 

# Short Red Spectral Sensitization of Emulsions for Color Negative Films

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## Abstract

This paper discusses criteria for selecting sensitizing dyes that are appropriate for use in a short red spectral sensitization of emulsions for a color negative film. A film that incorporates a red recording layer with peak sensitivity in the short red region of the spectrum better approximates the human eye's natural sensitivity to red light, and therefore is capable of more accurately recording visual colors.

## Introduction

Maxwell's principle states that any visual color can be reproduced by the appropriate combination of three independent color stimuli (primaries). The amount of each primary required to reproduce the spectral colors defines the three color matching functions for those stimuli. Each set of primaries has a different set of color matching functions, and all color matching functions are related by linear transformation. Furthermore, the effective spectral sensitivity of the human eye is also a set of color matching functions. A film having spectral sensitivities that correspond to a set of color matching functions is capable of accurately recording color scenes.

Although any set of color matching functions is equally capable of accurately recording colors, not all sets are equally practical to employ in the design of color recording films. Many sets of color matching functions have negative sensitivities. Silver halide films cannot readily achieve negative sensitivities, so it is important to choose a set of color matching functions that are all positive. Furthermore, there is significant overlap between the red and green sensitivities. Optical screening by overlying layers in a color negative film reduces the amount of light available to expose a red record if it has significant sensitivity at shorter wavelengths. Accordingly, it is important to choose a set of color matching functions that minimize the spectral overlap of the blue, green, and red sensitive layers. Figure 1 shows a set of narrowest color matching functions proposed by MacAdam[1] that are all positive. The constraint that there are no negative lobes results in a large degree of overlap between the green and red curve.

The accuracy of color recording for a film will be determined by how closely its spectral sensitivity approximates a set of functions like those shown in Figure 1. The spectral sensitivity of the film is determined by the light that is absorbed by the individual emulsion components. Light absorption in the film is a function of the spectral absorption profile of the individual emulsion components modified by optical screening that occurs in the multilayer structure. The conventional film structure of blue sensitive layers over green sensitive layers over red sensitive layers necessarily filters shorter wavelengths of light before they reach the emulsions coated closest to the support. This places practical limits on how far the red sensitive layer can be shifted hypsochromically without incurring large speed penalties.

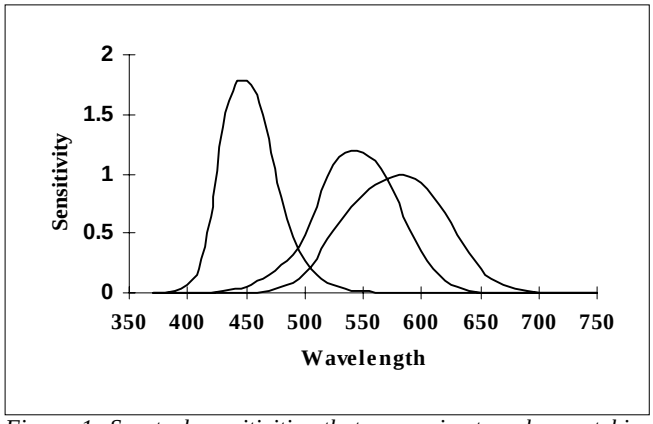


*Figure 1. Spectral sensitivities that approximate color matching functions.*

Figure 2 compares the light absorption of a long red and a short red sensitive emulsion with the red color matching function of Figure 1. Although the long red emulsion (650 nm) is quite bathochromic to the red color matching function in Figure 1, many films have been designed with such a red spectral sensitivity. The longer wavelength absorption increases the light absorbed by the emulsion in the multilayer structure and decreases the overlap with the green sensitive layer. As the chemical technology for silver halide films has improved over the years, it has become more practical to use short red sensitive emulsions (625 nm) like that shown in Figure 2. The light absorption of the short red emulsion is closer to the red color matching function resulting in increased capability for accurate color recording. The short red emulsion sensitivity shown in Figure 2 is a good compromise between the ideal color matching function and the capability of silver halide emulsion technology in a multilayer film structure.

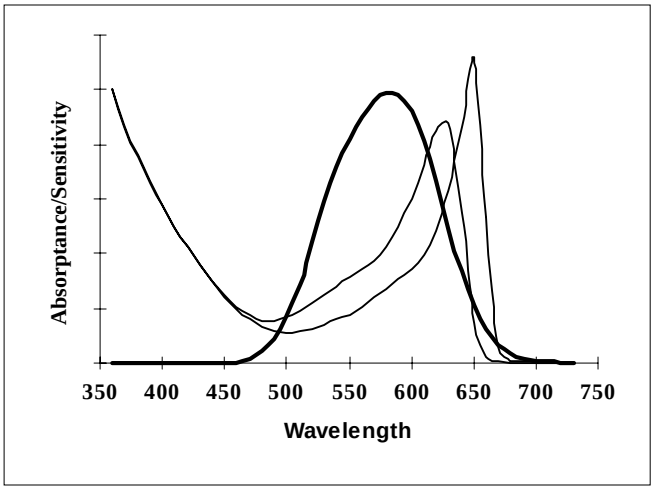


*Figure 2. Comparison of a short red and a long red emulsion to the red sensitivity shown in Figure 1.*

## Dye Selection

The task of the emulsion scientist is to find spectral sensitizing dyes that will provide the desired 625 nm sensitivity without sacrificing photographic efficiency. The best sensitizing dyes from a light absorption perspective are the J-aggregating cyanine dyes. These dyes have narrow, intense absorption spectra that arise from a close packed array of dye molecules on the surface of the silver halide crystal. However, if one considers the most widely used cyanine chromophores, it becomes clear that 625 nm sensitization is not easy to achieve.

| Dye Structure | J-aggregate Peak |
|---|---|
| ThC | 640-660 nm |
| OxC | 540-560 nm |
| BImC | 570-590 nm |
| OxThC | 590-610 nm |

*Figure 3. Common cyanine dye chromophores and J-aggregate peak positions.*

The symmetrical dyes shown in Figure 3 have J-aggregates that absorb at wavelengths longer than or shorter than 625 nm. Even unsymmetrical oxathiacarbocyanine dyes like OxThC in Figure 3 generally form J-aggregates between 580 nm and 610 nm. Therefore, in order to dye an emulsion so that its wavelength of maximum absorption is approximately 625 nm, a mixture of dyes is required.

When two J-aggregating cyanine dyes are mixed, the resulting mixture can retain properties of the individual dyes or exhibit properties that are intermediate between the individual dyes. If the individual dye properties are retained, a J-aggregate of the "persistent" type is formed. When the mixture behaves like an average of the pure dyes, it is called a J-aggregate of the "amalgamation" type. This is analogous to the electronic states of mixed crystals.[2] It would be desirable to achieve a 625 nm sensitization with a mixture of two cyanine dyes that form an amalgamation type aggregate. These aggregates have a single absorption maximum that is adjustable by changing the ratios of the two dyes. In Langmuir-Blodgett films of cyanine dyes, Yonezawa[3] has suggested that the amalgamation type aggregate might be expected when the quantity $\Delta_{DA}/T_{DA}$ is less than about 0.4, where $\Delta_{DA}$ is the difference in energy of the J-bands for the individual dyes, and $T_{DA}$ is the average of $T_D$ and $T_A$, twice the energy difference between the monomer and J-aggregate transition for the donor and acceptor dye, respectively.

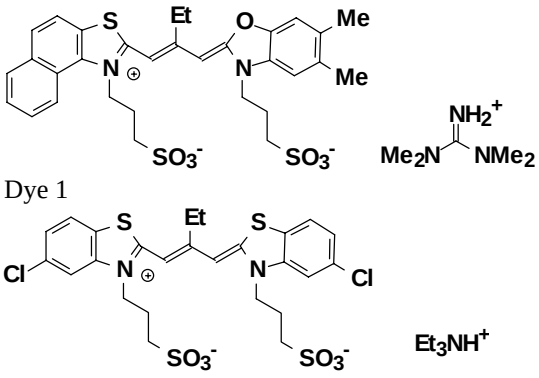


*Figure 4. Two dyes that produce an amalgamation type J-aggregate.*

The two dyes[4] in Figure 4 have a $\Delta_{DA}/T_{DA}$ value of 0.19 and might be expected to form an amalgamation type mixed aggregate. However, we have found that when adding dyes to a silver halide emulsion where they are strongly adsorbed, the proper energy relationships between individual dye aggregates is necessary, but not sufficient to form the desired amalgamation aggregate. In addition, it is also necessary to control the manner in which the dyes are added to the emulsion. When the dyes are added separately, the first dye will rapidly adsorb to the silver halide surface forming islands of pure aggregate before the second dye is added. The only way to achieve a uniform amalgamation aggregate is to add both dyes simultaneously.

This is demonstrated in Figure 5, where the light absorptance spectra of coated emulsions are shown. Curve A shows the result of dying an iodobromide tabular emulsion with a 2 to 1 molar ratio of dyes 1 and 2 where dye 1 is added first, followed after 15 min by dye 2. Curve B shows the result for the opposite order of addition. Curve C shows the result for simultaneous addition of both dyes. Only in the third case is the desired amalgamation type aggregate obtained, demonstrating a single absorption peak.

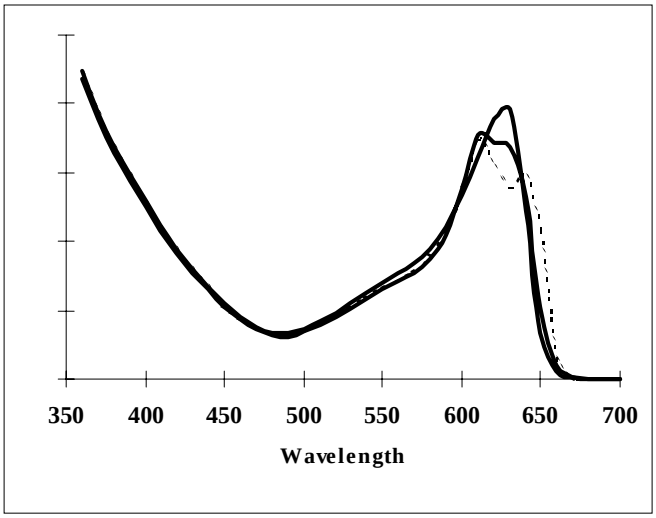


*Figure 5. The effect of dye addition order for dyes 1 and 2 on the resulting absorption spectrum of the dyed, coated emulsion. Curve A (solid) - Dye 1 added first, then dye 2 after 15 min. Curve B (dashed) - Dye 2 added first, then dye 1 added after 15 min. Curve C (bold) - Both dyes added simultaneously and held 30 min.*

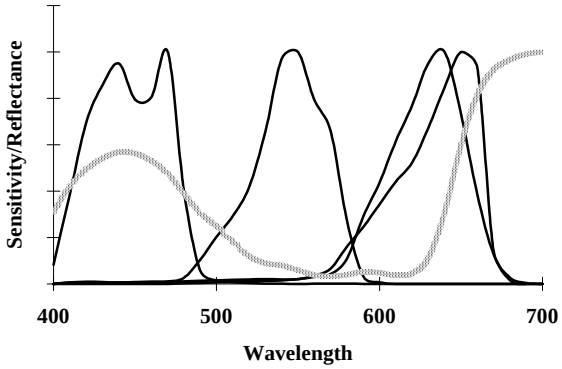


*Figure 6. A multilayer film spectral sensitivity showing the shortened red response achieved with the mixed aggregate of dyes 1 and 2 in Figure 4. The broad jagged line is the reflectance spectrum of the lobelia flower*

## Spectral Sensitivity

Using red sensitive emulsions like curve C in Figure 5, it is possible to construct a multilayer color negative film with improved color recording accuracy relative to a film containing long red sensitive emulsions. The spectral sensitivity of two films with a long or short red spectral sensitivity is shown in Figure 6. The film with the short red spectrally sensitized emulsions has a red sensitivity that is shifted 20 nm hypsochromic from the long red sensitivity at 650 nm. Nevertheless, the green sensitivity of the red emulsion is little changed. The careful formation of the amalgamation type J-aggregate allows the desired spectral distribution, i.e., reduction of the long red response while maintaining a narrow absorption band. Minimizing the green absorption also minimizes any speed penalty caused by filtration of light by the overlying green sensitive layers, and reduces the need for large film color correction effects.

## Color Reproduction

Figure 6 also shows the reflectance spectrum of the lobelia flower. Many blue flowers and certain fabric dyes have strong infrared reflectance. A film designed with long red sensitive emulsions records more of the infrared reflectance than the eye sees. This causes the color of the flower to be reproduced more magenta than it appears visually. The short red sensitive film records less of the infrared reflectance resulting in an improved capability to reproduce the color of the flower relative to its visual appearance.

## Conclusion

A shorter red spectral sensitivity, rather than the traditional 650 nm sensitivity employed by many color films, allows improved color reproduction by moving the peak closer to that of the human eye. The actual amount of hypsochromic shift will be limited in a practical sense because of screening of light by overlying layers in a multilayer film element. Because of the limited range of wavelengths where common cyanine dyes form J-aggregates, it is necessary to mix several dyes together to achieve the desired peak wavelength sensitivity. Ideally, one hopes to form an amalgamation type mixed aggregate where the two dyes have a single absorption band. Amalgamation type J-aggregates allow a narrow light absorption profile that minimizes both the unwanted long wavelength response and undesirable green response. The wavelength of maximum sensitivity can then be controlled by changing the ratio of the two dyes.

In practice, even if the two dyes have the proper energetic relationship to form an amalgamation type J-aggregate, the dyes must be added to the silver halide emulsion simultaneously to allow the desired aggregate to form on the silver halide surface. Two dyes were shown that form an amalgamation type J-aggregate. A 2 to 1 molar ratio of the short wavelength dye to the long wavelength dye was used to sensitize silver iodobromide emulsions to a peak sensitivity of 625 nm. Incorporated into a multilayer color negative film, these emulsions offer an improvement in color recording capability, especially for objects that have a high infrared reflectance.

## References

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3. Y. Yonezawa, T. Miyama, and H. Ishizawa, *J. Imaging Sci. Technol.*, **39**, 331 (1995).
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