KODAK T-Grain Emulsions in Color Films

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Abstract

The history of the development of KODAK T-Grain emulsions was traced over the last 10 years. Four advantages resulting from the use of T-Grain emulsions in color films were delineated: increased minus blue to blue sensitivity ratio, improved speed/granularity ratio, reduced background radiation sensitivity at equal speed/quality ratio and increased sharpness through improved emulsion optics.

Kodacolor VR 1000 film, announced at Photokina in 1982, was the first color negative film with a four-digit ASA speed rating, that is, an ASA speed rating of 1000 or more. An essential part of achieving such high sensitivity was the selective use of Kodak T-Grain emulsions (Figure 1). Here we will describe some of the history of the development of this technology, the benefits we feel make T-Grain emulsions worth pursuing in building color films and finally, some reasons that explain these benefits. For brevity, this paper will cover materials, although T-Grain emulsions have many useful applications in other areas.

This work is the result of many people's efforts over several years. Before the concepts we are about to discuss could be realized, the building blocks—high-aspect-ratio tabular-grain emulsions, their precipitation, including halide control and location, and their chemical sensitization—all had to be devised. For color films there is a never-ending quest for higher speeds and better picture quality at these higher speeds. In the mid-1970's a special group was formed in the Kodak Research Laboratories, the Interdivisional Investigative Team, to redefine this quest. Many chemical, film structure, amplification, and emulsion approaches were considered. One aspect of the project was to analyze the emulsion technology in color films of that vintage to determine if the desired improvements in speed and quality were possible and, if so, to indicate which approaches were the most promising.

Many facets were investigated, including spectral sensitization. Paul Gilman had given a paper at the ICPS meeting in Dresden in 1974 entitled “A Review of the Limiting Factors in the Spectral Sensitization of Silver Halide and Their Correction”, which cited three primary limitations: (1) desensitization, (2) recombination and inefficiency, and (3) poor dye adsorption. However, the
best emulsions of that period did not appear to be affected by any of the three limitations in a major way and in general seemed well optimized. In particular, concerning dye adsorption, these optimized emulsions were >90% covered with sensitizing dye, and there simply was no more surface area on which to adsorb more. For this and other reasons, the Interdivisional Investigative Team concluded that significant emulsion-related speed and quality improvements in high-speed color films would come from using new emulsion components, not from further reworking of the existing ones.

Photographic sensitivity, the response of a silver halide grain to light, can be enhanced in two ways: (1) by increasing the probability of light absorption and (2) by using more efficiently the photoelectrons generated by the absorbed light. The traditional approach to increasing the probability of absorption is to use emulsions with large individual grains. The result, up to a limit, is greater sensitivity and also, unfortunately, increased granularity, which degrades the photographic image. This undesirable granularity is due to the fact that the density is produced from fewer larger image centers that contribute more density per grain. Of course, the experienced film builder has a variety of tools to minimize this effect, but often other undesirable changes take place. For example, increasing silver to increase the number of image centers and reduce granularity decreases sharpness.

Increased sensitivity with increasing grain size is different in the intrinsic, blue region of the spectrum from that in the spectral green or red region—that is, the minus-blue region. This is because intrinsic speed increases with grain volume, whereas spectral speed is related to the amount of sensitizing dye that is adsorbed effectively, which in turn is related to the grain surface area. As shown in Figure 2 for increasing grain size of spherical or other relatively three-dimensional grains, the relative blue speed increases more than the minus-blue speed. This is a function of the surface-to-volume ratio.

This minus-blue to blue relationship poses a problem for the design of multilayer color films. Emulsions intended for red-sensitive and green-sensitive layers would be preferred to have no blue sensitivity at all. For films of even moderate speed, a blue-light-absorbing filter layer is necessary above the red-sensitive and green-sensitive layers, for example, in Kodacolor VR 400 film (Figure 3). The problem becomes more severe for higher speed films, where the choice is between degrading color reproduction or requiring more density from the blue-absorbing filter layer. Increasing the coverage of the blue filter layer incurs performance penalties because the most common filter materials, such as Carey Lea silver, absorb some green and red light, thus further reducing green and red speed (Figure 4). Also, more absorption by the filter layer removes
Fig. 4  Light absorption of a coating containing 0.069 g/m² of Carey Lea Silver.

blue light that would be reflected back to the blue-sensitive layer for faster speed. Therefore, the standard method of increasing sensitivity via increasing grain size has at least two major disadvantages: granularity increases, and the sensitivity ratio of minus-blue to blue decreases.

As we studied this problem, it suddenly occurred to us that a possible solution was to turn the different dependence of spectral or dyed speed, which is surface-area dependent, and intrinsic or blue speed, which is volume dependent, to our advantage. What if we were able to manipulate the surface area and the volume of silver halide grains independently?

But before we could pursue reducing silver halide grain volume independently of grain surface area, we had to address a more fundamental question: What determines the amount of silver that is coated in a color film? There must be enough silver to: (1) form a latent image, (2) act in a redox couple with the color developer to form the required amounts of image dyes, and (3) absorb sufficient light. Where sensitizing dyes primarily fill the absorption role, for example, in red-sensitive and green-sensitive layers, the silver is required to provide grain surface area for dye absorption. Since the grain surface area required for dye absorption controls the amount of silver coated in red-sensitive and green-sensitive layers, the possibility of reducing grain volume and to be the amount of silver coated appeared hence realistic.

Of the several different approaches for independently manipulating silver halide grain volume and grain surface area, we ultimately chose one particular approach, which has turned out to offer still other advantages. These ideas became Kodak T-Grain emulsions. These emulsions contain grains of high aspect ratio. Aspect ratio is defined as the ratio of the equivalent circular diameter to the thickness for a grain. T-Grain emulsions satisfy the requirements of better quality at higher sensitivity.

Although the precipitation and sensitization of high-aspect-ratio tabular-grain emulsions are not the topic here, we should mention that, prior to our investigations of using high-aspect-ratio tabular-grain emulsions in color materials, tabular-grain emulsions with aspect ratios of 3:1 to 5:1 were used in photographic products. Only later did we learn that high-aspect-ratio pure-bromide grains produced by Ostwald ripening were known. However, these emulsions were photographically inefficient, had a wide size frequency distribution, and had no commercial utility. Useful high-aspect-ratio tabular-grain emulsions were the product of our own investigations.

Now let us examine four advantages in color film performance realized by the use of T-Grain emulsions. Our appreciation of these advantages emerged during our investigations. One advantage is an improved
minus-blue to blue sensitivity ratio. Consider the idealized case of blue and minus-blue sensitivity dependence on grain size for the spherical grains, shown earlier, and tabular grains of increasing surface area while crystal volume is maintained constant by reducing grain thickness (Figure 5). Once our solution was conceived, the potential advantage was readily apparent. This advantage can be utilized directly to reduce color degradation due to the intrinsic sensitivity of emulsions in red-sensitive and green-sensitive layers, as shown in Figure 6, or it can be used indirectly by complete removal of the blue-absorbing filter layer for simplification of the film structure and reduced coating thickness. Of course, a combination of these two routes is also possible.

A second advantage is improved speed/granularity ratio. For simplicity in illustrating the concept, again consider a hypothetical example, in this case a film layer containing a spectrally sensitized monodispers-

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**Fig. 6** Relationship between log spectral sensitivity and wavelength for a conventional emulsion (-----) and a T-Grain emulsion (-- -).

**Fig. 7** Hypothetical speed/granularity characteristics of a 1 μm cubic emulsion.

**Fig. 8** Hypothetical speed/granularity characteristics of a 1.41 μm cubic emulsion.

**Fig. 9** Hypothetical speed/granularity characteristics of a 22.6:1 aspect ratio T-Grain emulsion.
would be increased to twice the original value because the surface area was doubled. Holding the silver coverage to the original level results in an RMS granularity decrease of 0.80 times as opposed to the 1.68 times increase of the 1:1 aspect ratio 1.41 μm cubic-grain emulsion coated at the same silver level. With higher-aspect-ratio T-Grain emulsions, the advantage is potentially even greater. Of course, this hypothetical case assumes that other features of the imaging system affecting granularity, for example, development characteristics, are equal. Also, all the emulsions must be sensitized to the same efficiency. Nevertheless, the hypothetical case suggests improved speed/granularity ratio at equal silver coverage or equal speed/granularity ratio at reduced silver coverage from the use of T-Grain emulsions. However, because the performance of practical emulsions is a function of many interacting variables, it required extended investigations to ascertain these advantages.

A third advantage is decreased sensitivity to high-energy radiation relative to film speed quality. Natural background radiation is both cosmic and terrestrial in origin and is a complicated polychromatic mixture of directly and indirectly ionizing high-energy particle fluxes. The radiation environment varies considerably, depending on factors such as the geography, latitude, and altitude of a location. Such background radiation is one of the factors that affects change in color films after manufacture, as Schiager has noted, and, therefore, it must be accounted for in product design by attempting to minimize as much as possible the sensitivity to this source of noise. (Other well-known factors that must be accounted for are temperature and humidity.) One of the important emulsion parameters that affects high-energy radiation sensitivity is the mass or volume of a grain. As shown in Figure 10, T-Grain emulsions, with their high surface-area-related sensitivity when spectrally sensitized, are advantageous because of lower sensitivity to radiation such as x-rays, cosmic rays, and gamma rays, which are volume related. In parallel to the earlier discussion of speed/granularity performance, T-Grain emulsions can be used for improved speed/quality ratio at equal radiation sensitivity, by maintaining the same silver level, or equal speed/quality ratio at reduced radiation sensitivity by reducing the silver level. Of course, this must be considered along with many other criteria in designing a color film.

The last advantage to be mentioned here is enhanced sharpness, a benefit resulting from the optical properties of coatings of high-aspect-ratio T-Grain emulsions. Light passing through a layer containing three-dimensional silver halide crystals becomes scattered. In a multilayer color film the lower layers are significantly less sharp than the upper layers for this reason. This is unfortunate, because the red-sensitive record, which is normally coated at the bottom of the structure, contains a high proportion of the image information. Phenomenologically, tabular emulsions lie with their long axis
parallel to the support because of the hydrostatic forces involved in coating and drying (Figure 11). This arrangement results in incident light being transmitted through layers containing T-Grain emulsions in a more specular fashion than light passing through layers containing conventional silver halide crystals (Figure 12). This can be shown by a graph of the cumulative transmission probability as a function of the collection half angle for normally incident light (Figure 13); T-Grain emulsions scatter much less light at large collection half angles than do more nearly three-dimensional particles. For light not normally incident, for example, if a layer containing T-Grain emulsion is coated below a highly scattering layer containing conventional grains, a net loss in sharpness can result. Therefore, care must be taken in building color films to use the optimum combination of crystal morphologies to obtain maximum sharpness.

In conclusion, we have demonstrated four distinct advantages that have resulted from the use of Kodak T-Grain emulsions in color films: (1) increases in minus-blue to blue sensitivity ratio, which give improved color separation and the possibility of removing the blue filter layer; (2) improved speed/granularity ratio at equal silver coverages or equal speed/granularity at reduced silver coverages; (3) equal speed/quality ratio at reduced background radiation sensitivity or improved speed/quality ratio at equal background radiation sensitivity; and (4) increased sharpness through improved emulsion optics. Finally, a fifth practical advantage is that only a fraction of the amount of silver coated in many existing color products is needed. We feel that advantages associated with three-dimensional emulsion technology, for example, optimization of emulsion size dispersity and specific placement of iodide for management of electron-hole separation, development characteristics, and inhibitor response, should be additive to the tabular morphology of T-Grain emulsions. Controlling the interior construction of silver halide grains to improve film performance is well documented. With the recognition of the role of shape, controlling grain interior construction and shape simultaneously is now a direction to follow.

It is important to recognize that manufacturers other than Eastman Kodak Company sell color films with speeds of ASA 1000 and above, based on low-aspect-ratio emulsion technology. However, as a result of the advantages discussed in this paper, Kodak T-Grain emulsions were instrumental in providing the world's first four-digit ASA color negative film. They have since permitted us to introduce other unique and desirable products. We expect that they will continue to enable us to use their advantageous properties to design valuable products for photography.

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