

# Dye Releasing (High Dye Yield) Couplers in Photothermography

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## Abstract

Yellow photographic dyes have low molar extinction coefficients, relative to those of magentas and cyans; therefore amplification of the yellow image by using dye-releasing couplers can be a key enabler for new imaging systems.

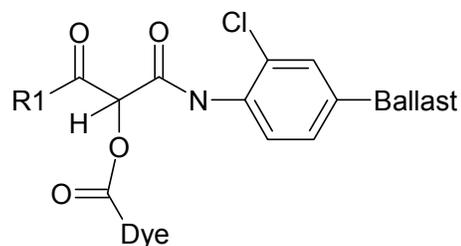
Successful color image-forming couplers for use in camera speed photothermography are not best designed using the established principle of balancing coupling site pKa and nucleophilicity, which has been used for aqueous-processed (conventional) couplers, even though the incorporation of the couplers in photothermographic film is most conveniently done, as in conventional systems, by using photographic dispersions in high boiling solvents. In photothermography, the absence of the alkaline processing solution removes the pKa constraint and enables the design of very low pKa but efficient dye-forming couplers.

## Introduction

Yellow photographic dyes have low molar extinction coefficients, relative to those of magentas and cyans; therefore amplification of the yellow image by using dye-releasing couplers can be a key enabler for new imaging systems. This led our group to develop photographic couplers that, upon reaction with oxidized color developer, form a yellow dye and release a high-extinction yellow dye. Such high dye-yield (HDY) couplers have found use in conventional photographic systems, but their application to photothermography offers a new set of challenges.

In yellow dye-forming HDY couplers<sup>1</sup> (Example 1), the dye chromophore is linked to the coupler through an oxycarbonyl group therefore shifting the hue of the dye to avoid speed losses in film. The dye structure is a methine type<sup>2</sup> to make use of the high extinction shown by these dyes. However, the properties required from the dye, with respect to stability and water insolubility, limit the structural changes that can be made to improve coupler availability and reactivity toward the developing agent. In conventional systems where post-process dye stability is important, the choice of R1 group on the coupler is limited to various

alkyl, aryl, heterocyclic, or the more common t-butyl groups. These choices limit the activation that can be achieved by lowering the pKa of the coupling site. Lowering of pKa also results in lower nucleophilicity of the coupler anion; therefore, these effects have to be balanced for best efficiency of dye formation.

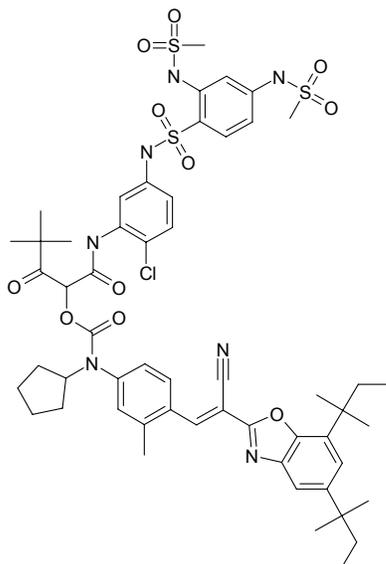


*Example 1. High dye-yield coupler*

With the electronic nature of the coupling site largely set by these restrictions, the design of the ballast is crucial in determining the coupler reactivity toward the developer. In photographic coupler dispersions used in films, the hydrophilicity of the ballast can be used to improve the reactivity toward the developing agent.<sup>3</sup> When the ballast contains one or more groups that are not ionized at the pH at which the film is coated, but contain acidic hydrogens with pKa less than about 8.8, the groups are largely ionized at the pH of the aqueous processing solution, and the reactivity of the coupler toward the oxidized developing agent is enhanced. A typical HDY coupler, where the low pKa groups used on the ballast are sulfonamides, is shown as Example 2.

In novel photothermographic systems where a camera speed, thermally developable film is used to capture the image, and the essentially dry chemical development is followed by immediate image scanning, the recorded digital image not the film negative—is the permanent record that accompanies the prints given to the customer. Thus, the longevity of the photographic material after scanning is less important. Lifting this constraint of image permanence in

the film negative has allowed the redesign of yellow HDY couplers for use in such systems.

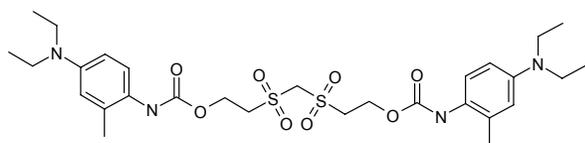


Example 2. Ballast-activated HDY coupler

### Camera Speed Photothermographic System and Components

The systems considered here<sup>4</sup> contain photosensitive silver halide emulsions, imaging couplers, a p-phenylene diamine developer precursor, (Example 3) from which the developer was released during heat processing, and thermal solvents such as salicylanilide. The image captured by the photosensitive silver halide emulsions acts as a catalyst for the reduction of silver salts of benzotriazole and 1-phenyl-5-mercaptotetrazole, the latter also acting as an antifoggant. There is concomitant oxidation of the developer leading to dye formation by reaction of Dev<sub>ox</sub> with the coupler.

The organic silver salts, blocked developer, and the thermal solvent are incorporated into the film as solid particle dispersions. The imaging couplers are incorporated as photographic dispersions in di-n-butyl phthalate or similar solvents.



Example 3. Blocked Developing Agent

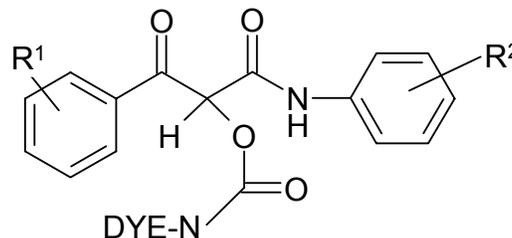
In evaluating the HDY couplers, monochrome filmstrips were exposed through a 0–4 density step wedge (3000 K, Daylight 5A, + appropriate Wratten filter, 0.5 s exposure). The film samples were processed on a heated drum at about 160 °C for 18 s. For ease of assessment, the strips were fixed using Kodak Flexicolor fixer and air dried.

The following measures were used to compare couplers from these coatings. We measured maximum density

obtained (D-max), maximum two-point photographic contrast (Gamma), and minimum density (D-min). We calculated a density range (D-range = D-max – D-min) and amplification (D-range/molar laydown per m<sup>2</sup> of coupler).

### HDY Coupler Design

Initial experiments showed that HDY couplers, like Example 2, were efficient dye formers in conventional (wet-processed systems) but were very poor in photothermographic film. Also, experiments using benzoylacetanilide couplers (Example 4) indicated that they offered better performance than similarly ballasted pivaloylacetanilides. We discovered that more efficient dye formation was obtained from couplers where electron withdrawing substituents (R1 and R2) on the benzoyl and/or the anilide rings, respectively, of the coupler were used to lower the pKa of the proton in the coupling site. In conventionally processed films, reducing the effective pKa of the coupler below the pH of the processing solution merely reduces the nucleophilicity of the coupling site anion and leads to lower reactivity toward oxidized developer. However, in the essentially non-aqueous development environment of photothermographic coatings, lowering the coupler pKa improved dye formation.



Example 4. Benzoylacetanilide HDY Coupler

The results for D-max and amplification shown in Figures 1–3 illustrate the trend for increased density formation and increased efficiency of imaging (amplification) with lowering of coupler pKa. In Figures 1 and 2, the responses from a conventional benzoylacetanilide imaging coupler are also shown.

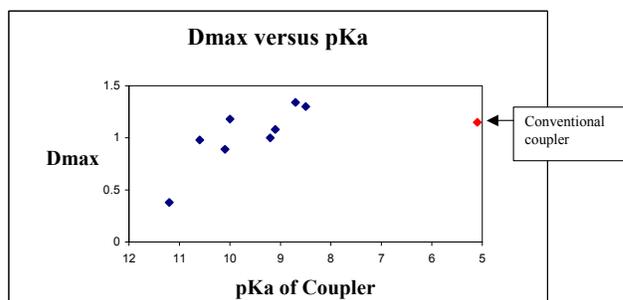


Figure 1.

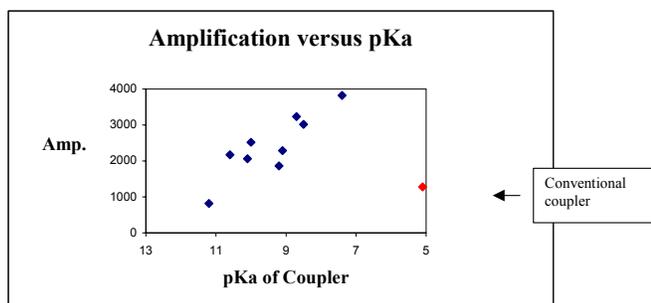


Figure 2.

Figure 3 shows the responses of coatings where coupler and silver halide emulsion laydowns were varied along with emulsion type. The trend of more efficient imaging from lower pKa couplers remains present.

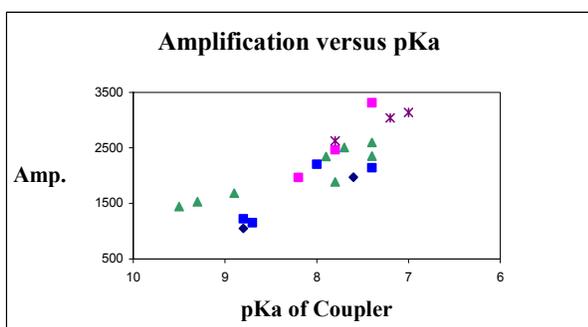


Figure 3

## Summary

We have shown that dye formation in photothermography can be improved by reducing the pKa of the HDY couplers below values that would be most advantageous for conventional processing. The most useful HDY couplers are based on benzoylacetyl yellow couplers with electron-withdrawing groups in the anilide and benzoyl rings.

## Acknowledgment

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## Biography

David Southby was educated in Britain, receiving a BSc (Honours) degree in Chemistry and Biochemistry and a PhD in Synthetic Organic Chemistry from the University of Cardiff, Wales.

He joined the Research Division of Kodak Limited in 1975 as a Research Chemist, transferring to Rochester, NY in 1987, where, in the Research & Development Laboratories of the Eastman Kodak Company, he has continued with chemical and film-building research toward new and improved photographic, and more recently, inkjet materials. In 2001 he was elected a Fellow of the Royal Society of Chemistry and is an IS&T member.