

# High-Extinction Dyes From Yellow Imaging Couplers: The Release of a Pre-Formed Dye from the Coupling-Off Group

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## Abstract

The design of blue light sensitive layers in film systems can be limited by the relatively low-extinction coefficients of chromogenically formed yellow imaging dyes. The release of a pre-formed dye from part of the coupling-off group of a coupler increases the effective extinction and is useful provided the dye is shifted to be colorless or nearly so, when part of the coupler. The overall hue of the dyes formed must be equivalent to the hue of the conventional dye system, and the incorporation of the dye into the coupling-off group cannot adversely affect the rate of reaction with oxidized color developer. Previous work on releasable dyes with phenolic chromophores suffered from the deficiencies that the hue was sensitive to pH, and often mordants were needed to prevent hue shifting. Such problems are overcome by using uncharged azo and methine chromophores. Release of the dye is made from carbamate precursors, which are, in turn, directly or indirectly linked to the coupling site of the coupler. The formation of the dye carbamate results in hypsochromic hue shifting of almost 100 nm.

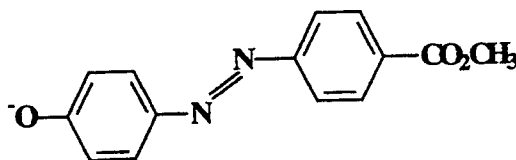
## Introduction

The release of photographically useful groups (PUG) from image couplers is well known, and imagewise release is achieved by having the PUG linked directly or indirectly to the coupling site of the coupler, so that reaction with oxidized color developer results in dye formation from the coupler and concomitant release of the PUG or a fragment containing it.<sup>1</sup> Such mechanisms are commonly used to release development inhibitors<sup>2</sup> and accelerators.<sup>3</sup> When the PUG is an image dye, the result is the formation of two dyes: the azamethine formed from the coupler and oxidized developer, and the released dye (from the PUG). This type of coupler has been termed "one-equivalent" as two molecules of dye are produced from the reduction of two silver halide molecules.<sup>4</sup>

Use as a high-extinction image coupler is possible if the hue of the released dye is similar to that of the azamethine dye, and, if the hue of the dye is sufficiently shifted when it is linked, as part of the PUG, to the coupling site of the coupler. These one-equivalent couplers offer advantages for film-building, particularly by allowing reductions in component laydowns. Further, use in the blue light sensitive layers can have the biggest impact as yellow imaging couplers, typically, form the lowest molar extinction dyes ( $\epsilon = 18-25,000$ ) of the three color records.

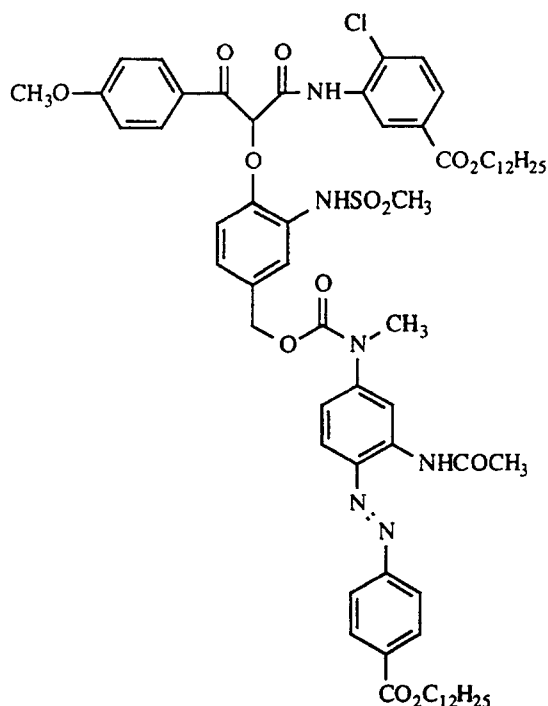
## Dyes as Coupling-off Groups

The imagewise release of dyes from the coupling-off group of a coupler has been described in the Patent literature,<sup>5,6</sup> but these disclosures are concerned with the release of anionic dyes (e.g., 1). Such dyes can be sensitive to the final pH of the film unless they are mordanted, and mordants introduce problems of stains by facilitating the retention of development by-products and sensitizing dyes. Metal ions are also used to chelate the released dye.<sup>6</sup> This involves introducing metal salts into one of the processing solutions. In order to make an advance in this one-equivalent coupler technology, a way was needed to release neutral dyes from the coupling-off group.



Example 1

Mooberry and Singer<sup>4</sup> disclosed the use of small linking groups, typically  $\text{CO}_2$  to convert neutral dyes into efficient PUGs for release from couplers (e.g., 2). We describe, here, the development of this work to release neutral yellow dyes from yellow image couplers. The couplers are colorless, or nearly so, when coated and form composite dye images with effective extinction of over  $\epsilon = 50,000$ .



Example 2. Azo Dye releaser

We have concentrated on two classes of yellow dyes to form into PUGs. Azo-dyes have extinctions in the region of  $\epsilon = 35,000$ . In most cases, it is not desirable to have the released dye be mobile and so incorporation of a ballast hydrocarbon is used to restrict the mobility of the dye. When the dye ballast was incorporated as an ester (as in 2), the hue was orange of the check coupler derived dye (Fig. 1). Ballasting via the less electron withdrawing amide ( $\text{CO}_2\text{C}_{12}\text{H}_{25}$  replaced by  $\text{CONHC}_{12}\text{H}_{25}$ ) moved the hue hypsochromically to give a closer match to the check coupler on the long wavelength side of the envelope.

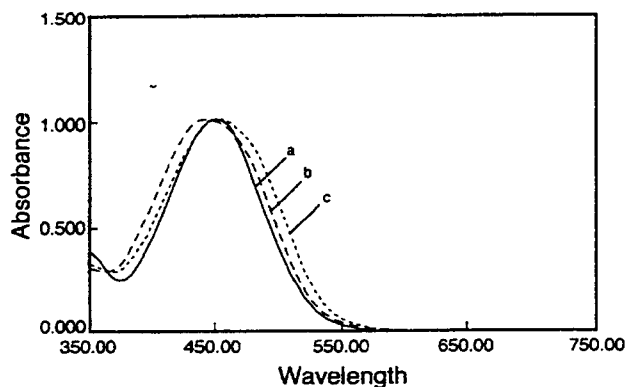


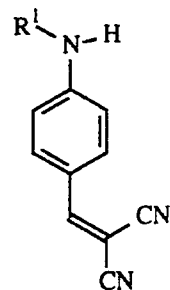
Figure 1. Azo dye spectra compared to conventional yellow coupler dye. (a) Conventional dye; (b) amide ballasted azo dye; (c) ester ballasted azo dye.

The broadness of the half-band-width (hbw) of the azo dyes could still be a problem for good color reproduction.

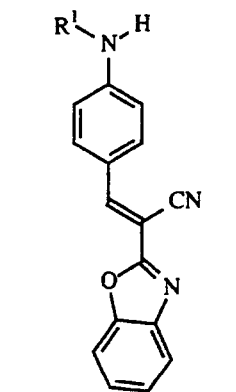
The shift form also showed the  $n$  to  $\pi^*$  absorption band from the azo group in the region of 450 nm, which, although weak, gave the coupler some residual color and could lead to blue speed losses, if the amount of coupler coated to reach a sensitometric aim was sufficiently high.

## Methine Dye Chromophores

Methine dye chromophores (3, 4) offer absorption envelopes with smaller hbw, more closely matching the absorption of conventional azamethine dyes, and cannot show the  $n$  to  $\pi^*$  absorption. Further, they have higher molar extinctions than azo dyes, of around  $\epsilon = 50,000$ . Simple dicyanomethines (3) have narrow absorption bands with hbw approaching 60 nm in solution, narrower than molecules where one of the cyano groups is replaced by a heterocycle (4). We have found benzoxazole based dyes to be particularly useful for matching the absorption of conventional azamethine yellow dyes.



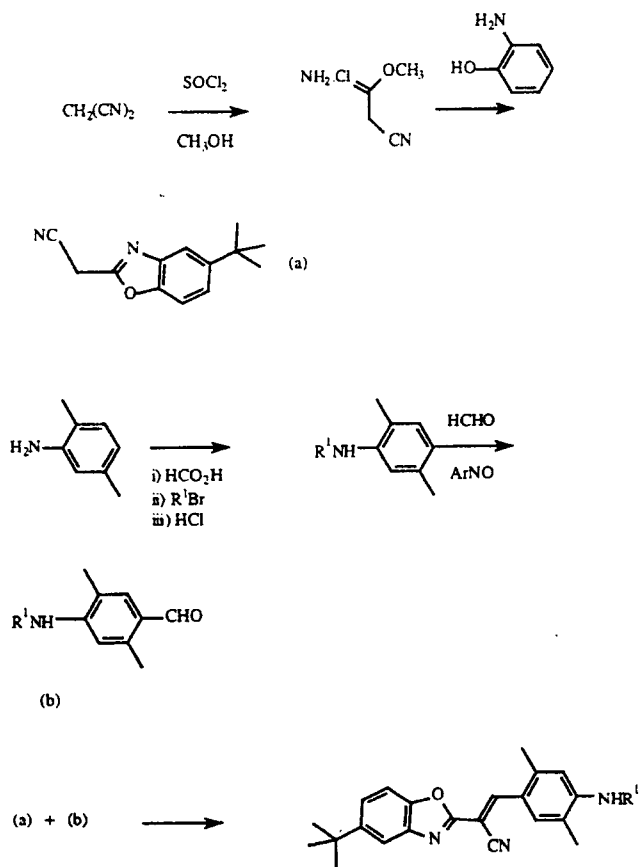
Example 3



Example 4

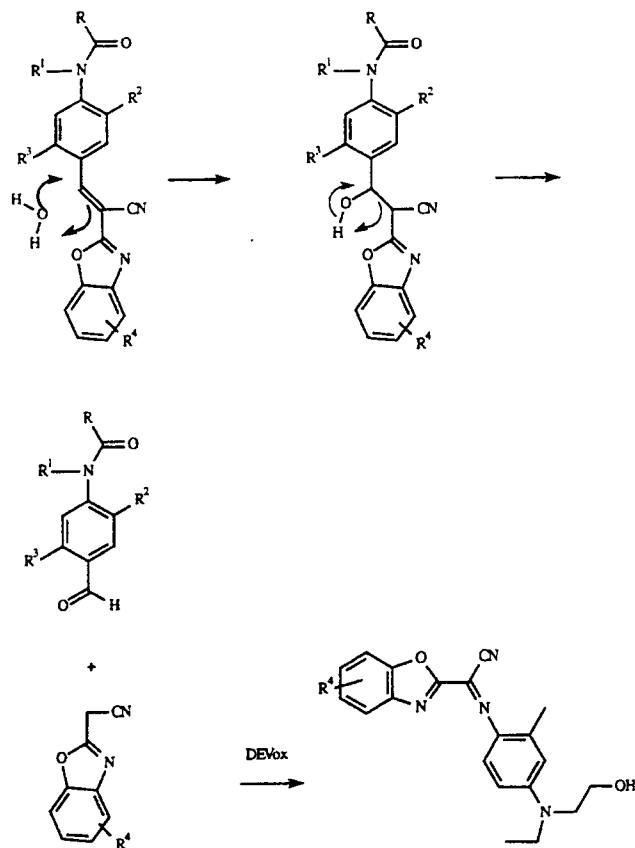
These methine dyes were easily prepared from commercially available materials<sup>7</sup> (Scheme 1). The benzoxazole moiety (a) was prepared by treating the iminoester of malononitrile with a suitable o-aminophenol. An appropriate alkylated aniline moiety was made by N-formylation, followed by treatment with an alkyl bromide and potassium t-butoxide followed by acid hydrolysis. The alkylated aniline was then treated with formaldehyde in the

presence of 4-nitroso-N,N-dimethylaniline, as oxidant, to give the aldehyde (b) needed to form the methine dye by reaction with the cyanomethyl-benzoxazole.



Scheme 1. Preparation of a Methine Dye

Methine dyes are very stable, but, the C-C double bond was found to be susceptible to nucleophilic attack when the electron donation given by the auxichromic nitrogen lone pair was unavailable. That is, when the dye was acylated as it is when linked to the coupling site to give the one-equivalent coupler. The decomposition (Scheme 2) involves a Michael-type addition of a nucleophile to the double bond followed by elimination of an active-methylene coupler, with the formation of an aldehyde when hydroxide ion was the nucleophile, or an oxime if attack was by hydroxylamine, from the developer solution. The other fragment formed, a cyanomethylbenzoxazole is an active methylene compound that was found to react with oxidized color developer to give a dye contaminant.



Scheme 2. Acylated methine dye decomposition where the nucleophile is water. R is a coupler residue, R1-R4 are, typically, alkyl substituents

The structure, and so the hydrophilicity, of the one-equivalent coupler and of the coupler solvent, affect the stability of the acylated dye to nucleophiles such as hydroxide ion and hydroxylamine. In Kodak process C-41 developer solution, the major nucleophile has been determined to be hydroxylamine. Relative rates of reaction for a coupler where  $R^1 = C_{12}H_{25}$ ,  $R^2 = R^3 = CH_3$ , and  $R^4 = H$  are given in Table 1.

Table 1. Relative rates of reaction of a coupler in Triton X-100 micelles at pH = 10.2, 23°C, with various nucleophiles found in developer solution. Nucleophile concentrations were those found in Kodak process C-41 developer solution

Nucleophile	Relative Rate
$NH_2OH$	160
$CO_3^{=}$	1
KODAK D-99 Developer / $CO_3^{=}$	45
$SO_3^{=}/CO_3^{=}$	1.7

Substituents on the dye can also greatly affect the stability of the acylated methine dye. The substitution of the benzoxazole ring ( $R^4$ ) had a large effect. Figure 2 shows a Hammett correlation of substituent sigma value with the relative rates of hydrolysis for a coupler where  $R^1 = C_{12}H_{25}$ ,  $R^2 = R^3 = CH_3$ , and  $R^4$  was varied. Electron donating groups in the benzoxazole aryl ring increased stability. Methyl and t-butyl examples are shown versus the electron withdrawing chlorine.

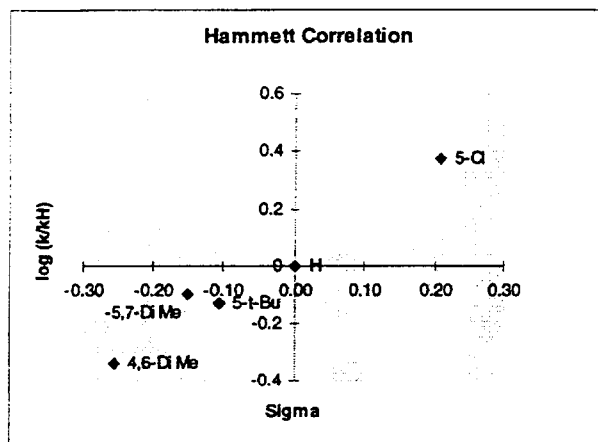


Figure 2. Hammett correlation, for coupler  $R^4$  group variants in Triton X-100 micelles at 23°C.

The substituents  $R^2$  and  $R^3$  in the aniline ring of the dye could also be modified to improve stability. Some paired examples are given in Table 2. For instance, a 3-iPr group offered steric hindrance to attack to retard the rate significantly.

Further, combining the 3-substituent in a ring with the benzylic carbon can also be used, although such changes have significant effects on the hue of the released dye making re-design of the dye molecule necessary.

Removal of the group ortho to the aniline nitrogen removed twisting of the bond between the nitrogen and the ring and increased electron density in the ring. This also improved hydrolytic stability, but decreased the shifting of the dye.

Table 2. Substituent effects on the stability of a coupler where  $R^2$  or  $R^3$  are varied. Results are for reaction with Kodak process C-41 developer solution at 23°C.

Anilide meta - substituent:  $R^3$

Substituent, $R^3$	Half-Life (min) in micelles	Half-Life (min) in film
$CH_3$	5.1	6.7
$CH(CH_3)_2$	6.8	14.0

Anilide ortho - substituent:  $R^2$

Substituent, $R^2$	Half-Life (min) in micelles	Half-Life (min) in film
$CH_3$	5.1	6.7
H	9.1	11.8

For HDY couplers to be practical, and not cause speed losses, the dye when acylated, must result in a coupler that is colorless, or almost so. Solution studies of dyes showed (Table 3) that acylation of methine dyes resulted in a hypsochromic shift of greater than 65 nm due to the electron withdrawing nature of the carbonyl group. A further shift was obtained by twisting the N-aryl bond out of plane ( $R^2 = H$  to  $CH_3$ ) and although other electronic and steric factors may have given rise to part of this shift (e.g.  $R^3 = CH_3$  to  $CH(CH_3)_2$ ), the overall result was that a dye with hue maximum of approximately 450 nm (in-film) was shifted to have maximum absorbance at about 360 nm, with less than half the extinction of the unshifted free dye (Fig. 3). Although twisting the acylated chromophore improved the shifting of the dye, this same twisting deepened the dye hue (e.g.,  $R^2 = H$  to  $CH_3$ ). This made careful choice of substituents necessary in order to balance hue of the dye with stability of the coupler.

Table 3. Substituent effects on the hue and the shifting of the dye. Data from acetonitrile solution.

$R^2$	$R^3$	$R^4$	DYE $\lambda_{max}$	ACYLATED $\lambda_{max}$
H	$CH_3$	Cl	447 nm	362 nm
$CH_3$	$CH_3$	Cl	453	353
$CH_3$	$CH(CH_3)_2$	Cl	450	346
$CH_3$	$CH(CH_3)_2$	H	443	343

Acylation by  $ArCH_2OCOCl$  to give  $DYE-N-CO_2CH_2Ar$

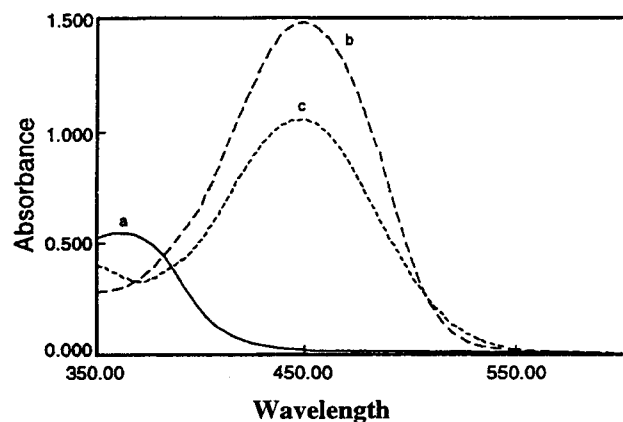


Figure 3. Hue of shifted coupler and composite dye image versus the dye image of a conventional coupler coated at twice the molar concentration. (a) Shifted coupler; (b) composite dye image; (c) conventional coupler dye.

In conclusion, we have developed a class of dyes, some previously used as textile or other dyes, that have absorptions suitable for use to make photographic images. A combination of these dyes and the coupler derived

azamethine make up the image. This combination has superior extinction, approaching three times the extinction of conventional azamethine yellow dyes when coated at equimolar levels. They enable new possibilities for the design of photographic materials.

### **References**

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2. US Patent No. 3,227,554.
3. US Patent No. 4,859,578.
4. US Patent No.4,484,840.
5. US Patent No.4,248,962.
6. European Patent No. 173,302.
7. US Patent No.5,457,004.