-blindness protection useful materials included polynuclear aromatic and heterocyclic compounds that give high concentrations of triplet states after exposure to an extremely intense flash. The triplet states often absorb strongly and broadly in the visible, and have lifetimes sufficient to protect the eye until alternative shutters can be activated. As practical drawbacks, the polycyclic compounds are often extremely tedious to prepare and purify to the degree necessary to give reproducible results, and are quickly fatigued.

Another advantage of organic dyes is the variety available. Many triarylmethane dyes can be purchased or readily synthesized (but purification can be tedious). The spiropyrans are even more prolific. Essentially they are prepared by the condensation of a heterocyclic quaternary salt having an active alkyl group, or the corresponding methylene base, with a β-hydroxyacrolein moiety. Because of the availability of the intermediates (namely, a 2-methyleneindoline–a so-called Fischer's Base–and a salicylaldehyde), the indolinospirobenzopyrans (acronym: BIPS, from an earlier-used name, BenzIndolinoPyryloSpiran) were most extensively investigated, at first chiefly by NCR in the US, by St. Gobain in France, and by several groups in the USSR, where much of the preparative work appears to have been carried out by Dzhaparidze in Tbilisi.

At NCR we had prepared about 75 different Fischer's Bases and 125 different salicylaldehydes, and made about 650 BIPS compounds. From the many other quaternary salts available, for example in the benzothiazolium, benzoxazolium, quinolinium, pyridinium, pyrylium, thiopyrylium, and isoxazolium series, the corresponding heterocyclylspiropyrans could be made; the salicylaldehyde could be replaced by other classes of compounds, and the salicylaldehydes could be condensed with ketones to give an extensive assortment of symmetrical and unsymmetrical spirobipyrans. I use the term "salicylaldehydes" to include hydroxynaphthaldehydes, *i.e.*, benzosalicylaldehydes. Since the nitroso group easily condenses with active methylenes in the same way as an aldehyde, in 1959 1-nitroso-2-naphthol was condensed with Fischer's Bases to give indolinospironaphthoxazines; I believe these were the first preparations of this class of photochromics. These dyes were useless for the flashblindness protection application, so they were put on the shelf and never touched again for years--at NCR, that is!

I've made the synthesis sound easy, and the condensation often is, at least for the BIPS: pour the two halves of the molecule together and the product precipitates in a rather pure form. However, after you've used the very few Fischer's Bases and the two dozen or so salicylaldehydes readily available, getting the intermediates may become a major research project in organic synthesis. The structures assigned to several substituted salicylaldehydes and naphthols in the literature are incorrect. Salicylaldehydes, hydroxynaphthaldehydes, and nitrosonaphthols having multiple additional substituents such as alkyl, alkoxy, halo, and nitro unequivocally in specified positions often require lengthy synthetic schemes. The nitrogen, sulfur, and selenium analogs of these compounds are formidable synthetic challenges. Authentic *ortho*-nitrosophenols, even simple ones, are difficult to prepare pure. Most Fischer's Bases are miserable to prepare. The cyclization step in both the Fischer and Bischler syntheses gives a mess, the yield often is very low, and there is an ambiguity in the direction of cyclization of *meta*-substituted anilines (the substituent may end up in the 6 or the 4 or both positions of the indole derivative). (Practical tip: unless you can purchase the phenylhydrazine, follow the Bischler route using acetoin whenever possible. However, some substituted Fischer's Bases are best prepared by routes other than these two classical ones.)

The spiropyrans originally used by Hirshberg and Fischer were observably photochromic only at low temperatures, since the thermal fading rate was so high that the color did not persist at room temperature. For most practical uses the color needs to persist for seconds, minutes, or hours in polymer films or microencapsulated fluid solutions. A strong electron-attracting group, conveniently a nitro, conjugated with the oxygen atom of the pyran moiety, reduces the thermal fade rate, usually enough to impart observable photochromism at room temperature. The thermal fading rate constants of substituted BIPS correlate well with the substituent constants in a Hammett-type equation. The correct structures of some substituted salicylaldehydes were deduced by this method prior to confirmation by more usual means.

During the 1960s the organizations mentioned and others throughout the world examined a large number of organic photochromics for many different applications. Among those in the US were Sperry Rand Corp. (anils), RCA (indigos), and American Cyanamid Co. (spiropyrans, metal dithizonates); and among others in the UK were Plessey Ltd. and Aberchromics Ltd. (fulgides, fulgimides). During these early attempts to develop useful products an important application of photochromics was to impress administrators with spectacular color magic shows in order to encourage continued funding for another year. Even a Nobel-prizewinning photochemist could be suitably impressed (but not mystified for long.) Such demonstrations in classroom lectures or as laboratory experiments turn on students to the wonders of organic photochemistry!

However, in spite of all this effort and impressive demonstrations with attendant publicity, organic photochromics had very little commercial success. The spiropyrans were used in a thermal, not photo, copy paper and in a recording medium for microimages, and that was it. The limited commercial success of organic photochromics during that period can be attributed almost entirely to "fatigue," a vague term that merely means "the dye did not cycle as often as desired when used in a particular way in our specific application." Most applications required the photochromic to undergo a very large number of cycles, or, more commonly, to be exposed continuously for a long time to sunlight. Non-photochemist manufacturers of sunglasses, automobile windshields, and T-shirt printing inks do not realize the enormous total energy in one day of bright sunlight, let alone two years.

In initial attempts to reduce fatigue rate, the usual antioxidants, free-radical traps, and just about everything on the shelf simply were added to spiropyran formulations. Such Edisonian experiments were not very helpful; many addenda significantly quenched the photocoloration reaction, and those that did not were insufficiently effective by orders of magnitude. To double the useful lifetime of a pair of sunglasses from one day to two days still does not produce a commercially viable product. The few studies of the mechanisms of fatigue and of the photocoloration confirmed one's suspicions that each case is unique, and that what happens in dilute fluid solutions is not necessarily what happens in more rigid polymer matrices. With practical limitations of organic photochromics becoming apparent, attention turned to "causing color changes" by means of liquid crystals and by "electrochromism," which is misnamed because what is usually involved is an electrochemical reaction cycle, often involving oxidation of a leuco dye at an anode. By about 1971, then, because of "fatigue," the development of other ways of controlling light and displaying color, and a worsening economic situation in the US, much organic photochromic research was essentially abandoned.

The time was ripe for a comprehensive summation of photochromism in all its aspects—organic, inorganic, biological, and applied—and particularly the preservation of the large amount of information in patent and unpublished government reports, still very useful even though denigrated for not being peer-reviewed. Thus in 1971 there appeared the book *Photochromism*, G. Brown, Ed., J. Wiley & Sons, New York. This volume was brought up to date by the publication in 1990 of *Photochromism: Molecules and Systems*, H. Dürr and H. Bouas-Laurent, Eds., Elsevier, Amsterdam, which followed the same format as the earlier volume. Additional reviews, valuable for the more thorough coverage of Soviet work, are the books by Dzhaparidze on spirochromenes, by Przhiyalgovskaya on the chemistry of Fischer's Bases, and the more general survey of Eltsov.

In spite of its early activity, NCR was inexperienced in protecting and exploiting this novel chemical technology, and its initial advantages were lost. After the termination of research and researchers at NCR in 1972, I found myself "overqualified" in the eyes of potential employers. One of my duties had been to provide free samples and advice in answer to inquiries about photochromics, so in accordance with the principle of "why give it away free when you can sell it," I founded Chroma Chemicals.

Organizations attempting to develop plastic photochromic ophthalmic lenses continued their efforts, however, because of the very considerable financial rewards for a commercially successful product. Goals were an acceptably small loss in photochromic performance during two years of normal use, a small temperature dependence of thermal fading rate, and a neutral gray or brown color. The dyestuff research was heavily biased towards the spironaphthoxazines, because of the presumed better fatigue resistance inherent to this class. The naive approach to the desired colors involved simply mixing two or more dyes of equal ultraviolet photosensitivity giving absorption bands of equal intensities in different regions of the spectrum and having equal thermal fade rates. Everyone is still searching for such a trio or even a pair of such dyes. A better approach is to find a dye having two (or more) equally intense absorption bands in the visible region. By this time, the mid-1970s and the 80s, one could calculate an approximate absorption spectrum for a given structure, conveniently with the semi-empirical PPP methods exploited by Griffiths, and a variety of organic dyes, including many novel spiro compounds, were proposed for synthesis on the basis of their calculated spectra. Nowadays more sophisticated calculations include non-planarity and many more configuration interactions. Out of such efforts came the spiroquinolinooxazines and the spirobenzoxazines. These latter give orange and red colors useful for brown-tinted lenses. Although benzothiazolo- and benzoxazolospiropyrans had been long known to give yellow and orange colors, they are not of practical use in this application. These colors were obtained from certain fulgides and from

2,2-disubstituted benzo- and naphthopyrans. Currently, much effort is being devoted to these non-spiro pyrans.

There is a limit to how much photostability even the cleverest organic chemist can build into a complex organic dyestuff. When it was finally realized that what is "fatiguing" is not just the photochromic dye, but the dye in its polymer matrix, the polymer chemists and engineers designed matrices specifically optimized for a given dye formulation by taking into account such parameters as glass transition temperatures, free volume in the matrix, and the activation volumes needed for the dye to convert from the spiro to the open form and vice versa. The many studies of photochromics dissolved in polymers, or structurally incorporated into them by grafting or co-polymerization, were reviewed by V. Krongauz in the 1990 *Photochromism* book. Such studies of dye-polymer interactions resulted in considerable improvements in fatigue resistance and other performance parameters Further improvements resulted from the use of newer types of stabilizers such as metal chelate singlet oxygen quenchers and "hindered amine light stabilizers," and from improved methods of sealing a lens against entry of oxygen and moisture. Currently, plastic photochromic ophthalmic lenses are pretty good and are going to get better both technically and economically because of the lively competition. Advances in polymer processing technology probably will be of greater value than advances in dyestuff synthesis.

Since the rise and fall of photochromics in the 1960s a whole new generation of scientists and engineers has arrived, to many of whom the phenomenon of photochromism is new. In the last seven or eight years many people have asked me about photochromics. The non-scientist would-be entrepreneurs usually intend to invent sunglasses or a sun-tanning doll or an instant photographic film. I give them their homework reading assignment (*i.e.*, the two *Photochromism* books) and never hear from them again. The serious investigators of the new generation are rarely synthetic organic chemists, but instead engineering physicists, materials scientists, polymer chemists, and molcular biochemists using the long-known photochromics in new and more subtle ways in applications. They don't need new dyes; there are plenty of tricks to play on the old ones! The published literature of the last few years and the papers and posters presented at the IUPAC Symposium in Warwick (1990), the two Symposia on the Chemistry of Functional Dyes (Osaka, 1989; Kobe, 1992), and this present Symposium exhibit the variety of ways organic photochromics are being studied today.

Currently, as far as I know, the commercial status of organic photochromics is simply: (1) a large and growing use in ophthalmic lenses; (2) a small and steady use in making microimage masters; (3) a small and slowly growing use as exposure indicators in photolithographic plates; and (4) a small and fluctuating use in inks, toys, and novelties. I should also mention continuing research uses as chemical actinometers and for visualization of fluid flow, for which a water-soluble material with good photochromic properties is still needed.

In the near future, I expect that plastic ophthalmic lenses will get better and almost entirely replace classical (i.e., Corning) glass. I have no idea whether photochromic contact lenses or photochromic glass lenses prepared by sol-gel processes will prove practical. If I had to guess what general area will next be a commercial success for photochromics, I'd choose physics over biochemistry. Color printing, optical recording, 3D-memories, storage, and holography using linear and non-linear properties of the dyes, the dyes not only in a bulk polymer matrix but oriented in films, adsorbed on solid substrates, or vapor deposited, seem promising to me. In this regard I will mention the efforts of Robillard and of Rentzepis and their respective associates.

Well, I have reminisced about old history; now it's time to make new history for future reminiscences.