

# A False-Sensitized Instant Film for LED Printers

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## Abstract

Polaroid's ColorShot™ printer is a recent example of the marriage of instant silver halide photographic film and digital printing. However, the history of digital printing on instant silver halide film goes back much further. In the early 1980's Polaroid launched an effort to develop a small portable printer based on gallium arsenide LED's with peak emissions at 635 nm, 720 nm and 820 nm. To utilize such a printer, the instant film would have to be sensitized to those wavelengths.

The purpose of this presentation is to describe our efforts to develop a unique set of dyes, which both sensitized at the appropriate wavelengths and had sufficient environmental stability. Sensitization at 635 nm presented no problems and was satisfied by the carbothiacyanine dye **1**. The initial attempt at sensitization at 720 nm was satisfied by carbothiacyanine **2**. However, this dye proved to be very unstable because of the chemical sensitivity of the thiomethyl group at the meso position. A substantial investigation finally led to the 2-furanyl dye **3**, that offered not only excellent photographic sensitivity at 720 nm, but also excellent storage stability. Sensitization at 820 nm was a challenge, which was satisfied in a unique way by dicarbothiacyanine dye **4**. Unlike the vast majority of dicarbothiacyanine dyes, dye **4** forms a J-aggregate, which shifts its peak absorbance to 820 nm. This formation of an aggregate is particularly notable in that dye **4** offers significant photographic sensitivity and stability advantages when compared to alternative sensitizing dyes.

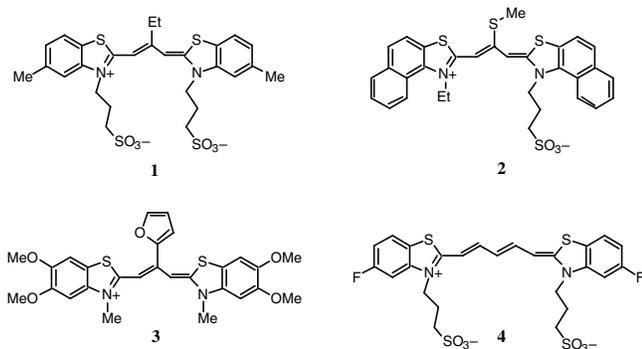


Figure 1. Sensitizing Dye Structures

## Introduction

The introduction of SONY's Mavica™ digital camera in 1980 indicated a strong future for digital image capture with a small handheld camera and subsequent printing of the images. It was strongly felt that a digital camera combined<sup>1</sup> with a portable, battery-powered printer was a winning strategy. Because of the low energy requirements of instant silver halide film and its relatively high quality it was felt that printing on instant silver halide film was a good option. However, the key problem was the choice of an exposure device. At that time light emitting diodes were chosen as the best option. However, blue LED's were unknown and the green LED's of that time were highly inefficient. The most promising, cost-effective LED arrays were based on gallium arsenide and had peak emissions at 635 nm, 720 nm and 820 nm. Consequently, the silver halide emulsion group and the sensitizing dye chemists were challenged to develop stable, high-speed emulsions, which were sensitive at those wavelengths. These emulsions could then be incorporated in a straightforward way into an instant film structure to create a key component of a mobile, high-quality digital printer. This work continued for approximately ten years and a stable, sensitive, false-sensitized color instant film was demonstrated.<sup>2</sup> However, over that ten-year period, exposure devices improved considerably. Options, including LED's, that could print on conventional film with visible light, were imminent. Consequently, a separate false-sensitized film made little sense either technically or from a business perspective. Nevertheless, this technological effort was a forerunner of the hybrid, silver halide-digital printers we see in the marketplace today.

## Sensitizing the False Blue Emulsion - The 635 nm LED

Just as in conventional instant film the top sandwich in the false-sensitized negative would control the yellow dye. However, unlike conventional film where this layer would be sensitive to blue light, this layer would be sensitized to the shortest of the LED's and be sensitized to 635 nm red light. This was easily achieved with either of the two red sensitizing dyes **1** or **5**. These dyes showed no issues with speed or stability.

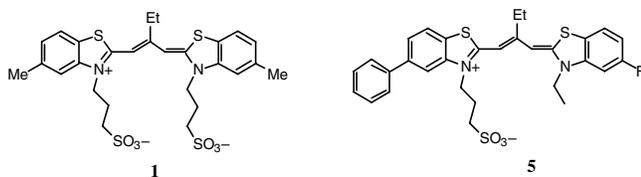


Figure 2. Structure of False Blue Sensitizers

### Sensitizing the False Green Emulsion - The 720 nm LED

Sensitizing the false green sandwich to adequately control magenta dye was our most significant challenge. Early on we decided to bathochromically shift traditional red sensitizers so that they would absorb in the near infrared. We quickly discovered that the electron rich carbocyanine dye **2** had the desired absorption properties and delivered excellent photographic sensitivity at 720 nm when freshly coated. However, this dye proved to be very sensitive to aging both in a pressurized oxygen environment<sup>3</sup> or when stored under ambient conditions. This instability was thought to arise either from the facile oxidation and displacement of the reactive thio-methyl group. However, the electron-rich thiomethyl group was intrinsic to the bathochromic shift to 720 nm. We immediately searched for an alternative electron-rich group that could produce a similar bathochromic shift but without producing an unstable dye.

Mechanistically we thought that either a 2-substituted thiophene or 2-substituted furan could produce a similar bathochromic shift. Furthermore, since the electron-rich thiophene or furan groups are aromatic and correspondingly much less reactive than the thiomethyl group, the environmental stability should be substantially improved. Our thinking proved to be correct. **Table 1** summarizes our efforts which culminated in the synthesis of dyes **3** and **6**. These dyes demonstrated substantial photographic sensitivity at 720 nm and were highly stable under either ambient conditions or under accelerated aging in a pressurized oxygen environment. Although, the thiophene substituted dyes afforded similar properties, the furan dyes J-aggregated to slightly longer wavelengths and were superior.<sup>4</sup> It was also found that the size of the alkyl groups on the N and N' nitrogens was also critical. It was discovered that the J-aggregation and the stability were optimal when the groups were as small as possible. For example, when the N,N' methyl groups in dye **3** were replaced with ethyl groups both the speed and stability were substantially less.

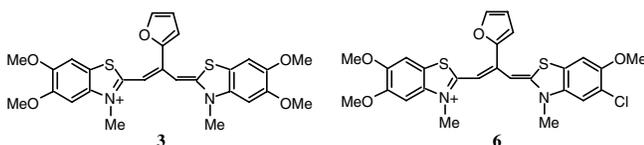


Figure 3. Structures of False Green Sensitizing Dyes

Table 1. Speed and Stability of the False Green Dyes

Dye	$\lambda$ max (solution)	Rel Spd @ 720 nm	Stability (300 psi O <sub>2</sub> )
<b>2</b>	578 & 626	1.64	-0.66
<b>3</b>	615	1.46	-0.09
<b>6</b>	605	1.83	-0.05

### Sensitizing the False Red Emulsion - The 820 nm LED

Efficient sensitization in the region from 750 to 850 nm is even more difficult to achieve than in the previously discussed region used for the false green. Carbocyanine dyes fall far short. Most dicarbocyanine dyes generally don't sensitize beyond 750 nm and suffer from poor sensitivity and poor stability. The traditional sensitizers used at these wavelengths, the tricarbocyanine dyes, are even slower and less stable. These dyes are often combined with supersensitizers to improve performance. In our laboratories only four dicarbocyanine dyes **4**, **7-9**, all having 5-fluorobenzothiazole bases, were reasonable sensitizers at 820 nm. These dyes among all dicarbocyanines were uniquely able to form stable J-aggregates.<sup>5</sup> Tables 2 and 3 summarize these dyes.

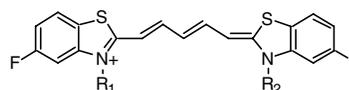


Table 2. Structures of the False Red Dyes

Dye	R <sub>1</sub>	R <sub>2</sub>
<b>4</b>	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
<b>7</b>	Ethyl	Ethyl
<b>8</b>	-(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> <sup>-</sup>	-(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> <sup>-</sup>
<b>9</b>	-(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	Et

Table 3. Speed and Stability of the False Red Dyes

Dye	$\lambda$ max (solution)	Peak Sensitization/ extent	Speed/ Stability
<b>4</b>	658	780/840	1.0/-0.18
<b>7</b>	656	780/840	0.88/-0.88
<b>8</b>	656	780/840	0.70/-0.09
<b>9</b>	660	780/840	1.20/-0.90

<sup>1</sup> Such a combination was envisioned early on to be either a single combined unit or a separate printer that could either dock with the camera or communicate via a cable or wirelessly.

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<sup>2</sup> In 1987 Fuji Photo Introduced Pictography 1000 in which a false-sensitized thermographic film was exposed by LED's emitting at 580nm, 680 nm, and 820 nm. Pictography 3000 was introduced in 1993 and the exposure source was changed to laser diodes emitting at 670 nm, 750nm and 810 nm.

<sup>3</sup> To accelerate the aging process, negative was stored for 3 days in an oxygen atmosphere at 300 psi. It was then processed and the sensitometry was measured relative to a control that was stored under ambient conditions.

<sup>4</sup> This work is partially covered by USP 5601963, M. P. Filosa, Z. J. Hinz and M. T. Spitler, February 11, 1997.

<sup>5</sup> This work is partially covered by USP 5254455, Z. J. Hinz and E. S. McCaskill, October 19, 1993.