

Factors in Modern Color Reversal Films

John D. Baloga

Eastman Kodak Company, Rochester, New York USA

Abstract

Modern color reversal films like Kodak Professional Ektachrome film E100S, the new Kodak Ektachrome 200 professional film, and many films from other companies, incorporate advanced design factors that differ from earlier films of this class. These new design factors provide improvements in the film's image structure, color, and customer use attributes. Unique layers added to the film's multilayer stack improve color fidelity and tone reproduction, thus rendering very accurate and pleasing scene colors under a variety of process conditions. Technical advances in silver halide emulsion design and new chemistry provide exceptional image structure and precise control of customer film use attributes such as push processing. This paper describes three new technical advances found in state-of-the-art films and explains how they contribute to the superior performance characteristics of modern color reversal films.

Introduction

Modern color reversal films must satisfy the needs of a wide range of customers from professional photographers to occasional amateur snap shooters. Some customer needs such as push processing have become more important to professional photographers in recent years. Other needs such as chemical retouching of original images on film have become less important (although not unimportant) due to the widespread use of scanning and digital manipulation of chromes on the computer. And some new customer needs have appeared that are related to scanning and digitizing images, then rewriting them by digitally controlled exposure devices onto new chromes.

Modern color reversal films are complex in film composition and construction. They typically contain over twelve optically and chemically interacting layers. Each layer possesses a unique and important function in the film that contributes to the film's performance. Careful design of light-sensitive silver halide emulsions, development modifying and image forming chemistry, and basic arrangements of the various layers in the film ultimately determine how well the film satisfies the customer's needs.

It is well beyond the scope of this article to discuss all emulsion, chemical, and film design properties that contribute to a color reversal film. Instead, I selected three design factors that have changed or have significantly improved in modern color reversal films compared to earlier versions, and to describe how these changes led to improved customer value.

I selected one topic from each of the three main categories of modern film design, namely chemistry, emulsions, and film structure. These topics are new chemistry for push processing, emulsion quantum sensitivity for improved speed and grain, and film technology for improved sharpness.

New Chemistry for Push Processing

Color reversal photographic films are very often push processed to recover images from underexposed films or to alter the contrast of images for aesthetic reasons. For example, push-processed films often show brighter highlights and whiter D-mins. Push processing is accomplished by prolonging the MQ black-and-white developing step in the E-6 color reversal process. This generally raises the contrast of the image as well as affording an apparent speed increase by making the dark underexposed image brighter.

Push processing has become increasingly important to professional photographers in recent years. It is not uncommon to underexpose a film by two stops and push process it to recover a useful and pleasing image. In some cases modern color reversal films can be pushed three stops with pleasing results. This is especially important for non-studio photography where natural lighting conditions may change dramatically over the course of a shooting event. It is essential that push processing not degrade the neutral tone scale of the image by giving neutral tones an undesirable color. To maintain acceptable tone scale after push processing, the various photographic emulsions that yield the final color image must all develop in a conforming manner.

Modern color reversal films may contain up to three emulsion layers for each of the three color records. It is challenging to construct a new film that has improved photographic reproduction characteristics and additionally maintains the consistent development of up to nine individual emulsion layers during push processing. In fact, emulsion layers in experimental films often do not develop in a concordant manner with some layers developing faster than the rest of the emulsion layers. This mismatch in developability can be corrected by redesign of the emulsion components; however, this nearly always leads to some compromise in other performance characteristics.

Some modern color reversal films employ a chemical, which when incorporated into a film layer slows down its development during push processing, thereby bringing it into alignment with the other layers in the film. This technology allows for fine tuning of emulsion component development, thereby ensuring that all the emulsion layers

in the film develop concurrently. This preserves neutral tones and maintains the film's intended color balance during push processing.

A modern chemical push-processing material satisfies six criteria:

1. It slows development of individual emulsion layers at extended development times.
2. It has minimal effect on development at normal development times.
3. It does not affect development of any other emulsion layer in the film.
4. It allows for good shelf life of the film product.
5. It does not contaminate processing solutions.
6. It does no harm to other film or emulsion characteristics.

In order to effectively incorporate a development restrainer into a film it is necessary to deactivate and immobilize it. During processing the blocked chemical is activated and released through chemical reaction with a component in the developer solution. In a reversal film this developer component is sulfite ion.

The integral parts of a blocked inhibitor for control of individual layers during push processing are shown in Figure 1. The electron-poor aromatic consists of a phenyl group substituted with two nitro groups, one each in the positions ortho and para to the inhibitor leaving group. The mercaptotetrazole inhibitor depicted has proven to be a strong inhibitor for the MQ development of typical reversal photographic emulsions. Additionally, this inhibitor has localized effects and does not migrate far in the film after it has been released during processing. The dodecyl ballast group imparts substantial hydrophobicity to the molecule ensuring that it remains substantially in place during preexposure storage of the film. Finally, the carboxylic acid moiety affords enough solubilization for the molecule that it can effectively interact with the sulfite in the developer solution.

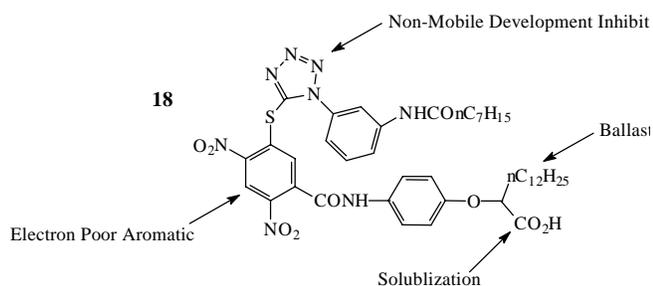


Figure 1: Structure of a blocked inhibitor for push-process control.

An example of how this works is shown in Figure 2. The film containing the blocked inhibitor chemical shows the desired behavior. At the short development time corresponding to normal development the profile is virtually identical to the check film that contains no blocked inhibitor. No MQ development inhibition is evident. At the longer development time corresponding to a push-process condition MQ development inhibition has clearly occurred. This results in higher color densities throughout the sensitometric curve. Free inhibitor shows unwanted

development restraint at 4 minutes in addition to 11 minutes, thereby showing the need for a blocking group.

While not depicted, intermediate MQ development times show progressively more MQ inhibition with increasing development time. Furthermore, changing the amount of blocked inhibitor coated in the film allows for fine tuning of the amount of development restraint to the level needed to bring this layer into conformance with the other layers in the film.

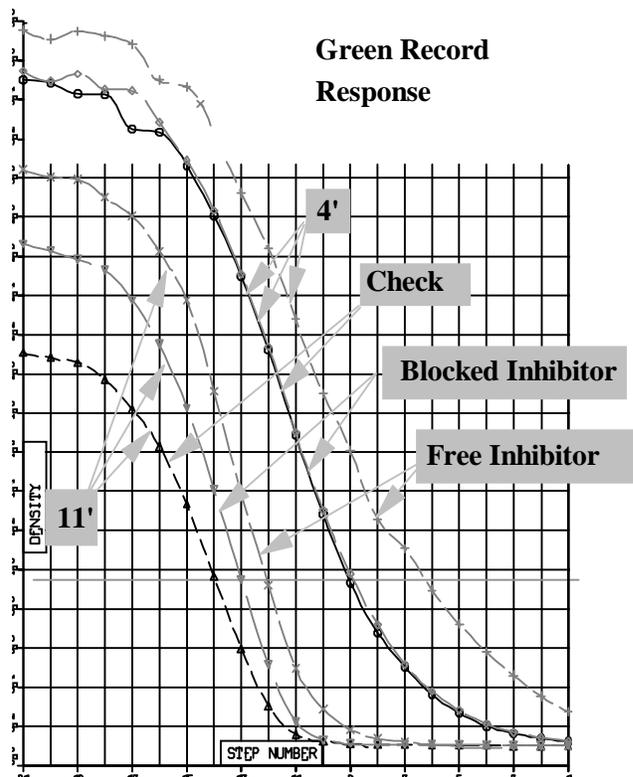


Figure 2: Sensitometric curves at normal and push process showing development restraint by the blocked inhibitor at push process times.

Further evaluations of this technology show that it does not adversely affect a film's shelf life or other film characteristics in any substantial manner. It has proven useful in many types of emulsion layers. Finally, it does not contaminate processing solutions so as to cause undesirable sensitometric effects in subsequently processed films.

In summary, new chemical blocking technology has proven useful in color reversal films and has been used to incorporate inhibitors into films. The inhibitors are activated and controllably released during processing, which then retards the rate of MQ silver development of individual layers in the film. This technology was perfected by careful optimization of aromatic ring substitution, balanced hydrophobicity, and development inhibitor performance. Examples of this technology have been used to fine tune and adjust push-processing characteristics in modern color reversal films. This technology has been disclosed in US Patent 5,567,577.¹

Quantum Sensitivity of Color Reversal Emulsions

Quantum sensitivity² (QS) is a measure of the average number of photons absorbed per grain to produce developability. Since developability is a function of the number of absorbed photons, QS is usually quoted in terms of the number of photons absorbed to cause 50% of the emulsion population's grains to develop and is denoted $QS_{0.5}$. This microscopic parameter provides an estimate of the photoefficiency of a given emulsion; the lower the QS value the more efficient is the emulsion. The quantum sensitivity measurement provides a cumulative measure of the latent image formation, detection, and amplification stages of the imaging chain. Post-development processes such as dye image formation are not included.

Quantum sensitivity has been measured for many emulsions. For example, Hailstone and colleagues³ reported a QS measurement on an octahedral emulsion in 1988. The most efficient hydrogen hypersensitized emulsions yield a QS of about 2 to 3 photons per grain. Although hydrogen hypersensitization is not useful for general use films, this sensitivity represents an ambitious goal for practical emulsions used in commercial film products.

Modern tabular emulsions have been made for color reversal films that are highly monodisperse.⁷ We have obtained QS results for the monodisperse color reversal tabular AgBrI (3% bulk Iodide) emulsion shown in Figure 3. This emulsion has a median grain size of 2.00 microns diameter by 0.133 microns average thickness. Electron microscopy image analysis indicated tabular grain content greater than 98% by area weighting and greater than 85% by number weighting. The mean grain volume was 0.29 cubic microns. Figure 3 shows the emulsion as observed under a scanning electron microscope.

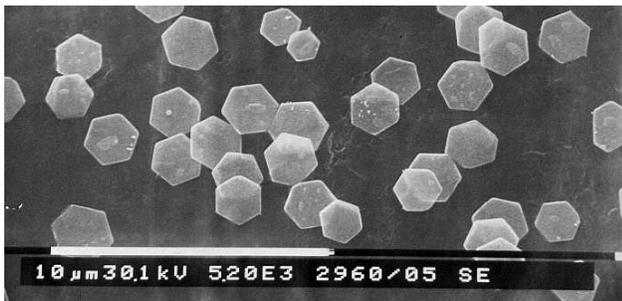


Figure 3: SEM of tabular emulsion used for QS studies.

Special processing for QS measurements was carried out in a time of development series in MQ, followed by a stop bath, wash, and dry-in total darkness. The general experimental methods and calculations used to determine the quantum sensitivity were similar to those described by Hailstone in reference 3. To confirm that sample preparation was not distorting grain counting statistics, a control experiment was carried out in which known quantities of undeveloped and developed grains were mixed. The resultant sample showed the correct proportions of developed and undeveloped grains.

Grain counting on our emulsion yielded a developed grain fraction for each step of the sensitometric exposure with 1% to 2% statistical error. This yields an average

number of absorbed photons per grain (the quantum sensitivity for a given exposure step) according to the following equation.

$$P = (T 10^{-\Delta} \Sigma A_{\lambda} I_{\lambda}) (V\rho / 10^{-4} SW) \quad (1)$$

where P = absorbed photons per grain
 T = exposure time
 Δ = step tablet density
 A_{λ} = absorptance at wavelength λ
 I_{λ} = incident intensity at wavelength λ
 V = grain volume
 ρ = silver halide density
 S = silver laydown on the film
 W = weight conversion factor

The summation $\Sigma A_{\lambda} I_{\lambda}$ is carried out over the exposure bandwidth. The first term within the first set of brackets yields the number of absorbed photons per unit area. The second term within the second set of brackets calculates the inverse of the number of grains per unit area.

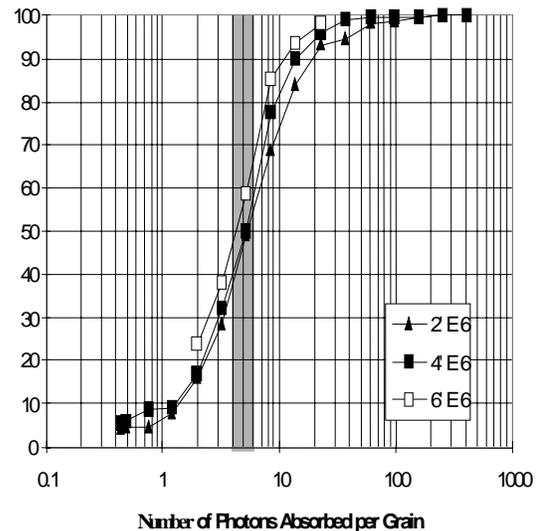


Figure 4: Quantum sensitivity plot.

Processing a special experimental single-layer film containing this emulsion for 4 minutes in MQ resulted in a high photoefficiency QS of 5 photons per grain. This is illustrated in Figure 4, where the percentage of developed grains is plotted as a function of absorbed photons per grain. Additional curves for 2 and 6 minute MQ processing are shown. All process times show a QS of 5 photons per grain within experimental error, with the longer times of development mainly showing increasing efficiency in the high exposure shoulder region of the curve. The shaded portion of the figure represents an error of plus/minus one photon per grain in the measurement.

These quantum sensitivity values imply that the emulsion is highly photoefficient. It is approaching the hydrogen hypersensitized value of 3 photons per grain. However, these results must be understood within the

limitations of the quantum sensitivity measurement. This efficiency represents only latent image formation and detection and amplification by the MQ black-and-white developer. The ensuing chemistry and dye cloud formation, which are critical for complete analysis of photographic performance in a detective quantum sensitivity² (DQE) sense, have not been considered.

These results serve to benchmark the QS of a highly efficient yet practical color reversal emulsion and indicate much progress has been made to improve the light detection and amplification steps that are critical to the overall speed and granularity of modern color reversal films.

Optical and Chemical Sharpness Effects in Modern Color Reversal Films

A color reversal film's sharpness-its ability to image and display fine detail and sharp edges with high resolution-is broadly controlled by two factors. These factors are light scattering and reflections during the exposure step, and chemical adjacency effects during the development step. Light scatter plays the dominant role because silver halide emulsions, being tiny particles, scatter light at visible wavelengths. Scattering is most intense when the emulsion dimension ranges from 0.30 to 0.80 microns, roughly comparable to the wavelengths of visible light. Unfortunately, we are often compelled to use emulsions having these dimensions in order to achieve photographic speed.

Tabular emulsion grains offer a way to achieve typical photographic speeds using larger dimension emulsions (typically 1.0 to 2.0 microns in diameter) that do not scatter light so strongly. However, reflections can become a detrimental factor with tabular emulsions because light reflecting from the upper and lower face of the crystal interferes, leading to resonances in reflection depending on the thickness of the tabular crystal. This is the same phenomena that causes multicolored light reflections from oil spread thinly over water. In an extreme case, tabular emulsions can act like partial reflecting mirrors bouncing light from grain to grain over some distance from its point of origin. This is called light piping by analogy with light traveling through an optical fiber.

Light piping is especially harmful when a tabular emulsion contains conventional octahedral or cubic emulsions either deliberately added or present as a contaminant in the emulsion's grain population.⁴ The highly turbid conventional emulsion, even if present in small quantities, can scatter light at angles sufficient to induce severe light piping through the tabular grain matrix. Modern emulsion science takes great pains to precipitate tabular emulsions free from contaminants of this type.

The thickness of a film plays an important role to minimize harmful effects from light scatter. Kodachrome film enjoys its significantly high degree of sharpness due to the thinness of its layers. This is made possible by the fact that it contains no incorporated coupler chemistry which adds considerable thickness to process E-6 films like Ektachrome, Fujichrome, Agfachrome, and others. Because typical modern color reversal films are structured with the yellow record near the top-closest to the light exposure

source-it is especially important to minimize thickness of all film layers below the yellow record because red and green light scattered by the yellow record progressively spreads as it passes to layers below.

Light-adsorbing interlayers between color records are another factor used in modern film design. For example, many Ektachrome films have a magenta filter dye interlayer between the magenta and cyan records. In addition to its usefulness to reduce "light punch through" (green light passing through the magenta layer to expose the red-sensitized layers), this filter layer helps eliminate harmful reflections of green light off cyan record emulsions and back into the magenta record. These reflections, although potentially useful for photographic green speed, can be very detrimental to magenta record sharpness in a high-quality film.

Chemical-related contributions to film sharpness arise from the well-known Eberhard effect⁵ whereby certain byproducts of silver halide development restrain further development. In color reversal films these inhibitors are primarily Iodide ion gradients. This "negative feedback" leads to restrained development in the interior of large area densities because development inhibitors accumulate, but less inhibition near the edge since the inhibitors are free to diffuse away from the edge. Iodide gradients also lead to interlayer interimage effects (IIE) for color correction in color reversal films because they carry an inhibitor message between color records in addition to acting within a developing layer.

We typically determine a film's sharpness by two measurements. The film's modulation transfer function (MTF) is an acutance measurement that describes its ability to reproduce terms in an exposure pattern's Fourier series without distortion, and therefore mathematically describes the cumulative optical and chemical distortions that arise in the film. A typical modern color reversal film's MTF is shown in Figure 5. Each color record produces its own curve. They differ due to differences in light scatter and chemical effects within each color record.

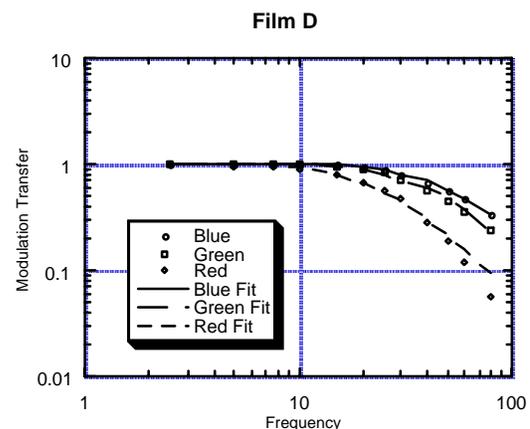


Figure 5: MTF data and curve fit for Film D.

Another acutance measurement results from a sharp edge imaged using X-rays. Being much smaller in wavelength than typical emulsion crystals, X-rays do not

scatter in color reversal films and therefore produce images of sharp edges free from light scattering. What remains are edge distortions solely related to chemical effects in a pattern that typically looks like Figure 6. The height of the "ear" and extent of its spread into the interior of the edge determine the characteristics of the chemical edge effect and are related to the film's chemical spread function.

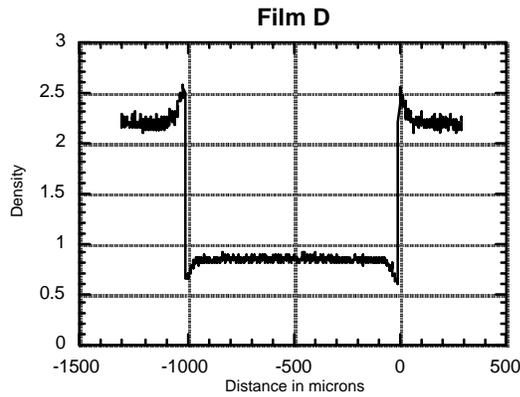


Figure 6: Sharp edge exposed by X-Rays onto Film D.

Using well-known theoretical concepts⁵ it is possible to decouple a film's MTF curve into separate optical and chemical components. The total MTF_T of a film follows equation (2).

$$MTF_T(k) = MTF_o(k) (1 + \langle D \rangle [B - \beta(k)]) / (1 + \langle D \rangle M^2 MTF_o^2(k) [B - \beta(k)]) \quad (2)$$

where $k = 2\pi\nu$ and ν is the frequency of the Fourier term
 $MTF_o(k) =$ optical MTF
 $\langle D \rangle =$ density at the mean exposure level
 $B =$ a parameter that describes the potency of the chemical inhibitor
 $\beta(k) =$ Fourier transform of the chemical spread function
 $M =$ modulation of the sine wave exposure in the MTF measurement

We have found the optical line spread function in a color reversal film is often well described by a simple exponential. Its Fourier transform gives the optical MTF in equation (3).

$$MTF_o(k) = (1 + [\kappa k]^2)^{-1} \quad (3)$$

where κ is a parameter that describes the extent of light spread from its point of origin on the film.

The chemical spread function is determined from sharp edge exposures using X-rays. Equation (4) describes the density from an X-ray exposure of a edge.

$$D_c(x) = D(x) + B D^2(x) - D(x) \int_{-\infty}^{+\infty} b(\zeta) D(x-\zeta) d\zeta \quad (4)$$

where $D_c(x)$ is the density at position x , $D(x)$ is the nominal density that would be calculated by use of the macro sensitometric curve for the film for the given exposure profile, and $b(\zeta)$ is the chemical spread function at point ζ .

In many color reversal films we have found the chemical spread function is well represented by an exponential cusp, as in equation (5).

$$b(x) = (B/2) \alpha \exp(-\alpha|x|) \quad (5)$$

where B is a parameter that describes the potency of the inhibitor and α describes the extent of diffusion of the inhibitor in the film. B is related to the X-ray "ear" height.

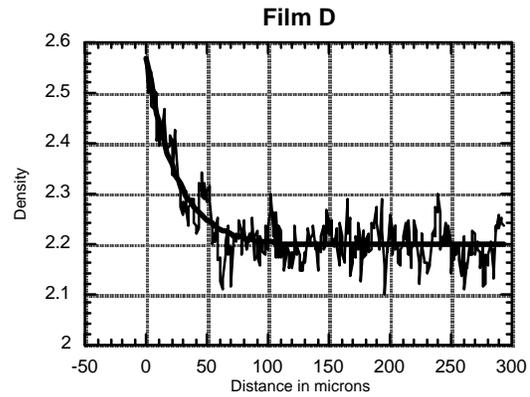


Figure 7: Curve fit of sharp edge exposed by X-Rays for Film D.

Using this formalism, X-ray exposures of sharp edges were analyzed to determine the α and B parameters of their chemical spread functions. These were done on older (pre-1990) as well as modern color reversal films processed in the process E-6 system. A typical fit is shown in Figure 7. The fits were generally quite good indicating a good correlation to an exponential chemical spread function.

It is difficult to measure the optical spread function of a film independent of chemical effects introduced during processing, although it can be done with difficulty by micro turbidity measurements on film raw stock. However, we chose to parametrically extract the optical contribution from an analysis of the film's total MTF combined with the chemical spread function data obtained in the X-ray line experiments. Equation (2) was used with the optical spread function parameter κ being the only adjustable parameter used to fit the total MTF data. It was then possible to separately calculate the optical MTF and the total MTF of each film for each color record. One such fit for the total MTF is shown in Figure 5.

It is often useful to simplify MTF data into a single number descriptor of acutance obtained by cascading MTF functions of an entire imaging chain and integrating over all frequencies. The process we used is similar to that described by Gendron.⁶ Our cascaded number represents an imaging system that includes a color reversal film viewed on a light table through an 8X magnifying loupe. These acutance numbers, designated 8X DMT, are shown in Figures 8 and 9 for a variety of color reversal process E-6 films, both old and new. One unit increase in 8X DMT signifies a statistically noticeable improvement in film sharpness. The optical MTF contributions, when separated from chemical contributions, more clearly display film advances in both terms.

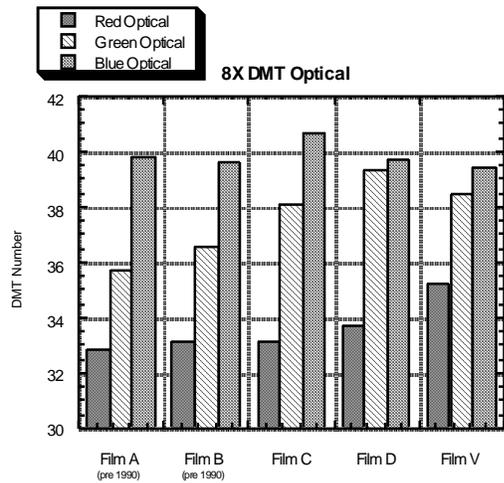


Figure 8: 8X DMT for the optical acutance of selected color reversal films.

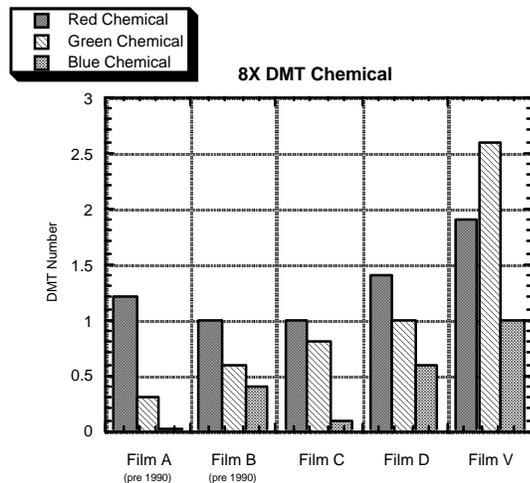


Figure 9: 8X DMT for the chemical acutance of selected color reversal films.

Figure 8 shows that yellow record optical acutance has not significantly improved over the years with the exception of Film C, which contains a tabular emulsion yellow record. However, magenta and cyan record optical acutance has improved in modern color reversal films due mainly to layer thinning below the yellow record and special care to prepare and use low-scattering emulsions.

Figure 9 shows that yellow record chemical acutance is generally weaker than magenta and cyan chemical acutance. We believe this is largely due to the yellow record's location near the top of the multilayer stack where development inhibitors more easily diffuse out of the film.

Conversely, cyan record chemical acutance is generally strong due to this color record's location at the bottom of the multilayer stack. Because the human eye is most sensitive to magenta dye, acutance in the magenta record is critical. Chemical acutance has generally improved in the magenta record in modern color reversal films due mainly to promotion of solution physical development effects, which are most susceptible to inhibition by Iodide in the MQ developer.

Film V shows the strongest chemical acutance effects in Figure 9. This special low-speed film was specifically designed to deliver very high acutance (and low granularity). It also features very high color saturation due to high IIE effects.

In summary, improvements to both optical and chemical acutance have been made in modern color reversal films. These were accomplished by combinations of layer thinning, improvements to emulsion crystal structure leading to low-scattering morphologies, use of light-absorbing interlayers, and judicious control and use of MQ development inhibitors to produce chemical acutance effects. Attention has focused on magenta record improvements since that record's dye is most critical to human perception of film sharpness.

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