

# AgX Photographic Technologies: Present and Future

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## Abstract

*Recent big change in photographic industries was caused by rapid popularization of digital still cameras (DSCs) owing to the facts that the image qualities of the pictures taken by DSCs as well as by color films have become to be totally good enough for amateur consumers, and that DSCs are more convenient than color films. However, comparisons between color films and DSCs have revealed that color films have still several advantages over DSCs in capability and image quality. The advantages are explained on the basis of the differences in technologies between them, and provide a good reason to predict that people will continue to use color films together with DSCs in the future. It is also stressed that silver halide technologies are so elaborated that they are being applied to various technical fields.*

## Technologies in Color Films<sup>1,2</sup>

A color negative film is composed of a photosensitive layer with thickness of  $\sim 20 \mu\text{m}$  on a TAC film base with thickness of  $\sim 100 \mu\text{m}$ . The photosensitive layer is composed of  $\sim 15$  sub-layers, which have different functions and are coated one on another. They include layers, each of which is sensitive to one of three primary colors (i.e., blue, green, and red) for capturing a full-color image. Furthermore, they also contain layers with high, medium, and low sensitivities for capturing an image with wide dynamic range. Recently, the fourth layer has been introduced into color films to achieve faithful color reproduction<sup>3</sup>. Namely, the three-dimensional structure of the photosensitive layer of a color film makes it possible for it to capture an image with faithful color reproduction and wide dynamic range.

A color film contains silver halide (AgX) grains as photosensitive materials, and especially in highly sensitive layers thin tabular AgX grains. Tabular grains were proposed<sup>4</sup>, and have been refined on the basis of nanotechnologies for many years. It is also noted that a TAC film for a color film has been improved and refined for many years to give a very flat and an optically uniform base for a photosensitive layer in a color film<sup>5</sup>.

Incident blue, green, and red lights are mainly absorbed by sensitizing dyes on the above-stated grains in the green-, and red-sensitive layers, and even in the blue-sensitive layer, since thin tabular AgX grains are weak absorbers for blue light. Then, excited dye molecules inject into the conduction band of the grains electrons available for the formation of latent image centers composed of silver clusters in collaboration with interstitial silver ions. A latent image center initiates photographic development, by which the exposed grain is reduced by a developer to give a silver grain and a dye, whose color is complementary to that of the absorbed light in each layer.

The theory and mechanisms of photographic sensitivity have been studied for many years<sup>6</sup> and have made it possible to grasp the present state properly and predict the possibility and ways for further improvements in the performance of color films<sup>2</sup>. They include the enhancement of light absorption by thin tabular grains

with antenna dyes<sup>6</sup>, the refinement of the technology to create two electrons by one absorbed photon<sup>7</sup>, the improvement in the efficiency of latent image formation by Se and Te sensitizations<sup>8</sup>, and the depression of recombination by localizing photoelectrons in the area with dislocations along the edge of a tabular grain<sup>9</sup>. It is predicted that the room for the increase in photographic sensitivity is several times owing to the results of the above-stated efforts<sup>2</sup>.

## Comparison in performance and technology between Color Films and DSC<sup>2</sup>

It is obvious that the image qualities of pictures taken by color films and DSCs with CCDs and CMOS as photo-sensors are already good enough to satisfy many ordinary consumers. However, careful comparisons in capabilities and image qualities of pictures between color films and DSCs have revealed several essential differences between them.

According to Uchida and Takada<sup>10</sup>, the advantages of color films over CCDs are high sensitivity (2 steps) and wide dynamic range (6 steps). They have brought about a new AgX product with a highly sensitive color negative film (ISO sensitivity of 1600) and a compact camera having a bright lens (1.9), by which we can take pictures of most objects without any flash light<sup>11</sup>. Color negative films with wide dynamic range are useful to develop attractive single-use cameras and motion pictures<sup>12,9(a)</sup>.

We have compared in image quality between the pictures of various objects as taken by color films and DSCs, and found several essential differences between them<sup>2(c),(d)</sup>. Among those pictures, two examples were taken and analyzed. Namely, a color film could describe the details of the face skin of a lady more precisely than DSC (Example 1), while a DSC could describe an airplane more sharply than a color film (Example 2)<sup>2(c)</sup>. As analyzed below, the depression of the response of a CCD in higher frequency region by a low-pass filter is responsible for Example 1, while the enhancement of the response of a CCD in the medium frequency region is responsible for Example 2. The above-stated two kinds of image processing technologies in a DSC would be the reasons why people sometimes feel that the pictures taken by CCDs are unnatural.

Then, comparisons are made on the differences in technologies between color films and DSCs, which bring about the above-stated differences in performance between them<sup>2</sup>. One of the most important differences is in that a color film has such a three-dimensional structure as to establish a pixel, which is sensitive to three primary colors (i.e., blue, green, and red) with wide dynamic range, while a CCD with two dimensional structure is composed of pixels, each of which is sensitive to one of three primary colors with limited dynamic range. In addition, the increase in the frame area to increase the number of pixels per frame is much easier in a color film than in a CCD. These differences are the main causes for the fact that a color film is superior in sensitivity and dynamic range to a CCD, as indicated by Uchida and Takada<sup>10</sup>.

It is noted that photosensitive elements in a color film are AgX grains, which are as small as 0.2 ~ 1 $\mu$ m and much smaller than photosensitive elements (i.e., pixels) in a CCD. Since a CCD is composed of many pixels, which are regularly arranged and electrically connected in series, it is probable for only one defect or dust to deteriorate the function of a CCD. Since the function of a pixel in a color film is the result of the responses from several hundreds independent AgX grains, defects and dusts hardly deteriorated the function of a pixel, when their numbers are much smaller than that of AgX grains in it. This is the reason why the increase in the frame area for the increase in the number of pixels per frame is more difficult in CCDs than in color films.

The modulation transfer function of a CCD becomes to be very strange when the frequency of the input sign signal becomes to be close to and larger than that of the regularly arranged pixels. This means that a CCD is not available for taking a picture of a regularly arrayed object owing to the occurrence of such problems as aliasing and false color when its frequency is close to or larger than that of the pixels on a CCD. In order to escape from this problem, the depression of the response of a CCD in higher frequency region is carried out by use of a low-pass filter, and therefore responsible for the poor description of the details of the face skin of a lady by a DSC. On the other hand, the enhancement of the response of a CCD in the medium frequency region is brought about by an image processing technique and responsible for the sharp description of the edges of an airplane by a CCD. Such image processing treatments as the depression of the response in higher frequency region and the enhancement of the response in medium frequency region bring about unnatural description of some objects in the pictures taken by DSCs.

As stated above, the efficiency of image formation by color films is still low, and has a room for further improvement. On the other hand, the efficiency of image formation by CCDs is already high, and little room for improvement. However, the possibility for the improvement in capability by image processing technologies is larger for CCDs than for color films. One of the most effective technologies seems to be the interpolation, by which the response at a deficient pixel can be supplied by the responses at its neighboring pixels, and makes it easier to increase the frame area of a CCD for the increase in the number of pixels per frame.

As stated above, there are the differences in capability and performance between color films and DSCs, which are ascribed to the differences in technologies between them. It is therefore considered that people will use color films in addition to DSCs for taking pictures, depending on their purposes and conditions.

## New Technologies from AgX Photography

It is noted that various kinds of technologies have ever been introduced into color films, and refined them for many year to realize such fine and highly composite systems as color films. Efforts to extend the technologies in AgX photography to other fields are therefore thought to be attractive and promising. Some of such efforts are new nuclear emulsion coatings with resetting function for the study of neutrinos<sup>13</sup>, application of AgX emulsion technologies to nano-particles of AgX available for holographic materials<sup>14</sup> and new nuclear emulsions to detect unknown materials present in the space (i.e., dark matter)<sup>13</sup>, a new technology to put AgI grains into practice to create photothermographic materials, in

which unexposed photosensitive grains (i.e., AgI grains) are fixed during thermal development<sup>15</sup>, application of flat and optically uniform TAC film bases of color films<sup>5</sup> to films for liquid crystal displays<sup>16</sup>, application of characteristic technologies of AgX materials (i.e., three-dimensional structure and the fourth layer for faithful color reproduction) to new CCD and CMOS sensors to enhance their performance<sup>17,18,3(c)</sup>, and to new photo-sensors with thin organic layers<sup>19</sup>, extension of the knowledge and technologies of J-aggregated sensitizing dyes to thin organic layer devices<sup>20</sup>, extension of dye sensitization as developed for photographic materials to photo-catalys<sup>21</sup>, and dye-sensitized solar cells<sup>22</sup>.

## References

- [1] Tadaaki Tani, *Photographic Sensitivity: Theory and Mechanism*, Oxford University Press, New York, 1995.
- [2] (a) T. Tani, *Photogr. Sci. Photochem.*, **21**, 357 (2003). (b) T. Tani, *J. Dispersion Sci. Technol.*, **25**, 375 (2004). (c) T. Tani, 2005 Beijing Intern. Conf. on Imaging, May 2005, Beijing. (d) T. Tani, Intern. Gelatin Conf., September, 2005, Heidelberg, Germany.
- [3] N. Sasaki, K. Takahashi, and H. Ikoma, *J. Soc. Photogr. Sci. Technol.*, **52**, 41 (1989). (b) N. Sasaki, *J. Soc. Photogr. Sci. Technol.*, **67**, 504 (2004). (c) N. Ohta, Summer Seminar, sponsored by SPSTJ, Oct. 2004, Fujiyoshida, Yamanashi, Japan.
- [4] (a) Anonymous, *Res. Discl.* (Item 22534), **225**, 20 (Jan. 1983). (b) J. T. Kofron and R. E. Booms, *J. Soc. Photogr. Sci. Technol. Jpn.*, **49**, 15 (1986).
- [5] (a) *Principles of Photographic Science and Engineering (Shashinkougaku no Kiso)*, Revised edition, SPSTJ, ed., Corona Publishing Co., Ltd., Tokyo, 1998, Section 3.7. (b) *Neblette's Handbook of Photography and Reprography, Materials, Processes, and Systems*, Seven Edition, J. M. Sturge, ed., Van Nostrand Reinhold Company, New York, 1977, Chapter 6.
- [6] R. L. Parton, T. L. Penner, W. J. Harrison, J. C. Deaton, and A. Muentner, AgX 2004.
- [7] (a) I. R. Gould, J. R. Lenhard, A. A. Muentner, S. A. Godleski, and S. Y. Farid, *J. Am. Chem. Soc.* **122**, 11934 (2000). (b) T. D. Pawlik, A. A. Muentner, R. S. Eachus, and J. R. Lenhard, AgX2004.
- [8] K. Morimura, H. Sasaki, T. Kojima, M. Ihama, S. Yamashita, T. Tani, and H. Mifune, in Ref. 2(c).
- [9] (a) K. Makino, S. Yamaryo, Y. Mimaki, and K. Kawai, ICIS'02, (b) F. Ueda, M. Goto, S. Kuwashima, K. Morimura, N. Haraguchi, M. Toyoda, H. Fukuzawa, and H. Ikeda, ICIS'06.
- [10] M. Uchida and S. Takada, ICIS'02.
- [11] (a) H. Ikoma and M. Uchida, The 21<sup>st</sup> Seminar on Photographic Technology, Sponsored by SPSTJ and Japan Soc. for Arts and History of Photographs, March 3, 2005, Tokyo. (b) M. Uchida and H. Ikoma, Summer Seminar, Sponsored by SPSTJ, Oct. 2005, Fujiyoshida, Yamanashi, Japan.
- [12] (a) M. Moriya, The proceedings of the Annual Conference of SPSTJ, May, 2004, Tokyo, pp.72-73. (b) S. Takahara, Photo Imaging Expo Seminar, organized by SPSTJ, March 2006, Tokyo.
- [13] (a) K. Niwa, *J. Soc. Photogr. Sci. Technol.*, **67**, 561 (2004). (b) T. Toshito, *J. Soc. Photogr. Sci. Technol.*, **67**, 538 (2004). (c) K. Kuwabara and S. Nishiyama, *J. Soc. Photogr. Sci. Technol.*, **67**, 521 (2004).
- [14] Holography News, Vol. 20 (No. 1), January, 2006, p. 1&8.
- [15] (a) H. Mifune, T. Tani, S. Yamashita, S. Aiba, T. Ohzeki, and K. Yamane, ICIS'06. (b) H. Mifune, K. Yamane, T. Ohzeki, F. Nariyuki, K. Watanabe, M. Yoshikane, M. Nakanishi, and T. Maekawa, ICIS'06. (c) H. Mifune, T. Funakubo, T. Ohzeki, K. Ohzeki, and K. Yamane, ICIS'06.
- [16] H. Mori, *J. Display Technol.*, **1**, 179 (2005).

- [17] (a) K. Oda, H. Kobayashi, K. Takemura, Y. Takeuchi, and T. Yamada, *Image Information and Television Engineering*, **27** ( 25 ) 17 ( 2003 ), (b) T. Ashida, H. Yamashita, M. Yoshida, O. Saito, T. Nishimura, and K. Iwabe, *Sensors and Camera Systems for Scientific, Industrial, and Digital Photography Application V*, M. M. Blouke, N. Sampat, R. J. Motta, eds., Proc. of SPIE-IS&T Electronic Imaging, 2004.
- [18] (a) R. F. Lyon and P. M. Hubel, *IS&T/TSID 10<sup>th</sup> Color Imaging Conference Proceedings*, Scottsdale, AZ, USA; 2002, pp. 349-355.(b) P. M. Hubel, J. Liu, and R. J. Gutosch, Proc. SPIE Vol. 5301, pp. 402-407, 2004.
- [19] (a) S. Takada, M. Inuiya, and M. Ihama, *IS&T/SPIE's Electronic Imaging Science and Technology*, January 15-19, 2006, San Jose, CA, (b) S. Takada, M. Ihama, and M. Inuiya, ICIS'06.
- [20] T. Tani, K. Seki, K. Yoshihara, and J. Hanna, The 9<sup>th</sup> Intern. Conf. Solar Energy and Appl. Photochem. (SOLAR'06), Cairo, January 2006.
- [21] (a) A. Heller, *Acc. Chem. Res.*, **28**, 141 (1995), (b) A. L. Linsebigler, G. Q. Lu, and J. T. Yates, *Chem. Rev.*, **95**, 735 (1995), (c) A.

Fujishima, K. Hashimoto, and T. Watanabe, *TiO<sub>2</sub> Photocatalysis, Fundamentals and Applications*, BKS, Inc., Tokyo, 1999.

- [22] (a) A. Hagfeldt, M. Graetzel, *Chem. Rev.*, **95**, 49 (1995), (b) M. Graetzel, *Nature*, **2001**, 414, 338-334.

## Author Biography

*After Tadaaki Tani studied photographic science under the guidance of Prof. S. Kikuchi and Prof. K. Honda as a graduated student in the University of Tokyo, he was graduated there, and obtained the degree of Doctor of Engineering in 1968. In the same year, he became to be a member of Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., and has been involved in fundamental research of AgX emulsions and systems until now. He is concurrently a guest professor of Tokyo Institute of Technology since 1999.*