Progress and Future Prospects of Silver Halide Photography Compared with Digital Imaging

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The progress and future prospect of silver halide photography are analyzed by comparing the structure and efficiency of image formation of color films with those of CCDs in digital still cameras for amateur consumers. It is predicted that the efficiency of image formation by a color film, which is based on the efficiencies of absorption of incident photons and conversion of absorbed photons into latent image centers by silver halide grains, will be increased by several times in the future. It is also predicted that the superiority of color films over digital still cameras in terms of image quality and cost will remain in the future, because the efficiency of image formation by CCD is based on the efficiencies of absorption of incident photons and conversion of absorbed photons into photoelectrons, both of which are very high and have therefore little room for improvement. The characteristics of photographic systems with color films were also analyzed in comparison with those of digital imaging systems with CCDs.

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Introduction

IS&T, the Society for Imaging Science and Technology, celebrates its 50th anniversary in 1997. Various kinds of photosensitive materials have been developed and studied during these years. Among them, only silver halide photographic emulsions could provide materials with the high sensitivity necessary for taking pictures, until charge-coupled devices (CCDs) appeared recently.[1] The progress and future prospect of silver halide photography and electronic photography with CCDs as sensors have attracted the keen interest of imaging scientists and engineers. Several important publications have made the comparison between silver halide photography and electronic photography from various viewpoints.[2–8]

Because digital still cameras with CCDs as sensors have become popular recently owing to the increase in the popularity of personal computers, analyses and discussion on the future of imaging systems are occurring more often than before. Taking into account this condition, the present author has tried to analyze this subject again according to the session on AgX and Si arranged by M. Kriss on the occasion of the 50th anniversary of IS&T.[9]

The present author has been involved in studies on the mechanisms of photographic sensitivity for many years and noticed that the capability and future trend of imaging systems mostly depended on the structure, mechanism, and efficiency of image formation by their photosensitive materials. The present author, therefore, considered that the most reliable future prospect of silver halide photography in comparison with that of electronic photography should be given by the analysis of the photosensitive materials in those systems.

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Various kinds of digital still cameras have been produced recently, not only for amateur photography but also for office and professional uses. The image quality of pictures taken by digital still cameras sharply depends on their cost. It is now possible to take pictures with high quality by use of digital still cameras, although those cameras are too expensive for amateur consumers to purchase. However, such expensive cameras could be acceptable to office and professional uses. It is, therefore, confusing to compare silver halide photography with electronic photography from a general aspect.

To make clear the point of discussion on the present state and future prospect of silver halide and electronic photography in this paper, analyses focus on color films and digital still cameras for amateur consumers, which are representative of photography and also constitute the major part of photographic market.

Characteristics of Color Films and CCDs

Figure 1 shows the scanning electron micrograph of emulsion layers in a color negative film with silver halide grains as white spots in gelatin layers. A suspension of silver halide grains in gelatin or in its aqueous solution is called a photographic emulsion. There are three major emulsion layers, which are sensitive to blue, green, and red lights. In each major layer, there are three sub-layers, sensitivities of which are high, medium, and low. The multilayer structure with different functions makes it possible for a color film with a small frame area to capture a large amount of image information with full color and large dynamic range.

The photosensitive materials in color films are a large number of silver halide grains randomly arranged in emulsion layers as seen in Fig. 1. As shown in Fig. 2, silver halide grains absorb incident photons to create electrons, and the created electrons take part in the formation of latent image centers composed of silver clusters on the grain surface. Only the grains with latent image centers on their surfaces are reduced by a developer to give developed silver

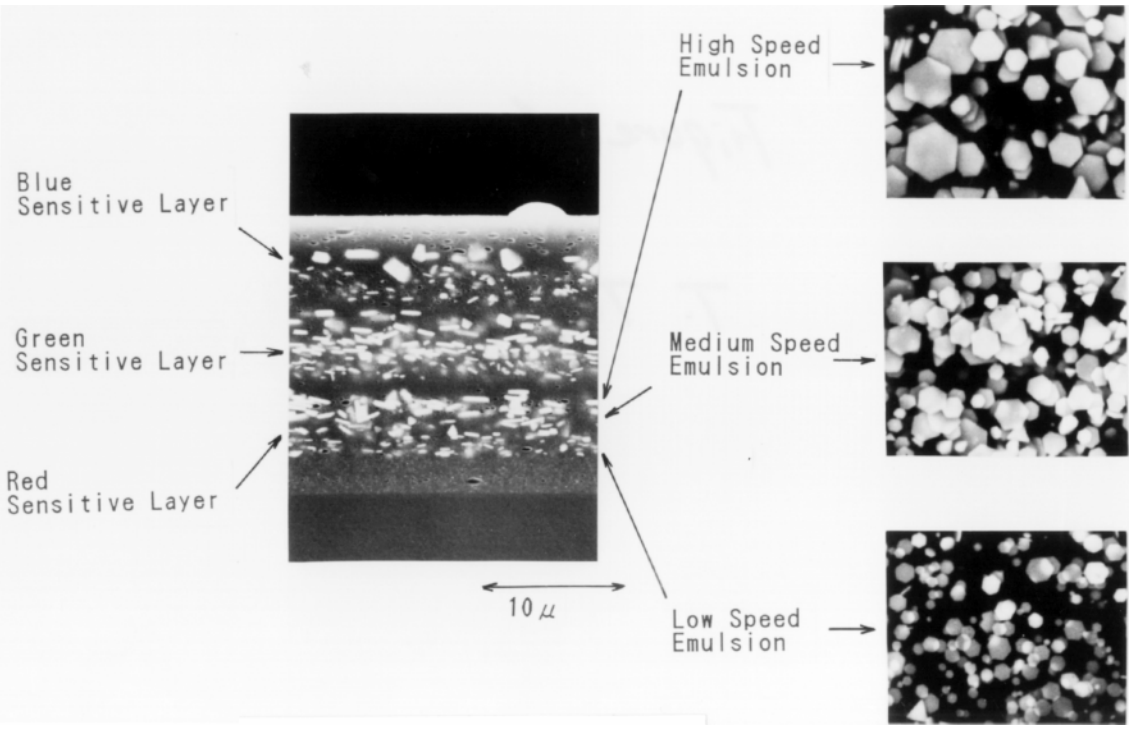

Figure 1. (Left) A scanning electron micrograph of a cross section of photosensitive layers of a color negative film with ISO sensitivity of 400, showing three major layers sensitive to three primary colors. White spots are silver halide grains. (Right) Scanning electron micrographs showing silver halide grains in high-speed, medium-speed, and low-speed sublayers in a red-sensitive major layer (courtesy of N. Sasaki).

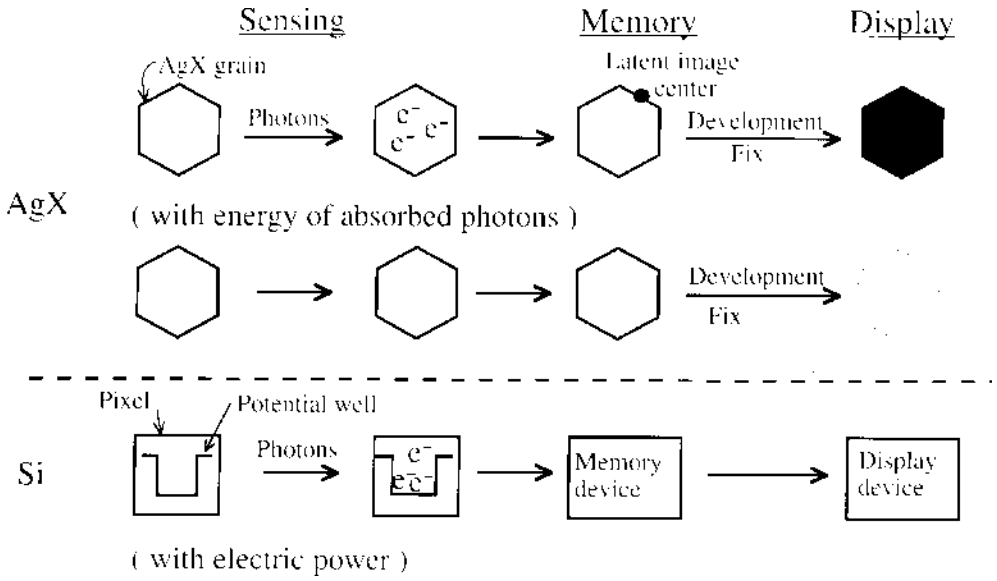

Figure 2. Processes for image formation in AgX and Si systems, where e^- is a photoelectron.

grains and oxidized agents.[1] The oxidized agents react with couplers to give dyes. It is believed that the smallest latent image center formed on a grain in a color film is composed of three atoms.[10–15] Because a highly sensitive grain in a color film contains several tens of billions of silver ions, the degree of the amplification caused by photographic development is as large as several billion times, making color films highly sensitive to light.

A silver halide grain itself absorbs only blue light in the visible region. In green- and red-sensitive layers, silver halide grains adsorb sensitizing dyes that absorb green and red lights, respectively. A sensitizing dye molecule is electronically excited by an absorbed photon and injects an excited electron into the conduction band of the silver halide grain.[16] An injected electron takes part in the formation of a latent image center on the grain surface.

The latent image formation is initiated by the reaction of a photoelectron with an interstitial silver ion to form a silver atom at a sensitization center and is followed by the formation and growth of a silver cluster there. It is known that a single silver atom on a silver halide grain is unstable and dissociates to give an original electron and

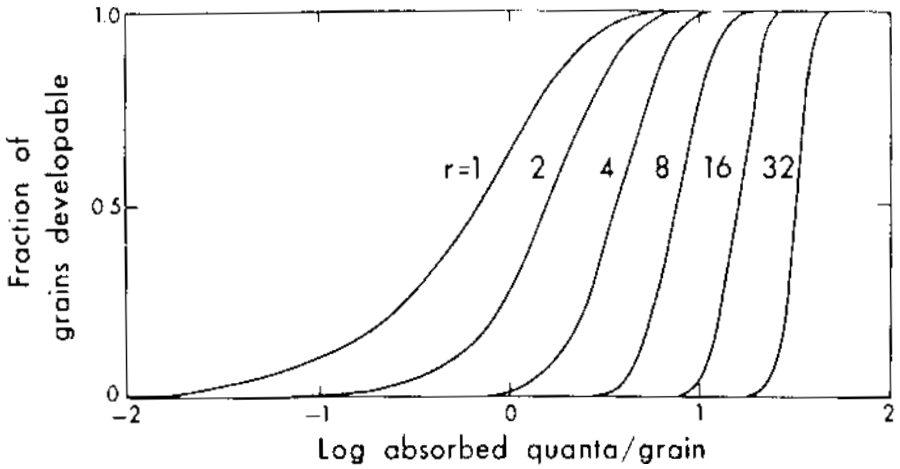

Figure 3. Characteristic curves of AgX emulsion layers with variation of quantum sensitivity, which is defined as the number of absorbed photons per grain (r) for the formation of the smallest latent image center.[17]

interstitial silver ion and that silver clusters including a dimer are stable.[1,15] Namely, a threshold exists for the formation of a latent image center between the formations of a silver atom and a dimer of silver atoms, and any stimulation that does not exceed the threshold does not change silver halide materials.[1] The presence of the threshold makes color films stable during long storage, although it makes them rather insensitive to very weak exposure for a long time.[1]

The characteristic curve of a silver halide material is represented by plotting the fraction of grains developable in the material or the optical density of the processed material, which is proportional to the fraction of grains developable, as a function of a logarithm of exposure or a logarithm of number of absorbed photons per grain. Fig. 3 shows such characteristic curves derived by Silverstein[17] as early as 1922 with variation of quantum sensitivity defined by the number of absorbed photons per grain needed for the formation of the smallest latent image center. Note that each curve is characterized by the presence of a long straight line portion. Thus, it is not the amount of developed silver or dyes formed during development, but its exponential that can be principally in linear relationship with the number of absorbed photons per grain, meeting the Lambert-Beer's law. Therefore, the characteristic curve of a color film is not suitable for displays with additive color processes, such as the display on a CRT, but is suitable for displays with subtractive color processes, such as the display on films and papers.

The working principle and an example of the structure of a CCD are illustrated in Figs. 2, 4 and 5. Each pixel has a potential well electrically connected with others in a series. Photoelectrons created by photons incident to a photosensitive area in each pixel are stored in the potential well, transferred from well to well, and taken out one after another to give an image signal in time series. The photosensitive area in each pixel in a CCD is limited and decreases with decreasing pixel size.[3] One of the most important advances in CCDs is the set-up of a microlens on each pixel to focus incident photons to a photosensitive area in a pixel.[18] To capture a color image, it is necessary to set up a microcolor filter on each pixel, and the development of an on-chip color filter in each pixel was an important advancement recently achieved in CCDs.[18] Captured electrons in each pixel form a captured image and are immediately taken out for memorizing. As shown in Fig. 6, the number of electrons per pixel is proportional to the

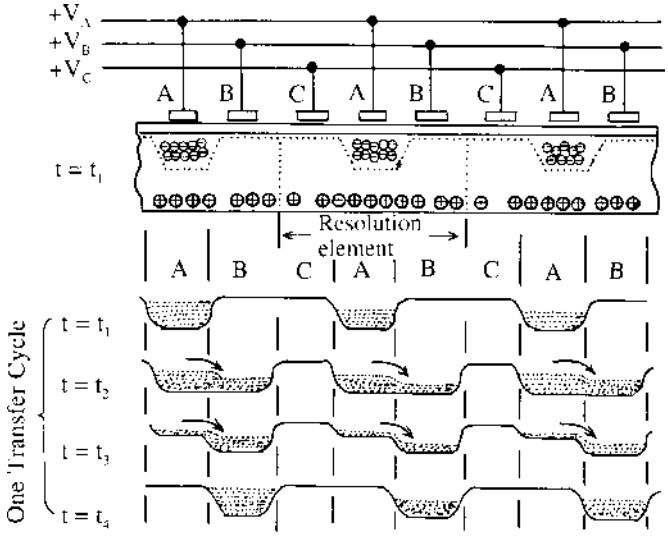

Figure 4. An illustration showing the working principle of a CCD.

number of absorbed photons per pixel.[19] However, the number of photoelectrons a pixel can store is limited and determines the dynamic range of a CCD. The number of photoelectrons that can be discriminated from the number of noise electrons determines the sensitivity of a CCD. The response of a CCD is linear and, therefore, suitable, not for the display with subtractive color process, but for the display with additive color process. Some kind of modification might be needed on the response of a CCD in order to display an image captured by it on a print.

Recent Progress in Color Films

According to the photographic processes as stated above, photographic sensitivity depends on light absorption, efficiency of the formation of a latent image center, and the size of the smallest latent image center.[20] In 1985, the present author analyzed these factors and predicted[20] the possibility for increase in photographic sensitivity as shown in Table I.

The light absorbance of a highly sensitive emulsion layer was judged to be ~1/3 according to the literature reported by Bird et al.[21] The efficiency of the latent image formation is usually represented by quantum sensitivity. Although the

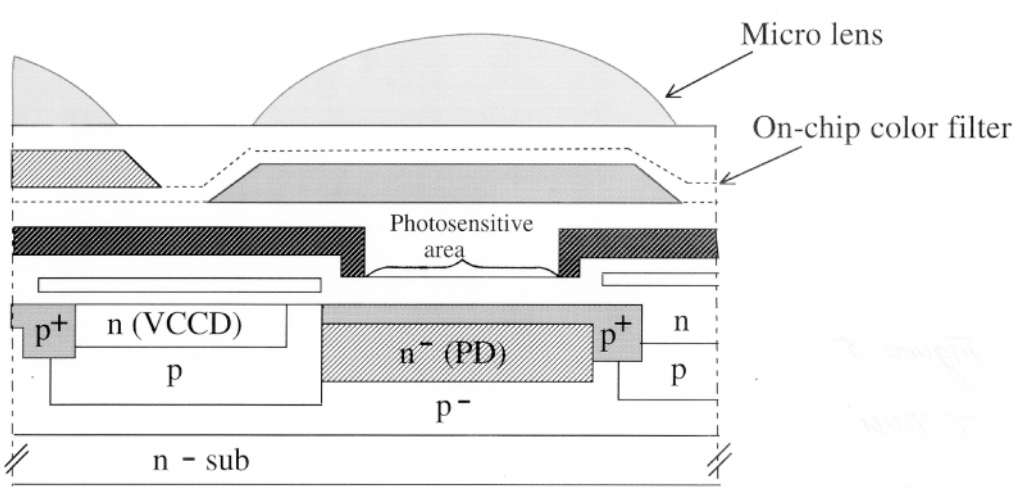

Figure 5. An illustration showing an example of the structure of a CCD.[18]

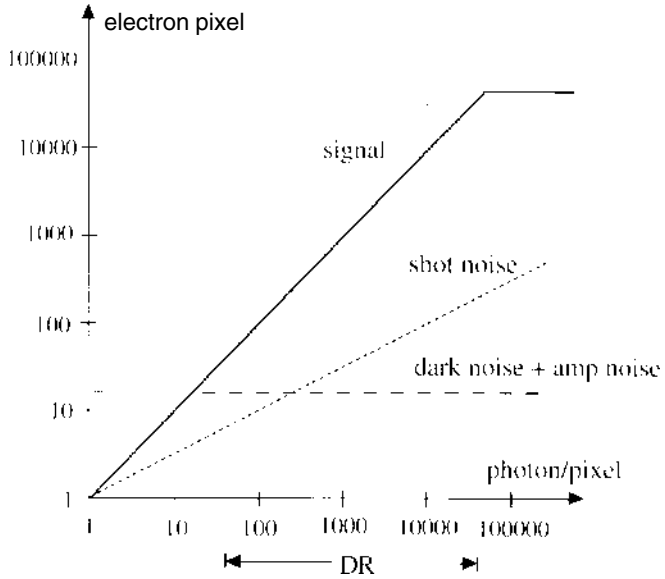

Figure 6. Characteristic diagram of a CCD with pixel size of 50 μm^2, where DR is its dynamic range.

quantum sensitivity of fine silver bromide grains, which were fully treated with sulfur-plus-gold sensitization and hydrogen hypersensitization, was already as high as less than 3 absorbed photons per grain in 1985, the quantum sensitivity of larger grains available for color films was evaluated to be ~10 absorbed photons per grain.[22] It was estimated that the smallest latent image center formed in a color film was composed of three atoms.[10–15]

The ultimate limit of the light absorbance is unity, and therefore, the room for improvement in the light absorption was evaluated to be ~3 times. It was considered that the ultimate limit of quantum sensitivity was 2 photons per grain,[14,23,24] and the room for improvement in efficiency of latent image formation was evaluated to be ~5 times. In total, it was predicted[20] in 1985 that the sensitivity of color films could be increased by more than 10 times.

Many efforts have been made to increase photographic sensitivity. Poor light absorption of the blue-sensitive layer in color film comes from the small absorption coefficient of silver halide in the blue region.[25] It is known that the absorption coefficient of silver bromoiodide in the blue region is much larger than that of silver bromide, although the rate of development for silver bromoiodide is smaller

TABLE I. Possibility for Increase in Photographic Sensitivity as Predicted in 1985

Factors	Present state	Ultimate limit	Room for improvement
Light absorption	~1/3	1	3
Quantum sensitivity (absorbed photon/grain)	~10	2	~5 >10
Size of the smallest latent image (atoms)	3	2	1.5

than that of silver bromide. To create grains with high capability of both light absorption in the blue region and high rate of development, double structure grains were developed by putting silver bromoiodide in their core and silver bromide in their shell.[26]

To improve the light absorption of green- and red-sensitive layers in a color film, it is necessary to increase the amount of sensitizing dyes adsorbed by an emulsion grain and, therefore, to develop silver halide emulsion grains with large specific surface area. One of the most important emulsion technologies for this purpose was the development of tabular grains[27] as shown in Fig. 7, and Marchant reported at the International Congress of Photographic Science in Cambridge in 1984 that, by using tabular grains, the absorbance of incident green and red lights by a color film could be as large as about one half.[28] Although the author did not report the details of his data and method, it is assumed that the above-stated absorbance was for the absorption maxima in green- and red-sensitive layers in a color film, and that the room for improvement in light absorbance would be nearly two times for the maxima and four times for the whole spectral regions of the above-stated layers.

The efficiency of latent image formation depends on the quantum yield of free electrons, the electron-trapping process at the sensitization centers, and the recombination process.

The absorption of a photon creates an exciton in silver halide. Because the binding energy of an exciton is some several tens of milli-electron-volts, it completely dissociates to give a free electron and a positive hole.[25,29,30] In addition, it has been verified that an absorbed photon in a silver halide grain gives two free electrons in the presence of R centers of reduction sensitization (Ag_2) according to Lowe's hypothesis.[31,32,22] As shown in Fig. 8, there are two types of silver clusters called R centers and P centers, which are formed at electrically neutral and posi-

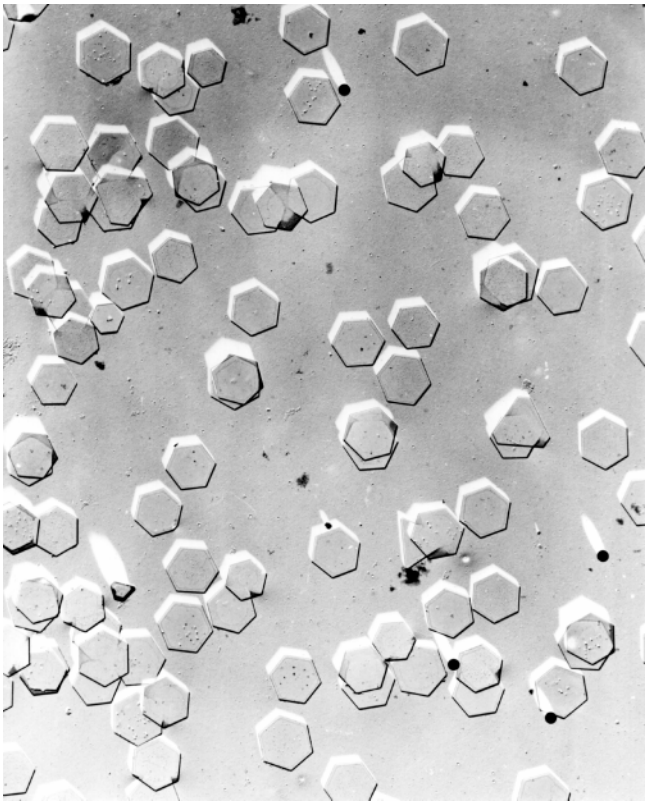

Figure 7. An electron micrograph of tabular AgBr grains, where the diameter of a black circle is 0.5 μm.

tively charged kink sites and are traps for positive holes and photoelectrons, respectively,[15,33–35] as shown in Fig. 8.[35(b)] The absorption of a photon by silver halide gives an exciton, which dissociates to give a free electron and a free positive hole. The reaction of a positive hole with Ag_2 gives Ag_2^+, which is unstable and dissociates to give a silver atom and an interstitial silver ion. As is well known, a silver atom is unstable and dissociates to give a free electron and an interstitial silver ion.[15] Therefore, the ultimate limit of the yield of free electrons is considered two. The realization of the ultimate limit of the yield of free electrons has not yet been achieved[22,36] and is one of the most important subjects for increasing high sensitivity.

In green- and red-sensitive layers, an absorbed photon excites an electron at the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in a sensitizing dye molecule and injects an excited electron into the conduction band of a silver halide grain.[16] The yield of free electrons in silver halide grains in green- and red-sensitive layers, therefore, depends on the quantum yield of the electron transfer from excited dye molecules to the grains.[16] Figure 9 shows the electronic energy level diagram of an excited dye molecule on a silver halide grain and potential energy profile of the electron transfer from the excited dye molecule to the grain in spectral sensitization, where ΔE is the difference in electronic energy between an excited electron and the bottom of the conduction band of the silver halide and is defined as the energy gap for the electron transfer. Because the reduction potential of a dye gives the electronic energy level of the LUMO of the dye,[16] it is regarded as the measure of the energy gap.

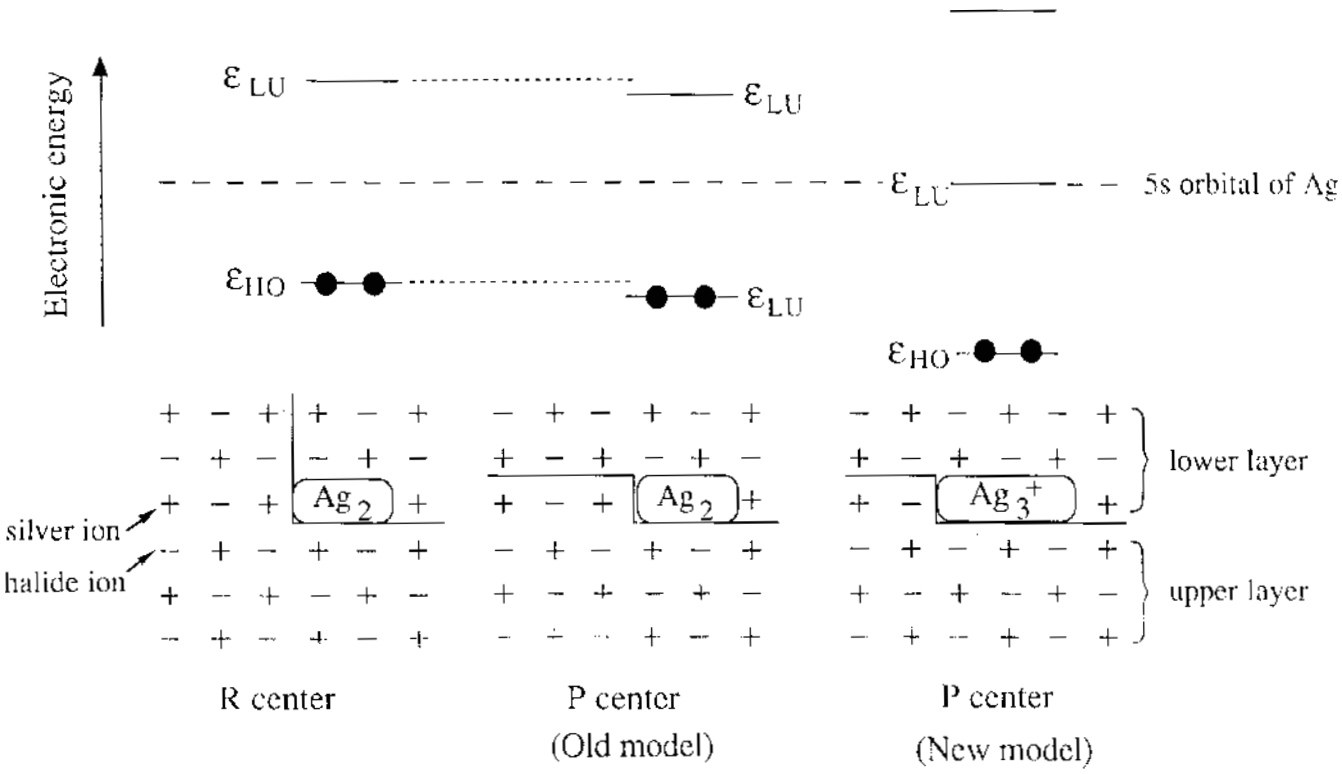

Figure 8. (Lower layer) Models for Ag_2 acting as a positive hole trap (i.e., R center) and as an electron trap (i.e., P center),[34,35] where + and – represent a silver ion and a halide ion, and solid lines indicate the position of steps on the surface. The old model for a P center was recently revised to give the new model.[35] (Upper layer) The electronic energy levels of an R center and P centers in old and new models.

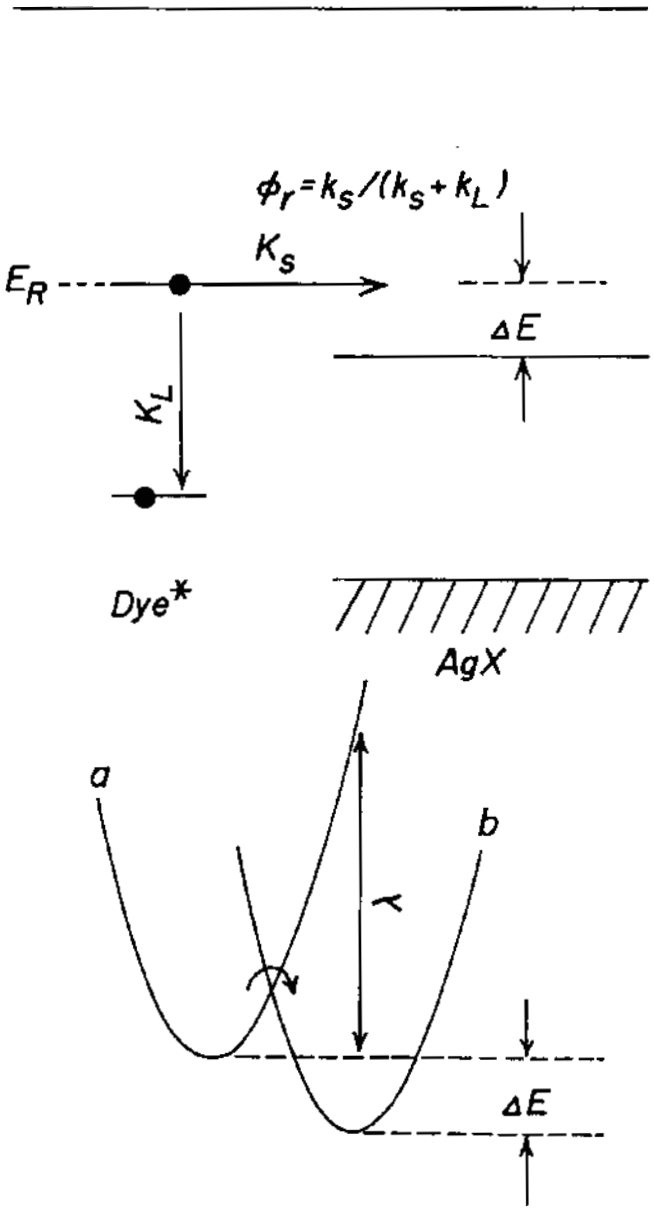

Figure 9. (Top) Electronic energy level diagram showing the electron transfer from an excited dye molecule (Dye*) to AgX, where k_s and k_L are the rate constants of the electron transfer (i.e., spectral sensitization) and deactivation processes, respectively; ϕ_r is the quantum yield of the electron transfer; and ΔE is the energy gap for the electron transfer. The reduction potential E_R is related to the height of the LUMO,[16] to which an electron at the HOMO is excited, and is used as the measure of the energy gap. (Bottom) Potential energy profile for the states (a) before and (b) after the electron transfer, where λ is the rearrangement energy.

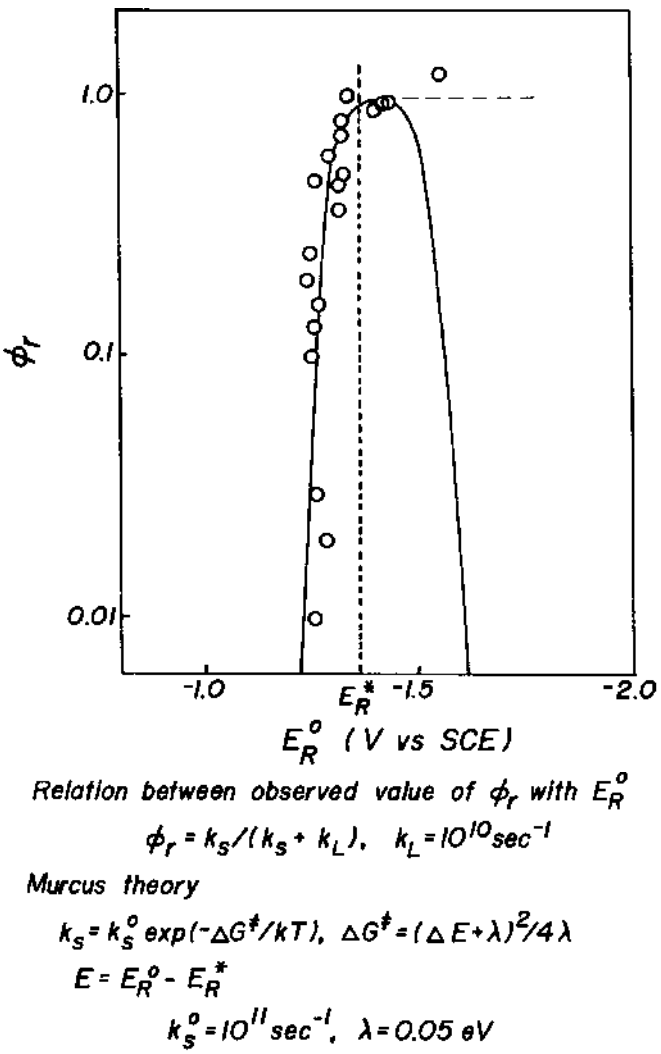

Figure 10. The energy gap dependence of the quantum yield (ϕ_r) of the electron transfer (i.e., spectral sensitization), which is plotted as a function of reduction potential (E_R) of dyes.[37] The rate constants of the electron transfer and deactivation processes (k_s and k_L, respectively) and ϕ_r were treated by the Marcus theory, where k^o is the maximum rate constant of the electron transfer; $\Delta G^{\ddagger}$ and ΔE are the activation energy and energy gap for the electron transfer; λ is the rearrangement energy; E_R^* is the reduction potential corresponding to the state where $\Delta E = 0$; and k and T are the Boltzman constant and absolute temperature, respectively.

In Fig. 10, open circles show the energy gap dependence of the quantum efficiency of the electron transfer for many sensitizing dyes in silver bromide emulsions, and the solid curve was derived from the Marcus theory with adjusted parameters.[16,37] It is realized that the electron transfer in spectral sensitization is characterized by the Marcus theory with small rearrangement energy and absence of the inverted region.[37] Although some dyes could achieve very high quantum efficiency, many dyes could not. The development of supersensitization technology, which improves the quantum efficiency of the electron transfer in spectral sensitization,[16] is one of the most important subjects for increasing photographic sensitivity.

It is considered that an electron-trapping sensitization center is composed of a dimer of silver sulfide,[38,39] and sulfide ions occupy the lattice positions (i.e., substitutional sulfide ions) on a silver halide grain.[38,40] Figure 11 shows the model for a sulfur sensitization center.[40] Because a sulfide ion has the electric charge of –2, a sulfide ion at the lattice position of silver halide should be associated with an interstitial silver ion for the compensation of its excess negative charge. Such a charged center as an interstitial silver ion has a hydrogen-like orbital, which loosely binds an electron with binding energy of several tens of milli-electron-volts.[25,41–43] Two hydrogen-like orbitals in a dimer of substitutional sulfide ions interact with each other to give a bonding orbital and an antibonding one. The bonding orbital in the dimer is deeper than the hydrogen-like orbital of an isolated interstitial silver ion and provides an electron trap suitable for the initiation of latent image formation.

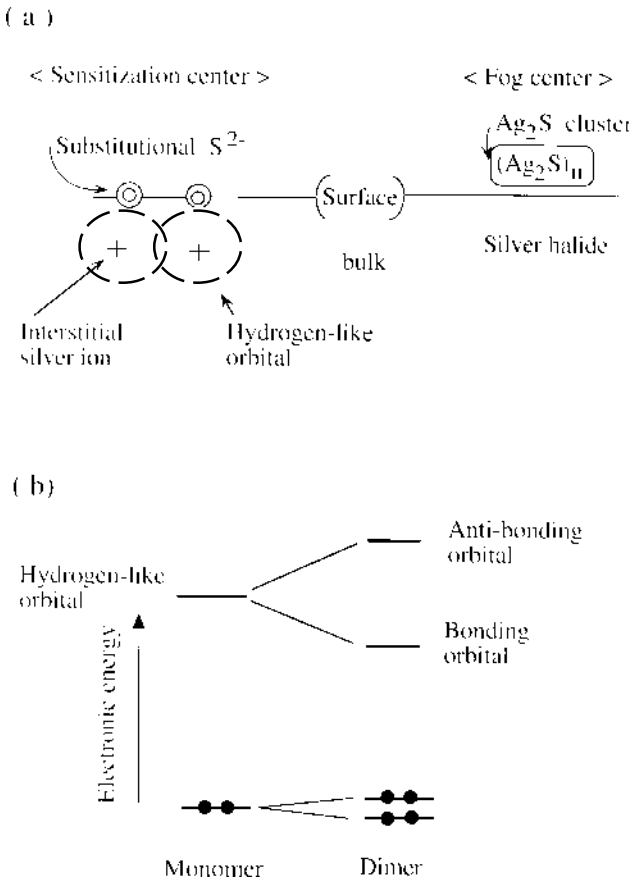

Figure 11. (a) Models for sulfur sensitization and fog centers and (b) electronic energy levels of a monomer and dimer of substitutional sulfide ions.[40]

The above-stated model predicts the possibility of modifying electron-trapping sensitization centers in such a way as to replace ions in the centers by other ions and to form the centers at some crystal defects on the grain surface. The replacement of an interstitial silver ion by a gold ion gives a sulfur-plus-gold sensitization center,[38,44] and the replacement of substitutional sulfide ions by selenium ions gives a selenium sensitization center.[45,46] Figure 12 shows the model for a sulfur-plus-gold sensitization center, which is a dimer of substitutional sulfide ions associated with an interstitial silver ion and an interstitial gold ion.[44] Because a gold ion is larger than a silver ion, the distance between two hydrogen-like orbitals in a sulfur-plus-gold sensitization center is larger than that in a sulfur sensitization center. Thus, the interaction between the two hydrogen-like orbitals in the sulfur-plus-gold sensitization center is weaker than that in the sulfur sensitization center. It is, therefore, predicted by the above-stated model, that an electron trap provided by a sulfur-plus-gold sensitization center is shallower and has a larger cross section than that provided by a sulfur sensitization center. The measured values[47,48] of the trap depths of sulfur sensitization centers were 0.33, and 0.39 eV,[47,48] whereas those of sulfur-plus-gold sensitization centers were 0.19 and 0.17 eV, which is consistent with the prediction by the model. The analysis of developer fog, which is initiated by electron transfer from a developer to the sensitization centers, could also support the above-stated model.[44] In a similar fashion, this model predicts a selenium sensitization center is shallower and has a larger cross section than a sulfur sensitization center, because a selenide ion is larger than a sulfide ion. The

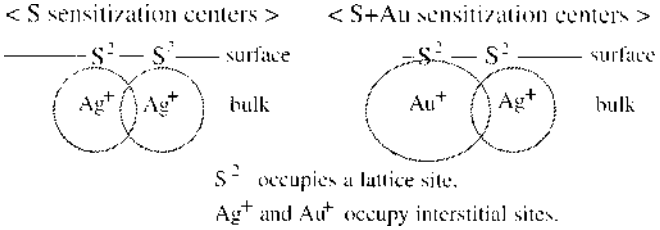

Figure 12. Models for sulfur sensitization and sulfur-plus-gold sensitization centers.[44]

technology for the optimization of the electron-trapping sensitization center is still being developed and is crucial for increasing photographic sensitivity.

The efficiency of latent image formation depends upon the recombination of positive holes with photoelectrons and/or image centers.[15] The most effective method to prevent the recombination is the realization of the Lowe's hypothesis[31,32,22] by putting R centers of reduction sensitization in emulsion grains.[15,33–35] Difficulties exist for the realization of the Lowe's hypothesis in practical emulsions. For example, the co-existence of reduction sensitization centers with gold sensitization centers tends to give fog centers, because it is known that stable and undevelopable silver clusters such as latent subimage centers and reduction sensitization centers could be converted into development centers by gold ions.[38,49,44] The hole-trapping ability of sensitizing dyes is inclined to prevent Lowe's hypothesis from taking place on silver halide emulsion grains. The technology for the prevention of recombination is still being developed and is important for increasing photographic sensitivity.

In green- and red-sensitive layers, an excited dye molecule transfers an electron to a silver halide grain and becomes a dye positive hole (i.e., a positive hole trapped by a dye molecule), which gives rise to an electron spin resonance (ESR) signal.[16,50] As shown in Fig. 13, both the intensity of the ESR signal and the degree of desensitization caused by dyes increase with an increase in the height of the HOMO of the dyes. This indicates that the dye positive holes, which gave rise to the light-induced ESR signal, cause the desensitization by recombining with electrons and/or image centers. This recombination is still severe in many cases and is one of the most important problems to solve for increasing photographic sensitivity.

As described before, it is believed that the smallest latent image center in a color film is composed of three atoms and that the ultimate form of the smallest latent image center, which is a dimer of gold atoms,[14,23,24] has not yet been realized and is a fascinating subject for achieving silver halide materials with very high sensitivity. A single-photon system has been proposed on the basis of the formation of a latent image center composed of a dimer of gold atoms by a single absorbed photon under the operation of Lowe's process.[36,51]

Some of the above-stated subjects have been recently solved in part and have contributed to recent remarkable progress in color films,[52] which is being utilized to increase sensitivity for some cases and/or to improve image quality for others. The increase in sensitivity thus achieved the development and improvement of color films with superhigh sensitivity (ISO sensitivity of 1600). The improvement in image quality brought about the enhanced popularity of color films with ISO sensitivity of 400, development and spread of single-use cameras, and development of color films with reduced frame area, i.e., Advanced Photo System (APS).

Figure 14 shows the change in the cross section of color negative films with ISO sensitivity of 400. Table II shows

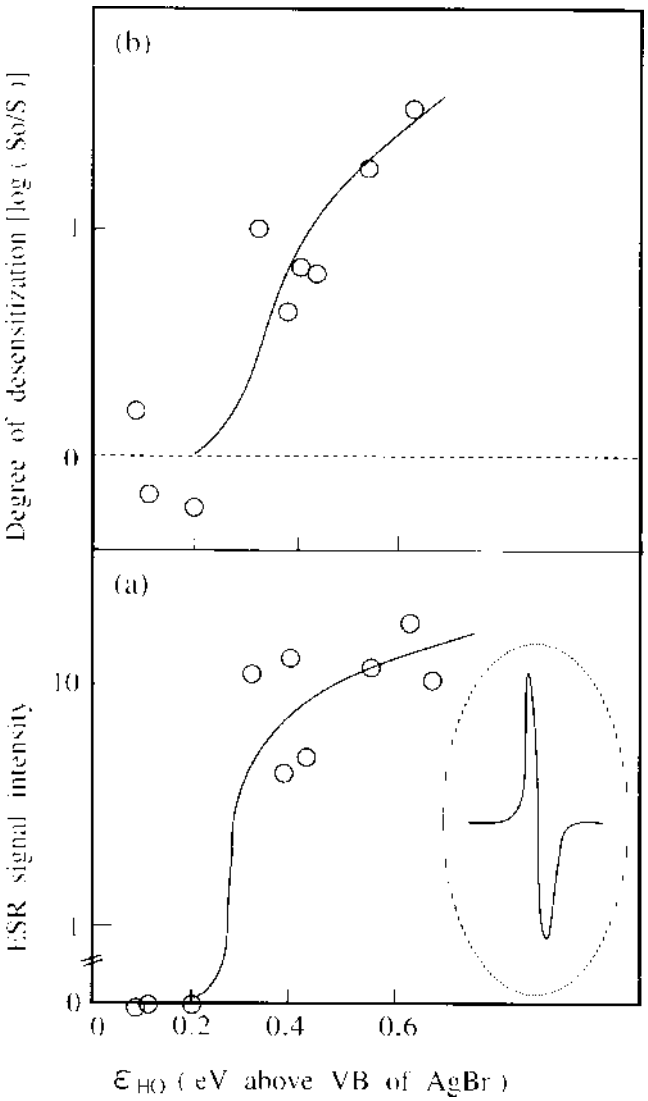

Figure 13. (a) Intensity of light-induced ESR signal at $g = 2.005$ and (b) degree of desensitization caused by dyes as a function of the electronic energy level of the HOMO of the corresponding dyes (ε_{HO}).[50] The degree of desensitization is expressed by $\log(S_o/S)$, where S_o and S are photographic sensitivities in the absence and presence of dyes. An example of an ESR spectrum is shown in (a).

the change in the structure of those films.[52] Note that the thickness of the photosensitive layers, total amount of silver halide, and average grain volume have been significantly reduced, and the number of grains has been much increased for those 16 years. Significant advances in the light absorption and efficiency of latent image formation probably contributed to the achievement of the above-stated results, although this has not been quantitatively reported.

Table III shows the predicted possibility for increase in sensitivity of color films. The light absorbance is estimated to be about one half, and the room for improvement in the light absorption is predicted to be about 2 times. The efficiency of latent image formation in terms of quantum sensitivity is estimated to be several but less than 10 absorbed photons per grain, and the room for improvement in the efficiency of latent image formation is predicted to be several times but less than 5 times. In total, it is predicted that large opportunities exist for the increase in sensitivity, which would be however less than 10 times. When one takes a single-photon system as the ultimate limit, the room for increase in sensitivity would be more than 10 times.

TABLE II. Progress of Color Negative Film (ISO 400)

Name	Year	Total AgX amount (rel.)	Grain volume (rel.)	Number of AgX grains (rel.)
F II 400	1976	100	100	100
HR 400	1983	92	54	213
HG 400	1989	58	23	487
G 400	1992	50	12	707

TABLE III. Possibility for Increase in Photographic Sensitivity

Factors	Present state	Ultimate limit	Room for improvement	
Light absorption	~1/2	1	2	
Quantum sensitivity (absorbed photon/grain)	<10	1.7	<5	<10
		(0.7)*	(>5)*	(>10)*
Size of the smallest latent image (atoms)	3	2	1.5	

* On the basis of single-photon system.

Color Film versus CCD

Figure 15 compares the efficiency of image formation between a color film and a digital still camera. As analyzed in the previous section, the efficiency of image formation of color film, which is composed of the efficiencies of its light absorption, creation of photoelectrons, and latent image formation, is still low because of poor light absorption and low efficiency latent image formation. Thus, significant room for improvement exists, whereas the efficiency of image formation of a CCD is very high,[19,53] because it is composed of such efficient processes as light absorption and creation of photoelectrons by silicon. Therefore, little room for improvement exits.

Figure 16 compares the capabilities of a highly sensitive emulsion layer useful for color film and a CCD. The pixel size of the emulsion layer is assumed to be 100 μm^2 on the basis of the fact that a color film with ISO sensitivity of 400 and 135 format contains 24 million pixels.[54] The pixel size of a CCD is assumed to be 50 μm^2. For a CCD, the number of photoelectrons in a pixel, which is used for image formation, is plotted as the number of absorbed photons by a pixel. For an emulsion layer, the fraction of developable grains is plotted as a function of the number of absorbed photons by layer with area equivalent to that of a pixel of a color film. The noise level was given by the standard deviation in the fraction of developable grains.

Note that the response of an emulsion layer that is a threshold sensor, reflected the threshold for latent image formation in a grain, which determined its sensitivity, and the reduction in its noise level did not seem to have a big influence on its sensitivity. But the response of a CCD was simply in linear relationship with the number of absorbed photons per pixel, and the reduction in its noise level resulted in notable increase in sensitivity.

As seen in Fig. 16, it seems the noise level of an emulsion layer was larger than that of a CCD. Because some kinds of technologies to reduce the noise level of emulsion layers are used in color negative film, the noise level of an emulsion layer as shown in Fig. 16 does not give the noise level of a color film. Noguchi and Ikoma[55] evaluated the image qualities of various pictures taken by color negative films and CCDs and printed on color papers with size of 96×144 mm^2, and they realized that the image

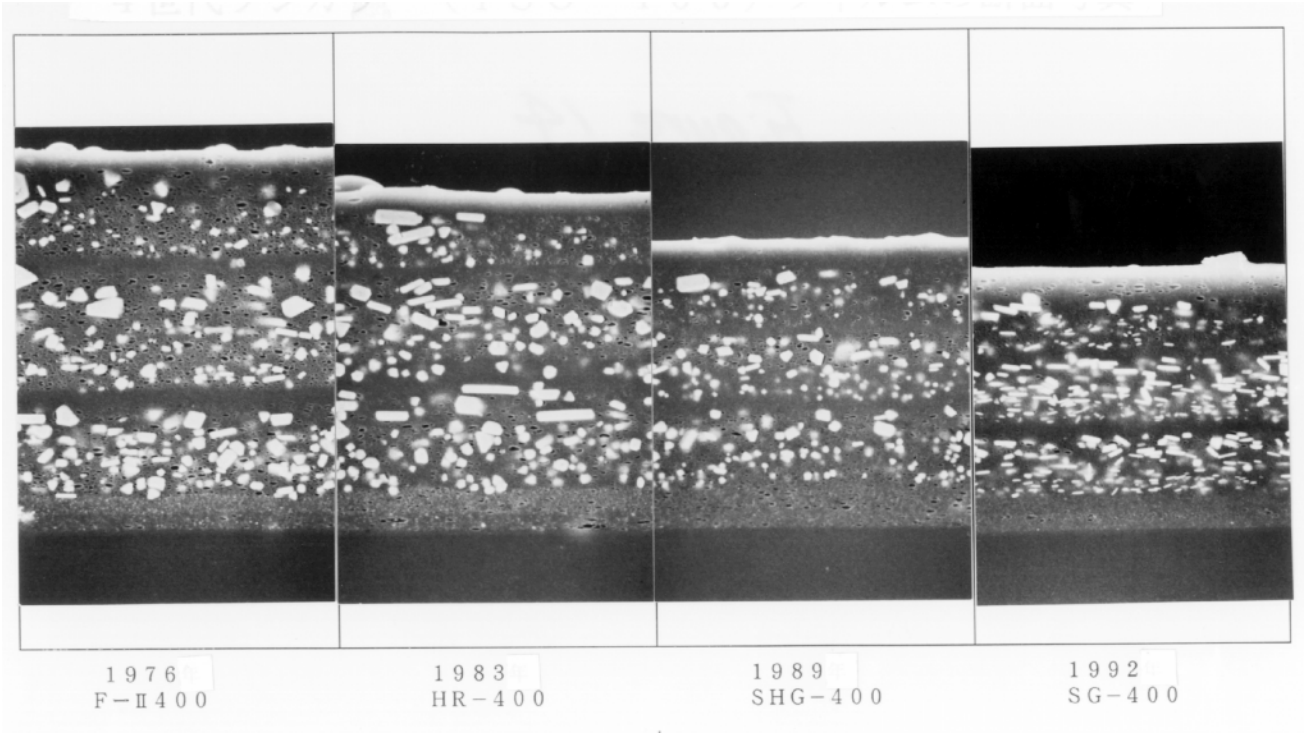

Figure 14. Change in the cross sections of color negative films with ISO sensitivity of 400, as observed by scanning electron microscopy.[52] White spots are silver halide grains (Courtesy of N. Sasaki).

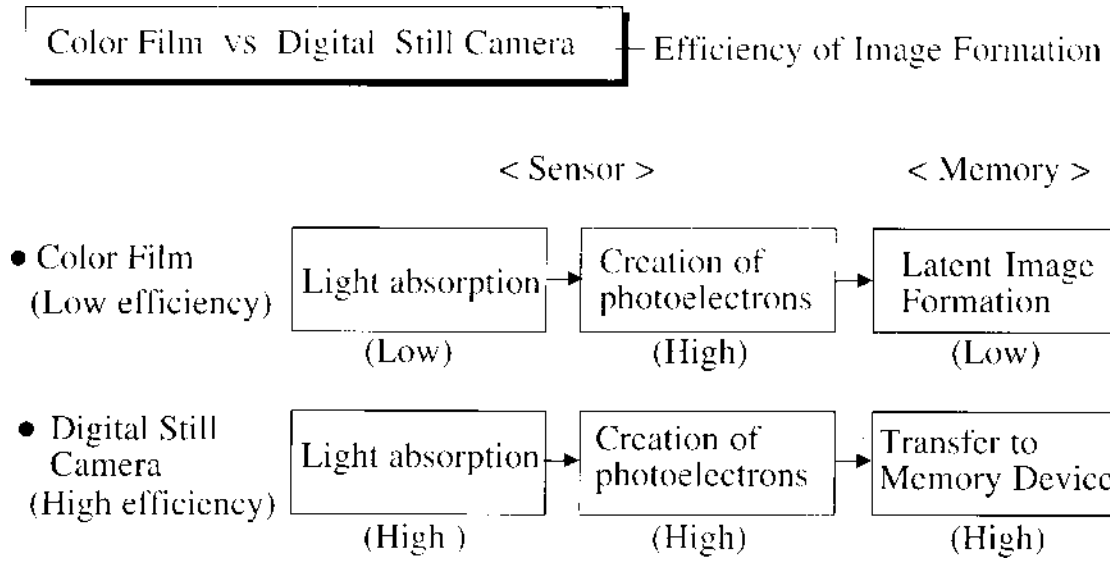

Figure 15. Comparison in efficiency of image formation between a color film and digital still camera.

quality of the pictures taken by color negative film with 135 format, ISO sensitivity of 400, and 24 million pixels was on a par with that of the pictures taken by a CCD with 6 million pixels. They considered a possible reason for the obtained result was that the noise level per pixel of the color film was larger by 4 times that of the CCD, although further investigations were needed for exactly evaluating the image qualities of pictures taken by color films and CCDs.

Note that the price of a CCD sharply increases with increase of its frame area for increase of its pixel number, and a digital still camera with a CCD having 6 million pixels is much too expensive for amateur consumers to purchase. Most digital still cameras for amateur consumers have around 0.4 million pixels.

As shown in Fig. 1, a color negative film has nine-fold emulsion layers, which are used for major layers sensitive to three primary colors and for three sublayers with different sensitivities in each major layer, giving a large number of pixels per area and a large dynamic range. The frame area of 135 format, which has the size of 24×36 mm^2 and is the most popular in color films, is larger by about 30 times that of the 1/2-in. format which has the size of 4.8×6.4 mm^2 and is the most popular in CCDs. By taking into account that the three major layers sensitive to three primary colors are coated one over another, the

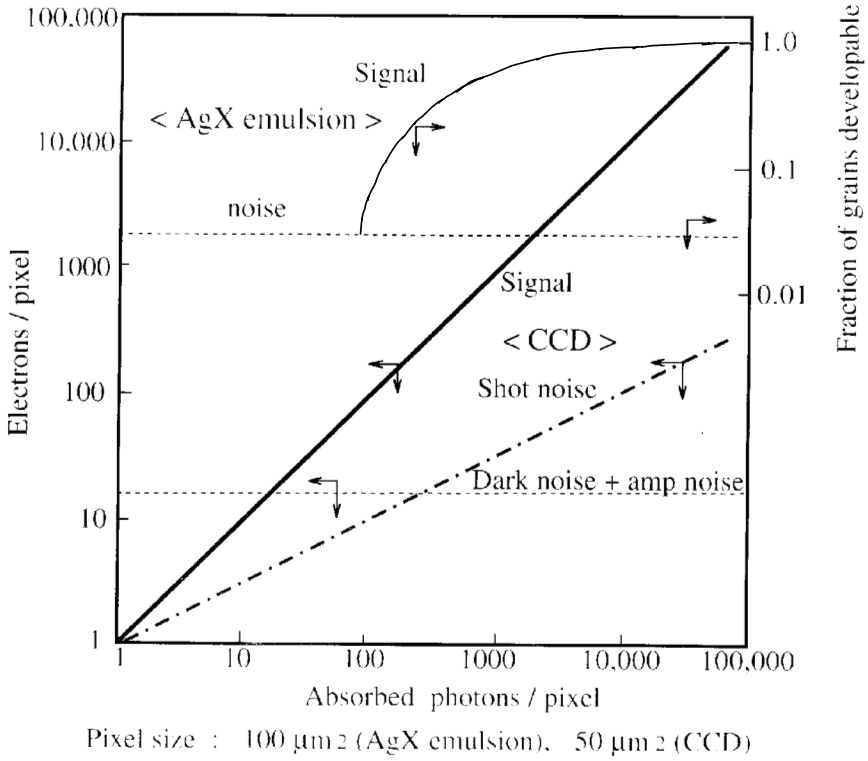

Figure 16. Comparison in signal and noise levels between a photographic emulsion layer available for a color film with pixel size of 100 μm^2 and a CCD with pixel size of 50 μm^2. In the case of an emulsion layer, the signal and noise levels are given by the fraction of developable grains and its standard deviation.

number of pixels in a color film of 135 format should be larger by about 90 times that of a CCD of 1/2-in. format, when the pixel size is the same for both. This is the reason why the number of pixels in a color film is much larger than that in a CCD and why the image quality of the pictures taken by a color film is overwhelmingly superior to that taken by a CCD used for digital still cameras for amateur consumers in spite of the noise level of the color film being larger than that of the CCD.

And increase in frame area and/or decrease in pixel size are needed for an increase of the number of pixels per frame in CCDs. However, it is difficult to increase the frame area of a CCD without increasing its production cost. Because CCDs take several months and more than 100 steps to produce on a silicon wafer, it is indispensable to make many CCDs on a silicon wafer to obtain CCDs, inexpensive enough to produce digital still cameras for amateur consumers. This is in contrast to the production of color films, where many layers are coated simutaneously and continuously on a large scale and high speed as shown in Fig. 1. In addition, the production yield of CCDs sharply decreases with increase in the CCD frame area.[3] But the production yield of color films is high and nearly independent of their frame area. The difference is because a CCD is composed of regularly arrayed pixels electrically connected with each other in series, while the function of a pixel in a color film is given by the integration of the functions of several hundreds of randomly arrayed fine silver halide grains that respond independently to incident photons.[1,8] Thus, it is probable that even a single small dust particle or defect can destroy the whole function of a CCD. Whereas, it is thought that because of the above-stated structure of a pixel in a color film a small number of small dust particles and/or deficient silver halide grains hardly deteriorate the function of a pixel in a color film.

Figure 17 shows the change in pixel size of color films and CCDs,[54] together with the change in the design rule of MOS memories. Note that a pixel in a color film contains image information of three primary colors. Although reduction in the pixel size of color films has been achieved by improvement in efficiency for image formation by silver halide grains, as described in Fig. 15, that of CCDs has been mainly achieved, not by the improvement in efficiency for image formation in a photosensitive area in each pixel, but by the set-up of a microlens and on-chip color filter on each pixel. By taking into account that the reduction in pixel size of some recently produced CCDs was associated with deterioration in sensitivity and/or dynamic range, the pixel size and its change of the CCD have been nearly equal to those of color films. The big difference in the number of pixels per frame between color films and CCDs in digital still cameras for amateur consumers mainly comes from the difference in frame area between and the three-dimensional structure of color films.

Figure 17 also shows that the rate of progress of CCDs in terms of reduction in their pixel size was much slower than the rate of progress of metal-oxide semiconductor, (MOS) memories in terms of reduction in their design rule, indicating an essential difference exists in the factor of progress between CCD and MOS memories. As Fig. 6 implies, reduction in pixel size of CCDs should be associated with decrease in the number of photoelectrons a pixel can capture and store and with decrease in CCD sensitivity and dynamic range. Thus, an increase in the number of pixels per frame without a decrease in sensitivity and dynamic range should be associated with an increase in the efficiency of image formation in CCDs. As shown in Figs. 15 and 16, the efficiency of image formation in CCDs is already very high and little room for improvement exists in the future. But the efficiency of latent image formation in color films is still low and has significant room for improvement in the future. Furthuremore, the fact that a lens with resolution that is high enough to meet a CCD with pixel size of less than 5 μm is expensive[56] and indicates the limit of the pixel size of a CCD in a digital still camera for an amateur consumer.

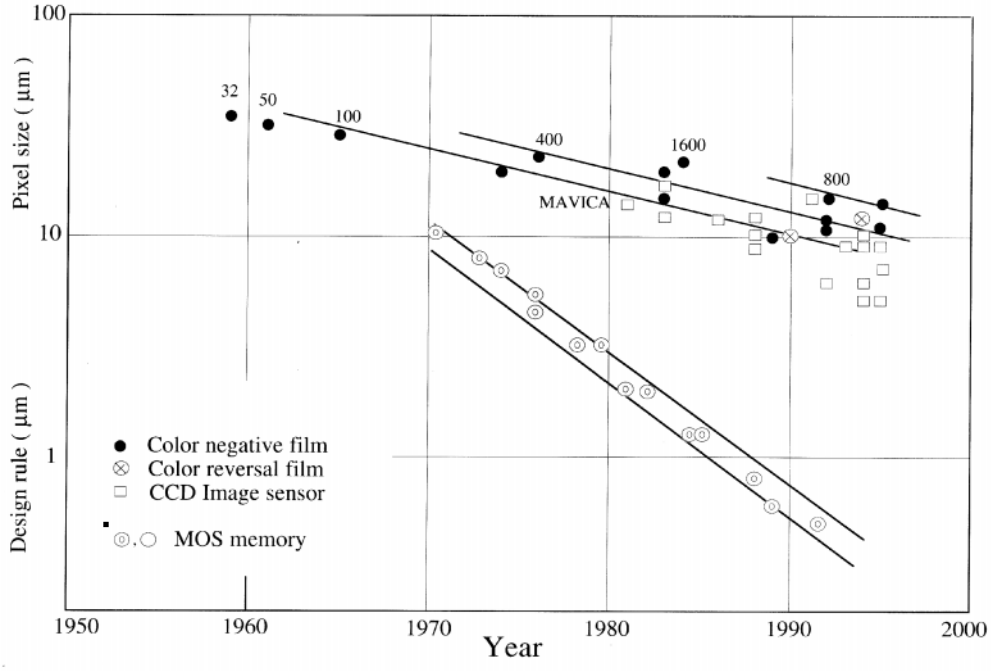

Figure 17. Changes in pixel size of color negative films, color reversal films, and CCD image sensors,[54] and in design rule of MOS memories. The numbers in the figure indicate the ISO sensitivities of the color negative films corresponding to the indicated closed circles.

Future of Color Films and Digital Still Cameras

As stated above, the comparison between color films and digital still cameras for amateur consumers on the basis of analysis of their photosensitive materials indicates the significant superiority of color films over digital still cameras in terms of image quality and cost. This is expected to continue in the future and cause amateur consumers to use color films for taking pictures. However, several other factors should be considered regarding the future of color films and digital still cameras.

Photographic Process

When taking a photograph with a camera and color film, incident photons as an image are captured by silver halide grains and memorized by the formation of latent image centers on the grains, as shown in Fig. 2. Because color film acts as a sensor and a memory device at the same time, the camera does not need to be equipped with a memory device. Because color film is composed of multilayers of photographic emulsions that can capture and memorize an image with three primary colors and a wide dynamic range, it has large image capacity per unit area. In addition, the capture and memorization of an image with incident photons can be achieved only by the energy of the absorbed photons. All these conditions make it possible to design very compact and easy to use cameras for color films. There are some advantages of digital still cameras that do not upset the above-stated condition. Namely, a digital camera uses a CCD that has a frame smaller than that of a color film, and stands still in the camera.

But a digital still camera should be equipped with several devices: a CCD, a memory device, and a liquid crystal display. In addition, these devices are operated by considerable electric power, which needs a secondary cell in many cases. It is quite troublesome to charge secondary cells in advance whenever one takes pictures.

In summary, cameras for color films are essentially more compact and easier to use than digital still cameras.

Display of Captured Images

To display a captured and memorized image in a color paper, an exposed color film is processed by sophisticated procedures with various chemical solutions. The display process of color films is, thus, too hard for amateur consumers to do by themselves. However, the above-stated processes are carried out as routine work for mass production by professional people, and amateur consumers can benefit the mass production, which provides them pictures with high quality and low price. Note that printing systems for digital imaging are not suitable for the mass production.[57]

Taking pictures by electronic photography, an amateur consumer can principally operate all the procedures including capturing images by a digital still camera, processing captured images on a personal computer, and making their prints at home by a color printer. Although the above-stated situation seems very attractive, it is a big investment for amateur consumers to purchase all that equipment. In addition, it requires considerable time and technique for an amateur consumer to process captured images on a computer. It is considered difficult for those printing systems to achieve such high quality and low cost as those achieved by printing systems for color papers when individual amateur consumers make prints by themselves.

In summary, it does not seem that the display process itself will influence the future of color films and digital still cameras.

Image Processing and Digitalization

In color film systems, various kinds of image processing are carried out during color development. Colored couplers[58–60] and development-inhibitor-releasing (DIR)[60,61] couplers are representative among them. Colored couplers could provide a technique to improve the colorfulness of colors of image-wisely formed dyes by substantially eliminating their side absorption bands, as illustrated in Fig. 18. DIR couplers are used to improve

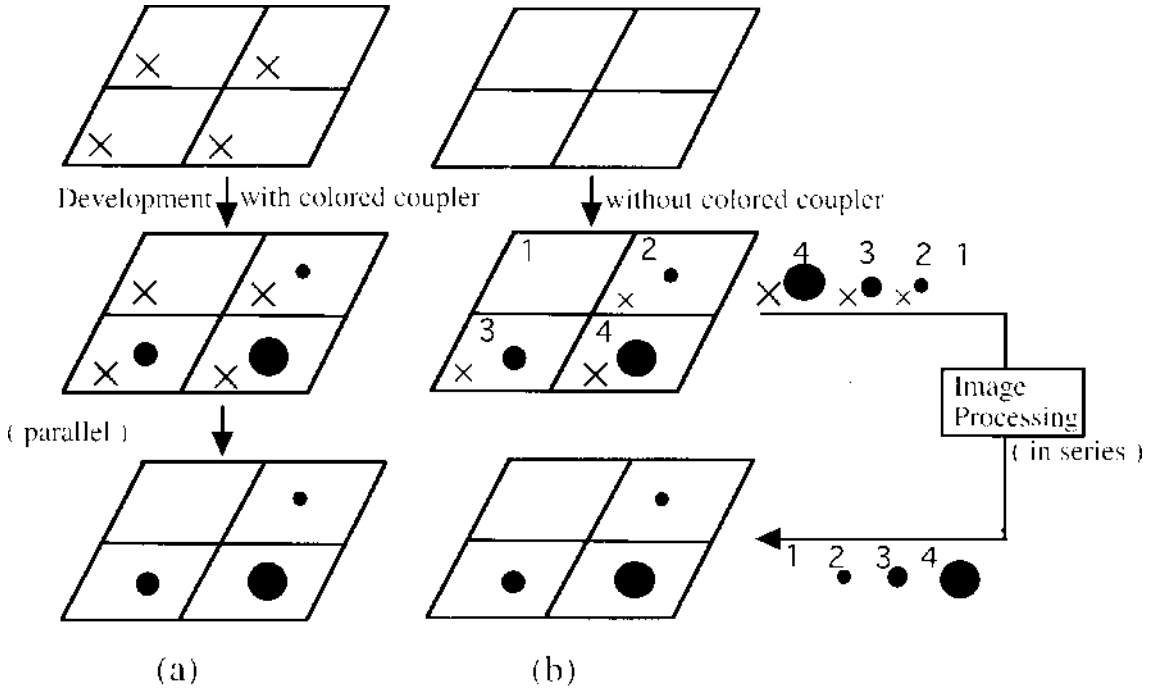

Figure 18. Illustrations showing chemical image processing taking place during development of a color negative film containing (a) a colored coupler and (b) the digital image processing as applied to a developed color negative film without a colored coupler, where ● and × are the main and side absorption bands of dyes formed in each pixel, respectively. Note that the chemical and digital image processings take place in parallel and in series, respectively.

granularity and saturation of colors by image-wisely releasing development inhibitors. Namely, image-wisely released development inhibitors decrease the size of dye clouds by depressing the development process in the layer where they are present and increase the saturation of colors in the same layer by depressing the development process taking place in the adjacent layers (inter-image effect). Figure 19 shows pictures made by simulation with and without image processing by use of a color coupler and DIR coupler giving the inter-image effect. As shown in Fig. 18, the above-stated processes take place in parallel at any place in a color film during color development regardless of the size of its frame area and the number of pixels in a frame.

The digitalization of analog images for image processing on computers has advantages and disadvantages. The most important merit is that digitalization makes it possible to process and transfer captured images. This is effective especially for pictures that will be reproduced many times and/or are valuable. The demerits of digitalization are the cost and time. The degree of cost and time probably will be in proportion to the number of pixels per frame. The digitalization should be effective when its merits overcome its demerits and is not necessarily effective for amateur photography because pictures for amateur photography should be inexpensive, of high quality with many number of pixels per frame, and not required to be reproduced many times.

Future of Color Photography for Amateur Consumers

The detailed analysis of photosensitive materials in the previous sections indicates that color films should keep their position in amateur photography in the future and not be replaced by digital still cameras. The analyses in this section on other functions should not exclude the above-stated conclusion.

However, it is highly expected that digital still camera systems will expand the photographic world by adding new attractive areas in amateur photography, despite providing color pictures with limited image quality.

Technical progress in color film systems in the future will expand the possibility of silver halide photography and achieve new attractive color film systems by improving the sensitivity and image quality of silver halide emulsions and by providing technologies that provide simpler, more rapid, environmentally kind, and/or dry processing. It is also probable that silver halide emulsions and color films will be designed to meet the demands of digital photography on the basis of hybrid technologies between silver halide and electronic photography. ▲

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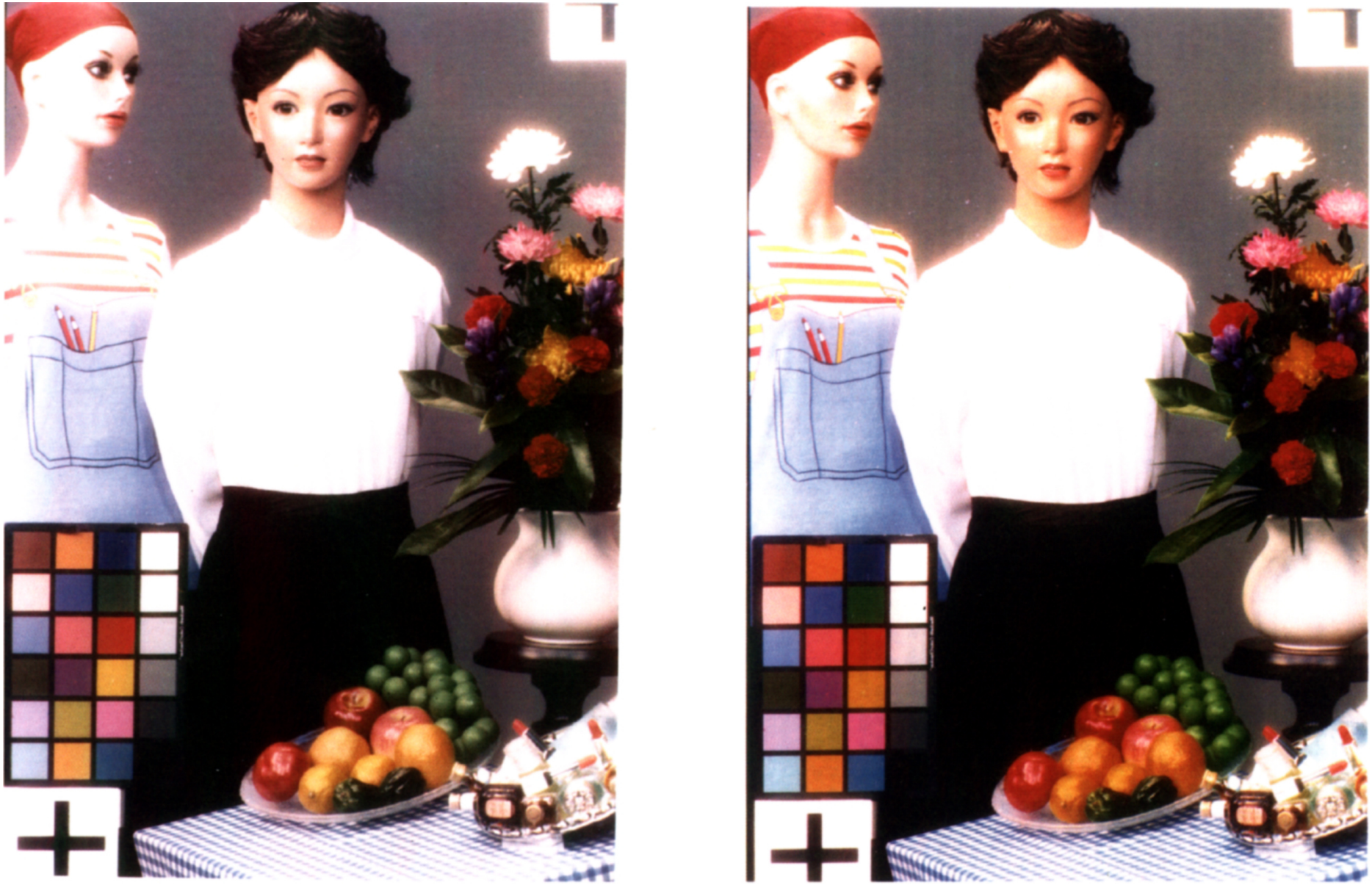

Figure 19. Pictures made by the simulation in the (left) absence and (right) presence of the image processing effects caused by a colored coupler and DIR coupler (Courtesy of K. Takahashi).

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