

New Coupler Technologies

Sundaram Krishnamurthy, John W. Harder, and Robert F. Romanet
Imaging Materials and Media
Research and Development Laboratories
Eastman Kodak Company
Rochester, NY, 14650 USA

Abstract

Silver halide imaging dyes play a major role in controlling the performance parameters, such as hue and extended image stability. The structure and molecular architecture of the parent image couplers from which the dyes are derived significantly influence such performance metrics. Recent molecular manipulations in this area have led to certain new coupler technologies.

These technologies have led to the discovery of certain specific structural features that are responsible for major advantages in performance characteristics of the resulting azomethine dyes. Especially significant are the remarkable hue control and image stability characteristics of these dyes derived from such couplers.

Pyrazolo[3,2-C]-5-triazoles (Fig. 1) represent an attractive class of magenta couplers.

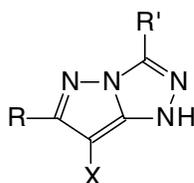


Fig. 1

These couplers have the advantage of low formaldehyde sensitivity, thermal yellowing, and photochemical printout. In addition, the unwanted absorption in the blue region is greatly reduced. While the dark stability of the dyes derived from these couplers are quite good, the light stability needed improvement.

The discovery that a tertiary butyl substituent at the 6-position (Fig. 2) increased the light stability enabled this class of coupler to be considered for use in color paper.

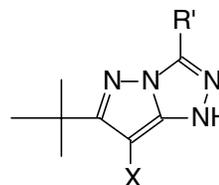


Fig. 2

There was, however, still a need for increased light stability. Investigation of other bulky substituents in the 6-position did not equate with increased light stability. For example, a 1,1-diethyl propyl substituted coupler (Fig. 3) had intermediate light stability between identical couplers containing methyl and tertiary butyl substituents.

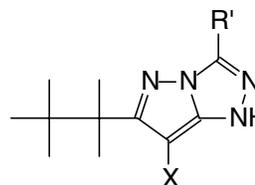


Fig. 3

Other factors such as substitution on the developer moiety and viscosity of the medium were studied to understand their influence on the light stability of the dyes.

The clue, however, to obtaining significantly increased light stability was found by considering the effect of the 6-tertiary butyl group. Compared to less bulky substituents, the hue was narrower and less aggregated. The light stability was also increased suggesting that the decrease in aggregation resulted in shorter singlet lifetimes, which had been shown to decrease fade time. This suggested that increased steric bulk in the 3-position might also be beneficial.

Many examples of pyrazolotriazoles have been synthesized with increased bulk in the 3-position and in some cases, modest gains in light stability have been realized. In particular, compounds with tertiary alkyl substituents in the 3-position were better than those having benzylic-like hydrogens.

However, it wasn't until the discovery of a sterically hindered β -amido group in the 3-position that significant

advances in light stability were realized. The general formula of such a compound is shown in Fig 4.

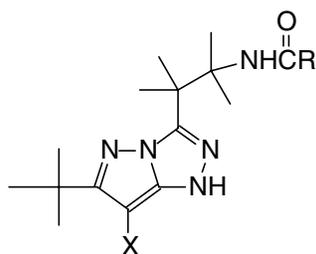


Fig. 4

Further investigations in this area revealed that the amido hydrogen was able to hydrogen bond effectively to the chromophore. The result were low energy conformations where the ballast was held over one face of the chromophore effectively decreasing aggregation and offering an energy wasting pathway leading to shorter singlet lifetimes. This resulted in dramatically increased light stability. Further hydrogen bond accepting and donating substituents on the amido portion such as found on the coupler in Fig. 5, further increased this effect.

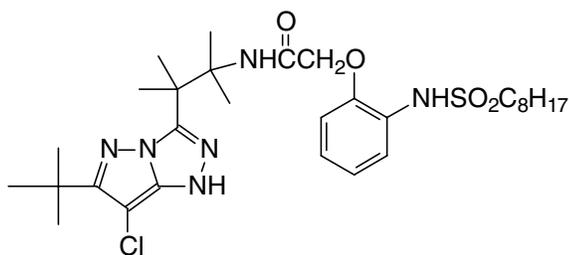


Fig. 5

Compounds such as this are finding use in current photographic products.

Phenolic couplers have historically been used for all photographic products in order to produce cyan dyes. 2,5-dicarbonamido phenols have been used for color negative films and 2-carbonamido-5-alkyl-6-chloro phenols have been used for color paper. The types of substituted phenols used in color negative produces dyes with good dark stability, but poor D-min yellowing. The phenols used in color paper produces dyes with good light stability, but poor dark stability. Both types of substituted phenols produce photographic dyes with broad dye hues and relatively low dye extinction.

Recent research explorations have led to a specific substitution type of the 2,5-dicarbonamido phenols that affect dye hues with less unwanted absorptions, higher extinctions, good dark stability, and light stability.

This improved dye performance is the result of highly ordered H-aggregates that can be achieved through

specific substitution patterns of the 2,5-dicarbonamido phenols.

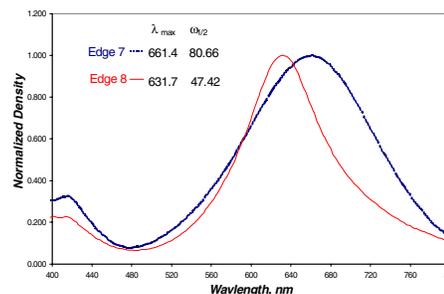


Fig. 6 Comparison of cyan dye hue

The H-aggregated dyes give a sharper-cutting absorption curve in paper coatings than the same dye gives in solution that is similar to the behavior of some types of sensitizing dyes. A key to this behavior is the chemical structure of the carbonamide substituents on the phenol. The most important feature is having an α -sulfo substituent on the 5-carbonamido group. Phenolic couplers with an α -aryloxy substituent on the 5-carbonamido group do not show the same behavior.

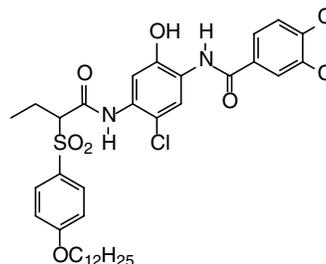


Fig. 7 Improved coupler structure

Also, the 2-carbonamido group can be varied, with aryl carbonamides giving good properties. With simple 2-alkyl carbonamido phenols the dyes are typically more hypsochromic.

It is believed that the sulfone substituted 5-carbonamide forms a bent structure in the dye molecule and the different amides form stacks or chains through H-bonding. Besides the sulfone, another 5-carbonamide based on proline gives a cyan coupler with similar behavior and proline is known to form " β -turns" in peptide structures.

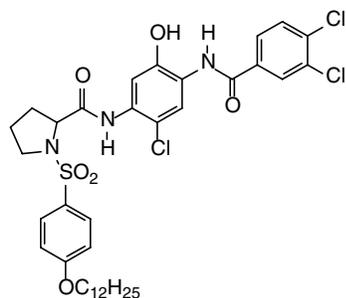


Fig. 8 5-Carboxamide-ballast based on proline

The technologies described herein illustrate that aided by modeling and theoretical energy calculations, the structural conformations of large organic molecules have been controlled in the careful design of magenta and cyan image couplers. This has resulted in improved photographic products now available in the marketplace.