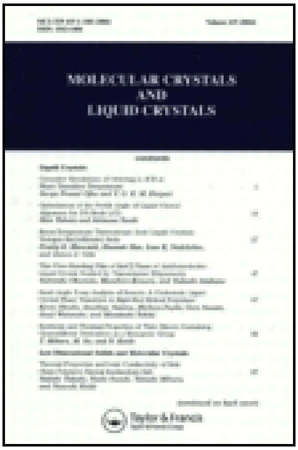

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The Commercialization of Plastic Photochromic Lenses: A Tribute to John Crano

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The Commercialization of Plastic Photochromic Lenses: A Tribute to John Crano

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With 1999 marking the 100th anniversary of the discovery of organic photochromic compounds[1], it is a fitting time to reflect back on commercial uses that have developed from this interesting class of organic compounds over the years. From the many applications that have been proposed, including security devices and optical memory storage, the one application that has achieved substantial commercial success is switchable lenses. Such lenses, based on inorganic photochromes (AgX), have been available since the mid 1960s, but it is only in the last 10 years that organic systems with acceptable performance have been available in the marketplace. From the mid 1980s until his sudden death in early 1998, John Crano lead the research effort at PPG Industries that developed the photochromic systems that have been commercialized by Transitions Optical Inc. under the name Transitions®.

Keywords: photochromism; naphthoxazine; naphthopyran; Transitions®

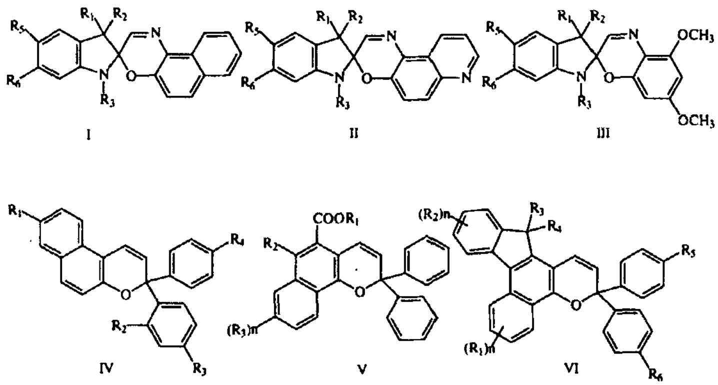
The story of the events leading up to the commercialization of Transitions lenses is rooted not in photochromism, but rather in a substance used to manufacture plastic lenses, CR-39® monomer. In the late 1930s, PPG Industries (at the time known as Pittsburgh Plate Glass Co.) was developing a series of allylcarbonate monomers[2] for possible plastic applications in World War II. The plastic resulting from polymerization of these monomers differed from materials known at the time (Plexiglas® from Rohm & Hass and Lucite® from DuPont) in that it was a thermoset as opposed to a thermoformable resin. The plastic from the 39th monomer prepared in the series (diethyleneglycol-bis-allylcarbonate, which later became well known simply as CR-39®) had particularly good mechanical properties and was used to manufacture fiberglass reinforced molded gas tanks for the B-17 bomber. When the war ended, so did the market for this monomer. For the next two decades, several entrepreneurs continued to examine this interesting material for applications where light-weight, strength, and optical clarity were required.

In 1964 Corning Glass scientists discovered silver halide based photochromic glass and two years later introduced a product in the US derived from this technology (the Photogray® lens). The photochromic borosilicate glass discovered by Corning contains 100 angstrom crystallites of copper-doped silver halide (too small to scatter and too transparent to absorb visible light). Ultraviolet light causes copper (I) ions in the crystallites to give up an electron, which is captured by silver ions. The resulting silver atoms aggregate to form small specks. These specks absorb visible light (they are too small to cause scattering) and turn the glass dark. When UV illumination ceases, the metallic silver releases electrons back to copper (II) and are themselves reconverted to visibly clear silver halide crystallites. This cycle can be repeated indefinitely with no degradation. The original product was enhanced with the introduction of the PhotoSun® lens in 1971 and the PhotoGray® Extra lens in 1978.

In 1972, to protect the public from an increasing number of eye injuries, The United States FDA set minimum standards for impact resistance for glass lenses that necessitated their being cut much thicker (2.2mm vs. 1.0-1.5mm). This occurred just when popular eyeglass styles were requiring larger and larger lenses. All at once it seemed that wearing eyeglasses had become very uncomfortable! At about the same time, plastic lens casters, who had been struggling for years to find a suitable material and conditions to manufacture consistently good plastic transparencies, were starting to achieve substantial success with CR-39® monomer. From 1970 to 1981, plastic lenses became a sensation in the United States, moving from 5% to 50% market share. Lens manufacturers looking to further capture market share from glass, came to PPG to ask for a photochromic version of their CR-39® to go up against the popular (nearly 20% of all lenses sold in the US at its peak) Corning Photogray® Extra product. Although this prompted some lowlevel experimentation, a serious effort did not start until some 10 years later (1982) when American Optical introduced its Photolite® plastic photochromic lens. The Photolite® lens, manufactured through a post-cure dyeing process, used an organic photochromic dye from a class of compounds called indolinonaphthoxazines (I). The oxazines had been patented[3] some 10 years earlier and possessed the unique property of having good photostability. Although they would eventually fatigue (unlike the inorganic silver halide system), they could be cycled between their clear and darkened state many times without showing signs of degradation. Clearly the Photolite® lens represented ground-breaking technology, but it was not successful in the marketplace, most people believed, because the activated color was blue as opposed to the more neutral sunglass colors of gray or brown. PPG therefore equated success with having a neutral activated color and set out to achieve that goal by developing its own organic photochromic compounds. The first fruits from this effort were the indolinoquinoxazines[4](II), a "knock-off" of the naphthoxazines that possessed improved photochromic properties. Unfortunately, much like the parent naphthoxazines, these compounds all had a blue activated color.

Concurrent with this dye research, the question of what substrate these compounds would be used in was being addressed. Recalling that PPG's interest in photochromism had been initiated by lens casters seeking a photochromic version of CR-39®, different methods were attempted to develop such a product. Unfortunately for the lens casters, because the use of high level of initiators required to polymerize allylic carbonate monomers would invariably destroy the photochromic dyes, such a product was not to be. Attempts to dye the polymer from CR-39® also posed a problem because it was found that very little photochromic could permeate due to its highly cross-linked nature. As a result, a new polymer was developed[5], based on CR-39®, that would accept photochromic dyes through a post treatment process. At a time when PPG was continuing its search for compounds with activated colors other than blue, it used the quinoxazine chemistry to launch a line of photochromic sunglasses called "Visensa" in 1986. These were available for only a short period before being withdrawn from the marketplace.

Figure 1. General Structures of Organic Photochromic Molecules



The second sub-class of photochromics that yielded some measure of success was the 5', 7'-dimethoxybenzoxazines[6](III). These compounds had a major absorption around 580nm and a minor absorption in the 460nm range. A lens prepared by mixing a representative member of this chemistry with the previously discovered quinoxazines, gave an activated color that was blue-purple. By today's standards, the lens did not approach the neutral gray that was desired, but it represented a substantial improvement over the AO Photolite® product.

In 1987 the facility that had produced the Visensa product was converted to produce development quantities of this lens and a limited test market was run around the US. Based on the success of these tests, PPG linked up with Essilor International of France in 1990 to form a joint venture to manufacture and market plastic photochromic eyewear. The joint venture, called Transitions Optical, built a manufacturing facility in Pinellas Park FL, and started manufacture of their first generation Transitions® lenses in early 1991. The joint venture partners complemented each other with their strengths: Essilor, the largest lens manufacturer in the world brought its knowledge of all facets of the lens business as well as the photochromic lens processing technology called "imbibition[7], while PPG brought the photochromic dye and polymer technology.

Fully realizing that the Gen-I product would have limit appeal in the marketplace, research into novel photochromic compounds continued. In late 1987 PPG had learned from an eminent photochromic chemist that had been retained as a consultant, that a family of photochromics called naphthopyrans[8] were photochromic at room temperature. This was very valuable information because the open literature at the time indicated that the compounds, although possessing a desirable activated color (yellow to orange) complementary to the quinoxazines, were photochromic only at reduced temperatures[9]. This information lead to a multi-year study of structure-property relationships within this class of photochromics. The 3,3-diaryl 3H naphtho[2,1-b]pyrans[10](IV) were the first compounds to be studied. This work produced orange compounds that were coupled with the blue quinoxazines to give the first commercial plastic photochromic lens that was a true gray when activated. Transitions Optical introduced the product (initially known as Transitions® Plus) in 1992. The lens was an instant success and demonstrated the commercial potential of such a product. Over the next 3 years, Transitions Optical became an international company by every sense of the word, establishing production facilities in Ireland and Australia.

While the Transitions® Plus lens was very successful, there were areas where photochromic dye chemistry could bring further enhancements. Consumers noticed the lens produced different activated colors depending on environmental conditions (UV and temperature), could flash shades of blue and brown during activation and fade, and would bleach out (not get as dark) at high temperatures. This was primarily a result of the difficulty of color matching photochromics from different families having different fade/activation rates as well as temperature dependencies[11]. This problem was addressed by the introduction of Transitions® III in 1996, a lens with a new all-naphthopyran dye package[12] based on the 2,2-diaryl 2H naphtho[1,2-

b]pyrans[13](V,VI). Both gray and brown versions of this product were developed to meet the needs of customers worldwide.

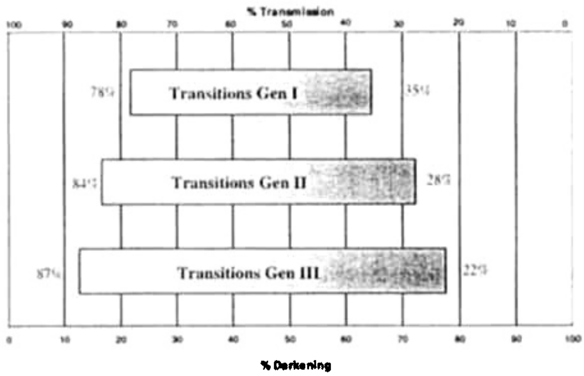


Figure 2. Performance enhancements of Transitions Lenses

Over the last decade, Transitions Optical has built and defined the plastic photochromic lens segment of the optical industry. Through the introduction of new products based on state of the art polymer and photochromic dye technology, performance properties (Figure 2.) have continued to improve. Much of the success that Transitions Optical has experienced during this period is a result of the determination and inspirational research leadership of John Crano.

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